Aquatic Chemistry for engineers

PHREEQXCEL-apps for water treatment

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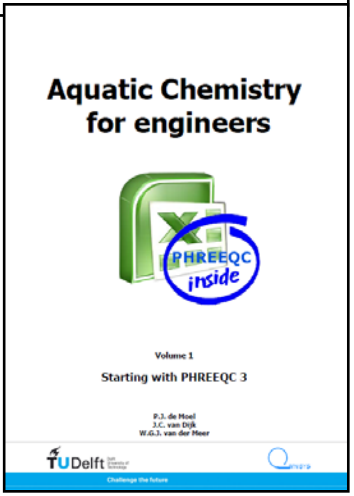
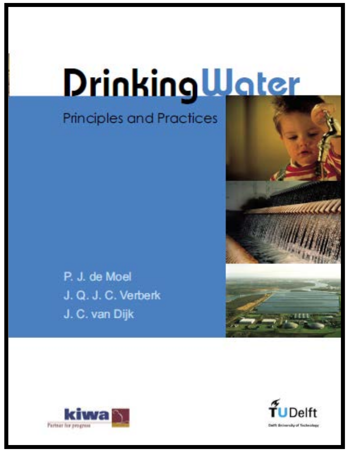
Course program

Aquatic Chemistry for engineers

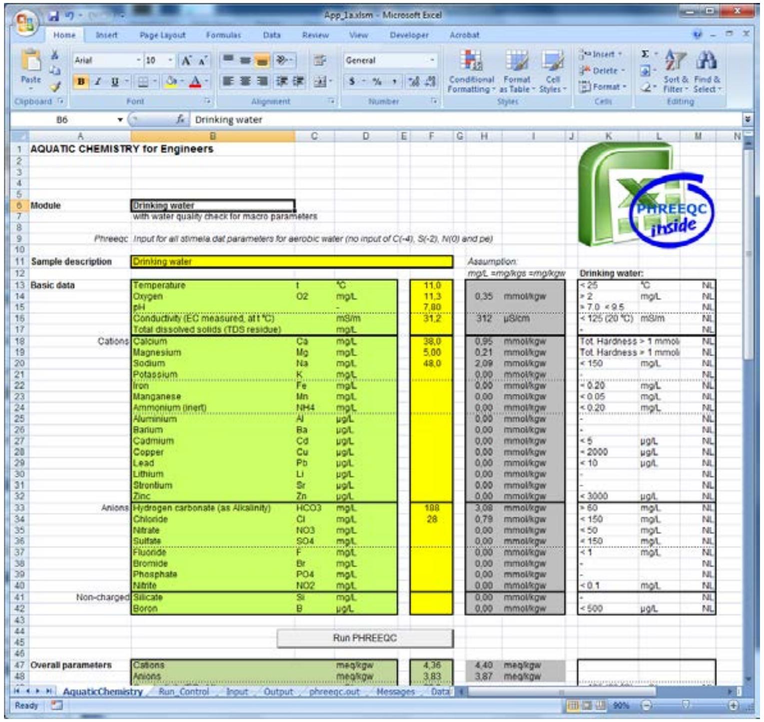
- Introduction (lecture + Starting with PHREEQC 3)
  - PHREEQC – PHREEQC Interactive – PHREEQC-COM
- Drinking water (App 1a+b)
  - Chemistry: SI / CCPP / Buffercapacity / Corrosion
  - Engineering: Ionic balance / Conductivity / Mixing
- Gases in water (App 2a+b+c)
  - Chemistry: solubility O_2, N_2, CO_2 , CH_4 etc
  - Engineering: P*V/T = R   / Biodegradation wastewater
- Hardness and pH (App 3a+b)
  - Chemistry: acid/base, solubility $CaCO_3$, $FeCO_3$, etc
  - Engineering: pH control / Neutralization / Softening





App 1a - Drinking water

- Open App_1a.xlsm:



Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

Module : Drinking water (aerobic water)

Water analysis report:

- Temperature 11 ^{0}C
- O_2 11.3 mg/L
- pH 7.8
- EC 31.2 mS/m (312 µS/cm)
- Ca 38 mg/L
- Mg 5 mg/L
- Na 48 mg/L
- Alkalinity 188 mg/L HCO_3
- Cl 28 mg/L

- O_2 > 0.1 mg/L
- So: no CH_4, no H_2S

AQUATIC CHEMISTRY for Engineers

Module Drinking water
with water quality check for macro parameters

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

Sample description Drinking water

Assumption: mg/L =mg/kgs =mg/kgw

							Drinking water:		
Basic data	Temperature	t	°C	11,0			< 25	°C	NL
	Oxygen	O2	mg/L	11,3	0,35	mmol/kgw	> 2	mg/L	NL
	pH		-	7,80			> 7.0 < 9.5		NL
	Conductivity (EC measured, at t °C)		mS/m	31,2	312	µS/cm	< 125 (20 °C)	mS/m	NL
	Total dissolved solids (TDS residue)		mg/L				-		NL
Cations	Calcium	Ca	mg/L	38,0	0,95	mmol/kgw	Tot. Hardness > 1 mmol/		NL
	Magnesium	Mg	mg/L	5,00	0,21	mmol/kgw	Tot. Hardness > 1 mmol/		NL
	Sodium	Na	mg/L	48,0	2,09	mmol/kgw	< 150	mg/L	NL
	Potassium	K	mg/L		0,00	mmol/kgw	-		NL
	Iron	Fe	mg/L		0,00	mmol/kgw	< 0.20	mg/L	NL
	Manganese	Mn	mg/L		0,00	mmol/kgw	< 0.05	mg/L	NL
	Ammonium (inert)	NH4	mg/L		0,00	mmol/kgw	< 0.20	mg/L	NL
	Aluminium	Al	µg/L		0,00	mmol/kgw	-		NL
	Barium	Ba	µg/L		0,00	mmol/kgw	-		NL
	Cadmium	Cd	µg/L		0,00	mmol/kgw	< 5	µg/L	NL
	Copper	Cu	µg/L		0,00	mmol/kgw	< 2000	µg/L	NL
	Lead	Pb	µg/L		0,00	mmol/kgw	< 10	µg/L	NL
	Lithium	Li	µg/L		0,00	mmol/kgw	-		NL
	Strontium	Sr	µg/L		0,00	mmol/kgw	-		NL
	Zinc	Zn	µg/L		0,00	mmol/kgw	< 3000	µg/L	NL
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	188	3,08	mmol/kgw	> 60	mg/L	NL
	Chloride	Cl	mg/L	28	0,79	mmol/kgw	< 150	mg/L	NL
	Nitrate	NO3	mg/L		0,00	mmol/kgw	< 50	mg/L	NL
	Sulfate	SO4	mg/L		0,00	mmol/kgw	< 150	mg/L	NL
	Fluoride	F	mg/L		0,00	mmol/kgw	< 1	mg/L	NL
	Bromide	Br	mg/L		0,00	mmol/kgw	-		NL
	Phosphate	PO4	mg/L		0,00	mmol/kgw	-		NL
	Nitrite	NO2	mg/L		0,00	mmol/kgw	< 0.1	mg/L	NL
Non-charged	Silicate	Si	mg/L		0,00	mmol/kgw	-		NL
	Boron	B	µg/L		0,00	mmol/kgw	< 500	µg/L	NL

Run PHREEQC

Aquatic Chemistry for engineers

Input - Output control

- PRINT
  - Alkalinity
- SELECTED_OUTPUT
  - for table output
  - parameters
- USER_PUNCH
  - for table output
  - special parameters
- CALCULATE_VALUES
  - Basic statements

```
PRINT
        -alkalinity          true                              # prints species that contribute to alkalinity. Default: false

SELECTED_OUTPUT
# Tip: use in/excluding # as line start for switching (defaults = true)
        -file                selected.out.txt                  # file name for tabulated output
#       -selected_out        false                             # set printing to the selected-output file on/off
        -reset               false                             # overwrites the default true values
        -simulation          true                              # prints simulation number
        -state               true                              # prints the type of calculation performed
        -solution            true                              # prints solution number
        -step                true                              # prints reaction step number for batch-reaction
        -pH                  true                              # prints pH
        -pe                  true                              # prints pe
        -temperature         true                              # prints temperature (Celsius).
        -alkalinity          true                              # prints alkalinity (eq/kgw)
#       -percent_error       true                              # prints percent error in charge balance
        -totals              C  C(4) C(-4)  Ca Mg Fe Fe(2) Fe(3) Mn Mn(# element total concentration (mol/kgw) (name from 1st column under _MASTER_SPECIES)
        -molalities          O2  CO2  HCO3-  CO3-2  CH4  Ca+2  CaH(# species concentration (mol/kgw) (name follows =-sign under SPECIES)
        -saturation_indices  Calcite Aragonite  Gypsum  Anhydrite  Dolo# SI-values for PHASES

USER_PUNCH
        -headings            Ion_Str  Conduct  Rho   Charge_Err   Charge_Bal   TotWat  Cation  Anion
        -start
                10           PUNCH MU
                20           PUNCH SC
                25           PUNCH RHO
                30           PUNCH PERCENT_ERROR
                40           PUNCH CHARGE_BALANCE                        # equal to TOTMOLE("charge")
                50           PUNCH TOT("water")
                60           PUNCH CALC_VALUE("Anion") + TOT("charge")   # Cation = Anion + ChargeBalans
                70           PUNCH CALC_VALUE("Anion")
        -end

CALCULATE_VALUES             # declaration of procedures (functions)
Anion                        # Calculate Anion concentration from Charge Balance (=Cat-An) and Error (=(Cat-An)/(Cat+An))
        -start
                10           DELTA = TOT("charge")                       # Charge Balance as Concentration (equal to CHARGE_BALANCE / TOT("water") )
                20           ERROR = PERCENT_ERROR/100                   # Error as Fraction
                30           AN = (DELTA/ERROR - DELTA)/2                # Calculate by substitution
                40           SAVE AN                                     # Algorithm less reliable at very small ERROR value
        -end
```

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Input - Simulations

- SOLUTION
  - water quality
- EQUILIBRIUM_PHASES
  - electron (pe)
  - solids
  - gases
- REACTION
  - adding chemicals
- REACTION_TEMPERATURE
  - other temperature

```
SOLUTION                    1
          -units              mg/kgs
          -redox              O(-2)/O(0)
          -density                     1
          -water                       1
          -pe                         14
          temp       11.0
          O(0)       11.3
          pH         7.80


          Ca         38.00
          Mg         5.00
          Na         48.00
          K          0.00
          Fe         0.00
          Mn         0.00
          [N-3]      0.00     as NH4
#         N(-3)      0.00     as NH4
          Al         0.00     ug/kgs
          Ba         0.00     ug/kgs
          Cd         0.00     ug/kgs
          Cu         0.00     ug/kgs
          Pb         0.00     ug/kgs
          Li         0.00     ug/kgs
          Sr         0.00     ug/kgs
          Zn         0.00     ug/kgs
          Alkalinity 188.00   as HCO3
          Cl         28.00
          N(+5)      0.00     as NO3
          S(+6)      0.00     as SO4
          F          0.00
          Br         0.00
          P          0.00     as PO4
          N(+3)      0.00     as NO2
#         N(0)       1        N2(g) -0,1079      # SI[N2(g)] = log(pa) = log(0.78) = -0.1079
#         Ntg        1        Ntg(g) -0,1079     # SI[Nga2(g)] = log(pa) = log(0.78) = -0.1079
          Si         0.00     as Si
          B          0.00     ug/kgs as B
END       # Simulation 1


TITLE     Simulation for calculating pe (redox equilibrium)
USE solution 1
EQUILIBRIUM_PHASES                           # dummy to start final calculation, with identical water quality
```

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Output

- Simulation results
  - Tabulated output

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	
1	sim	state	soln	step	pH	pe	temp(C)	Alk(eq/kgw	C(mol/kgw	C(4)(mol/kgw)	C(-4)(mol/k	Ca(mol/kgw	Mg(mol/kg	Fe(mol/kgw	F
2	1	i_soln	1	-99	7,80	14,00	11,0	3,08E-03	3,19E-03	3,19E-03	0,00E+00	9,48E-04	2,06E-04	0,00E+00	[illegible]
3	2	react	1	1	7,80	14,07	11,0	3,08E-03	3,19E-03	3,19E-03	0,00E+00	9,48E-04	2,06E-04	0,00E+00	[illegible]
4	3	react	1	1	7,78	14,09	11,0	3,07E-03	3,19E-03	3,19E-03	0,00E+00	9,42E-04	2,06E-04	0,00E+00	[illegible]
5	4	react	1	1	7,77	14,10	11,0	3,07E-03	3,19E-03	3,19E-03	0,00E+00	9,48E-04	2,06E-04	0,00E+00	[illegible]
6	4	react	1	2	7,55	14,33	11,0	2,98E-03	3,19E-03	3,19E-03	0,00E+00	9,48E-04	2,06E-04	0,00E+00	[illegible]
7	5	react	1	1	7,24	10,82	60,0	2,77E-03	3,04E-03	3,04E-03	0,00E+00	7,93E-04	2,06E-04	0,00E+00	[illegible]
8	5	react	1	2	7,05	9,19	90,0	2,41E-03	2,86E-03	2,86E-03	0,00E+00	6,12E-04	2,06E-04	0,00E+00	[illegible]
9															

Aquatic Chemistry for engineers

phreeqc.out

- Simulation results
  - Lined output

```
----------------------------Solution composition-----------------------------

        Elements           Molality       Moles

        Alkalinity       3.082e-003  3.082e-003
        Ca               9.484e-004  9.484e-004
        Cl               7.900e-004  7.900e-004
        Mg               2.057e-004  2.057e-004
        Na               2.089e-003  2.089e-003
        O(0)             7.065e-004  7.065e-004

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

                                       pH  =   7.800
                                       pe  =  14.000
       Specific Conductance (uS/cm, 11 oC) = 283
                          Density (g/cm3)  =   0.99985
                               Volume (L)  =   1.00063
                        Activity of water  =   1.000
                           Ionic strength  =  5.224e-003
                       Mass of water (kg)  =  1.000e+000
                    Total carbon (mol/kg)  =  3.194e-003
                       Total CO2 (mol/kg)  =  3.194e-003
                      Temperature (deg C)  =  11.00
                  Electrical balance (eq)  =  5.248e-004
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   6.41
                               Iterations  =   7
                                  Total H  = 1.110155e+002
                                  Total O  = 5.551638e+001

--------------------------------Redox couples--------------------------------

        Redox couple             pe  Eh (volts)

        O(-2)/O(0)          14.0741      0.7935

---------------------------Distribution of species---------------------------

                                                 Log       Log       Log    mole V
   Species          Molality    Activity  Molality  Activity     Gamma   cm3/mol

   OH-            2.189e-007  2.027e-007    -6.660    -6.693    -0.033     -4.89
   H+             1.697e-008  1.585e-008    -7.770    -7.800    -0.030      0.00
   H2O            5.551e+001  9.999e-001     1.744    -0.000     0.000     18.02
```

Aquatic Chemistry for engineers

Results for engineers

- Relevant results only
- Readable output
- Post-calculations
- Unit conversion
- Requirements checks
- Graphics (not shown)

Run PHREEQC

Overall parameters	Cations		meq/kgw	4,36	4,40	meq/kgw			
	Anions		meq/kgw	3,83	3,87	meq/kgw			
	Conductivity (EC at t)		mS/m	28,3			< 125 (20 °C)	mS/m	NL
	Total dissolved solids (TDS)		mg/L	307					
	Ionic strength		mmol/kgw	5,2					
	Total hardness		mmol/kgw	1,15	6,5	°D	> 1	mmol/L	NL
	Vapor pressure water		atm	0,01					
	Density		kg/L	1,000					
Redox conditions	Oxygen		mmol/kgw	0,35	0,21	atm			
	pe (electron activity)	pe	-	14,07					
	Redox potential	Eh	mV	793					
Correctness checks	Charge difference		meq/kgw	0,52	0,52	meq/kgw	< 0.2 meq/L (an < 3)		SM 1030E
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			6,4%			< 2% (3 < an < 10)		SM 1030E
	EC ratio, calculated/measured		-	0,91			>0.9 <1.1		SM 1030E
	TDS ratio, measured/calculated		-	-			>1.0 <1.2		SM 1030E
	Cations to measured EC ratio (*10)		meq.m/kgw.mS	1,54			>0.9 <1.1		SM 1030E
	Anions to measured EC ratio (*10)		meq.m/kgw.mS	1,35			>0.9 <1.1		SM 1030E
	TDS to EC ratio, measured (/10)		mg.m/L.mS	-			>0.55 <0.7		SM 1030E
	TDS to EC ratio, calculated (/10)		mg.m/L.mS	1,08			>0.55 <0.7		SM 1030E
	Oxygen saturation (to air at sea level)		atm/atm	102,7%			< 1.1		pr.
	pH change by electron balancing (Phreeqc)		-	0,000			< 0.01		pr.
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,80			>7.0 <9.5		NL
	Alkalinity	m	meq/kgw	3,08			>1	meq/L	NL
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	3,19	38	mg/L C			
	CO2	CO2	mmol/kgw	0,13	0,00	atm			
	HCO3 -	HCO3	mmol/kgw	3,02	185	mg/L	> 1	mmol/L	NL
	CO3 2-	CO3	mmol/kgw	0,01	0	mg/L			
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,25					
	Buffer capacity	BI	mmol/kgw /pH	0,32					
Calcite equilibrium	SI (calcite)	SI-c	-	0,02			> -0.2 < 0.3		NL
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,78					
	Calcite Precipitation Potential	CPP	mmol/kgw	0,01	1	mg/L CaCO3	> -0.05 < 0.2	mmol/L	DE + pr.
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,16	16	mg/L CaCO3			
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,34	34	mg/L CaCO3			
Other scaling solids	Aragonite	SI	CaCO3	-0,13			< 0.3		pr.
	Gypsum	SI	CaSO4.2H2O	-			< 0.3		pr.
	Anhydrite	SI	CaSO4	-			< 0.3		pr.
	Dolomite	SI	CaMg(CO3)2	-0,69			< 0.3		pr.
	Hydroxyapatite	SI	Ca5(PO4)3OH	-1000,00			< 0.3		pr.
Corrosion	Pb solvency potential	Pb	µg Pb / kgw	167			< 200		NL
	Cu solvency index	CuI	-	1,3			> 0		NL
	Corrosion index S1 (galvanized, pitting)		-	0,26			< 0.5		CEN
	Corrosion index S2 (galvanized, selective)		-	-			<1 or >3 or NO3<0.3		CEN
	Corrosion index S (copper, pitting)		-	-			> 1.5		CEN
Elements / Species	C (in TIC)		mmol/kgw	3,19					
	CO2			4,0%					
	HCO3 -			94,7%					
	CO3 2-			0,2%					
	Ca		mmol/kgw	0,95					

Drinking water

What causes the charge difference?

- Cations: 4.36 meq/kgw
- Anions: 3.83 meq/kgw
- Difference: 0.52 meq/kgw (6.4 %)

Run PHREEQC

Overall parameters	Cations		meq/kgw	4,36	4,40	meq/kgw			
	Anions		meq/kgw	3,83	3,87	meq/kgw			
	Conductivity (EC at t)		mS/m	[illegible]			< 125 (20 °C)	mS/m	NL
	Total dissolved solids (TDS)		mg/L	307					
	Ionic strength		mmol/kgw	5,2					
	Total hardness		mmol/kgw	1,15	6,5	°D	> 1	mmol/L	NL
	Vapor pressure water		atm	0,01					
	Density		kg/L	1,000					
Redox conditions	Oxygen		mmol/kgw	0,35	0,21	atm			
	pe (electron activity)	pe	-	14,07					
	Redox potential	Eh	mV	[illegible]					
Correctness checks	Charge difference		meq/kgw	0,52	0,52	meq/kgw	< 0.2 meq/L (an < 3)		SM 1030E
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			6,4%			< 2% (3 < an < 10)		SM 1030E
	EC ratio, calculated/measured		-	[illegible]			>0.9 <1.1		SM 1030E
	TDS ratio, measured/calculated		-	-			>1.0 <1.2		SM 1030E
	Cations to measured EC ratio (*10)		meq.m/kgw.mS	1,54			>0.9 <1.1		SM 1030E
	Anions to measured EC ratio (*10)		meq.m/kgw.mS	1,35			>0.9 <1.1		SM 1030E
	TDS to EC ratio, measured (/10)		mg.m/L.mS	-			>0.55 <0.7		SM 1030E
	TDS to EC ratio, calculated (/10)		mg.m/L.mS	1,08			>0.55 <0.7		SM 1030E
	Oxygen saturation (to air at sea level)		atm/atm	102,7%			< 1.1		pr.
	pH change by electron balancing (Phreeqc)		-	0,000			< 0.01		pr.
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,80			>7.0 <9.5		NL
	Alkalinity	m	meq/kgw	3,08			>1	meq/L	NL

- I give you 5 minutes....

Drinking water

What causes the charge difference?

- Answer:

Run PHREEQC

Overall parameters	Cations		meq/kgw	4,36	4,40 meq/kgw		
	Anions		meq/kgw	3,83	3,87 meq/kgw		
	Conductivity (EC at t)		mS/m	28,3		< 125 (20 °C) mS/m	NL
	Total dissolved solids (TDS)		mg/L	307			
	Ionic strength		mmol/kgw	5,2			
	Total hardness		mmol/kgw	1,15	6,5 °D	> 1 mmol/L	NL
	Vapor pressure water		atm	0,01			
	Density		kg/L	1,000			
Redox conditions	Oxygen		mmol/kgw	0,35	0,21 atm		
	pe (electron activity)	pe	-	14,07			
	Redox potential	Eh	mV	793			
Correctness checks	Charge difference		meq/kgw	0,52	0,52 meq/kgw	< 0.2 meq/L (an < 3)	SM 1030E
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			6,4%		< 2% (3 < an < 10)	SM 1030E
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	TDS to EC ratio, calculated (/10)		mg.m/L.mS	1,08		>0.55 <0.7	SM 1030E
	Oxygen saturation (to air at sea level)		atm/atm	102,7%		< 1.1	pr.
	pH change by electron balancing (Phreeqc)		-	0,000		< 0.01	pr.
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,80		>7.0 <9.5	NL
	Alkalinity	m	meq/kgw	3,08		>1 meq/L	NL

Drinking water

What causes the charge difference?

Run PHREEQC

Overall parameters	Cations		meq/kgw	4,36	4,40	meq/kgw			
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	TDS to EC ratio, calculated (/10)		mg.m/L.mS	1,08			>0.55 <0.7		SM 1030E
	Oxygen saturation (to air at sea level)		atm/atm	102,7%			< 1.1		pr.
	pH change by electron balancing (Phreeqc)		-	0,000			< 0.01		pr.
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,80			>7.0 <9.5		NL
	Alkalinity	m	meq/kgw	3,08			>1	meq/L	NL

- Answer:
- Missing anion
  - Cation > Anion 0.52 meq/kgw
  - EC measured = 31.2 mS/m > EC calculated = 28.3 mS/m
- Extra anions 0.52 meq/kgw =
  - NO_3 1- 0.52 mmol/kgw 32 mg/L 30.7 mS/m
  - SO_4 2- 0.26 mmol/kgw 25 mg/L 30.4 mS/m
  - F 1- 0.52 mmol/kgw 10 mg/L 30.2 mS/m
- Most probably:
  - SO4 only 16% of max. content for drinking water

Drinking water

Further output values in App Drinking water

- Drinking water regulations (Netherlands / SM / CEN)
- Overall parameters (Cation / Anion / Total hardness / EC etc)
- Redox conditions (O_2 / pe / redox potential)
- Analysis correctness checks, acc. Standard Methods 1030E
- Carbon equilibrium
  - TIC : CO_2 / HCO_3 / CO_3
  - bufferindex / dpH 0.1 mmol HCl/kgw
- Calcite equilibrium
  - SI calcite, pHs
  - CCPP (actual temp / 60 C /90 C)
- SI of other scaling solids
- Corrosion indices
- Major species

Run PHREEQC

Overall parameters	Cations		meq/kgw	4,36	4,40	meq/kgw			
	Anions		meq/kgw	3,83	3,87	meq/kgw			
	Conductivity (EC at t)		mS/m	28,3			< 125 (20 °C)	mS/m	NL
	Total dissolved solids (TDS)		mg/L	307					
	Ionic strength		mmol/kgw	5,2					
	Total hardness		mmol/kgw	1,15	6,5	°D	> 1	mmol/L	NL
	Vapor pressure water		atm	0,01					
	Density		kg/L	1,000					
Redox conditions	Oxygen		mmol/kgw	0,35	0,21	atm			
	pe (electron activity)	pe	-	14,07					
	Redox potential	Eh	mV	793					
Correctness checks	Charge difference		meq/kgw	0,52	0,52	meq/kgw	< 0.2 meq/L (an < 3)		SM 1030E
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			6,4%			< 2% (3 < an < 10)		SM 1030E
	EC ratio, calculated/measured		-	0,91			>0.9 <1.1		SM 1030E
	TDS ratio, measured/calculated		-	-			>1.0 <1.2		SM 1030E
	Cations to measured EC ratio (*10)		meq.m/kgw.mS	1,54			>0.9 <1.1		SM 1030E
	Anions to measured EC ratio (*10)		meq.m/kgw.mS	1,35			>0.9 <1.1		SM 1030E
	TDS to EC ratio, measured (/10)		mg.m/L.mS	-			>0.55 <0.7		SM 1030E
	TDS to EC ratio, calculated (/10)		mg.m/L.mS	1,08			>0.55 <0.7		SM 1030E
	Oxygen saturation (to air at sea level)		atm/atm	102,7%			< 1.1		pr.
	pH change by electron balancing (Phreeqc)		-	0,000			< 0.01		pr.
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,80			>7.0 <9.5		NL
	Alkalinity	m	meq/kgw	3,08			>1	meq/L	NL
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	3,19	38	mg/L C			
	CO2	CO2	mmol/kgw	0,13	0,00	atm			
	HCO3 -	HCO3	mmol/kgw	3,02	185	mg/L	> 1	mmol/L	NL
	CO3 2-	CO3	mmol/kgw	0,01	0	mg/L			
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,25					
	Buffer capacity	BI	mmol/kgw /pH	0,32					
Calcite equilibrium	SI (calcite)	SI-c	-	0,02			> -0.2 < 0.3		NL
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,78					
	Calcite Precipitation Potential	CPP	mmol/kgw	0,01	1	mg/L CaCO3	> -0.05 < 0.2	mmol/L	DE + pr.
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,16	16	mg/L CaCO3			
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,34	34	mg/L CaCO3			
Other scaling solids	Aragonite	SI	CaCO3	-0,13			< 0.3		pr.
	Gypsum	SI	CaSO4.2H2O	-			< 0.3		pr.
	Anhydrite	SI	CaSO4	-			< 0.3		pr.
	Dolomite	SI	CaMg(CO3)2	-0,69			< 0.3		pr.
	Hydroxyapatite	SI	Ca5(PO4)3OH	-1000,00			< 0.3		pr.
Corrosion	Pb solvency potential	Pb	µg Pb / kgw	167			< 200		NL
	Cu solvency index	CuI	-	1,3			> 0		NL
	Corrosion index S1 (galvanized, pitting)		-	0,26			< 0.5		CEN
	Corrosion index S2 (galvanized, selective)		-	-			<1 or >3 or NO3<0.3		CEN
	Corrosion index S (copper, pitting)		-	-			> 1.5		CEN
Elements / Species	C (in TIC)		mmol/kgw	3,19					
	CO2			4,0%					
	HCO3 -			94,7%					
	CO3 2-			0,2%					
	Ca		mmol/kgw	0,95					

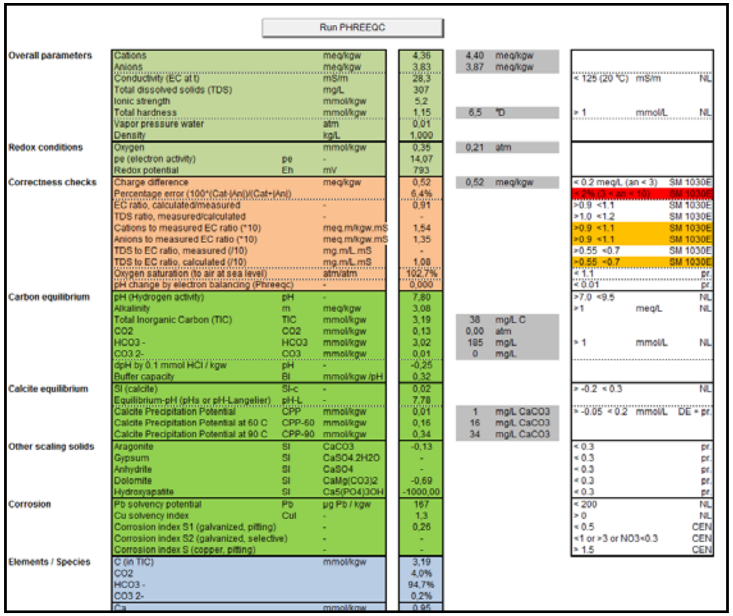
Conclusions - Lessons learned

Engineers versus Researchers

- Engineers use PHREEQC in predesigned Excel versions
  - no PHREEQC programming skills required
  - easy input with ‘normal’ units etc.
  - additional relevant output data provided

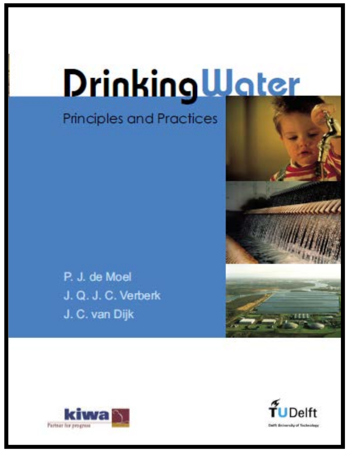
- Researchers use PHREEQC
  - in predesigned Excel versions
  - in Excel with own program lines
  - in Excel for addional graphs
  - developing Excel for Engineers

- Original PHREEQCI
  - only for input help / online manual



Drinking water

What causes the charge difference?



- Self study problem: Drinking water – P&P: page 225

Computation ionic balance

A single unknown concentration can be computed using an ionic balance.
In order to do this, the valence concentration for each component is computed:

Compound	Weight concentration (mg/l)	Molar mass (g/mol)	Molar concentration (mmol/l)	Valence	Valence concentration (meq/l)
Cations:					
Na^+	63	23	2.74	1	2.74
K^+	5	39	0.13	1	0.13
Ca^{2+}	45	40	1.13	2	2.25
Mg^{2+}	9	24.5	0.37	2	0.73
Fe^{2+}	4	56	0.07	2	0.14
Mn^{2+}	1	55	0.02	2	0.04
NH_4^+	2	18	0.11	1	0.11
Total	129				6.14
Anions:					
Cl^-	73	35.4	2.06	1	2.06
HCO_3^-	151	61	2.48	1	2.48
NO_3^-	1	78	0.01	1	0.01
SO_4^{2-}	Unknown	96	?	2	?
Total	?				6.14

From the ionic balance it follows that the total valence concentration of the anions should also be 6.14 meq/l.
Therefore, the amount of SO_4^{2-} should be 1.60 meq/l (= 6.14 - 2.06 - 2.48 - 0.01).
Conclusion: SO_4^{2-} = 1.60 meq/l = 1.60/2 = 0.80 mmol/l = 0.88 x 96 = 77 mg/l.
The total amount of dissolved matter amounts to 431 mg/l (= 129 + 73 + 151 + 1 + 77).

Note 1:
Use inert [Fe+2] and [Mn+2]

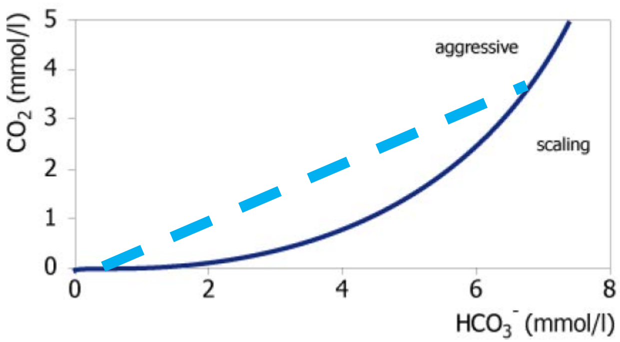
Note 2:
Cations and Anions are smaller in PHREEQC due to ion-pairs

Questions?

Aquatic Chemistry for engineers

Module : Mixing of water (App 1b)

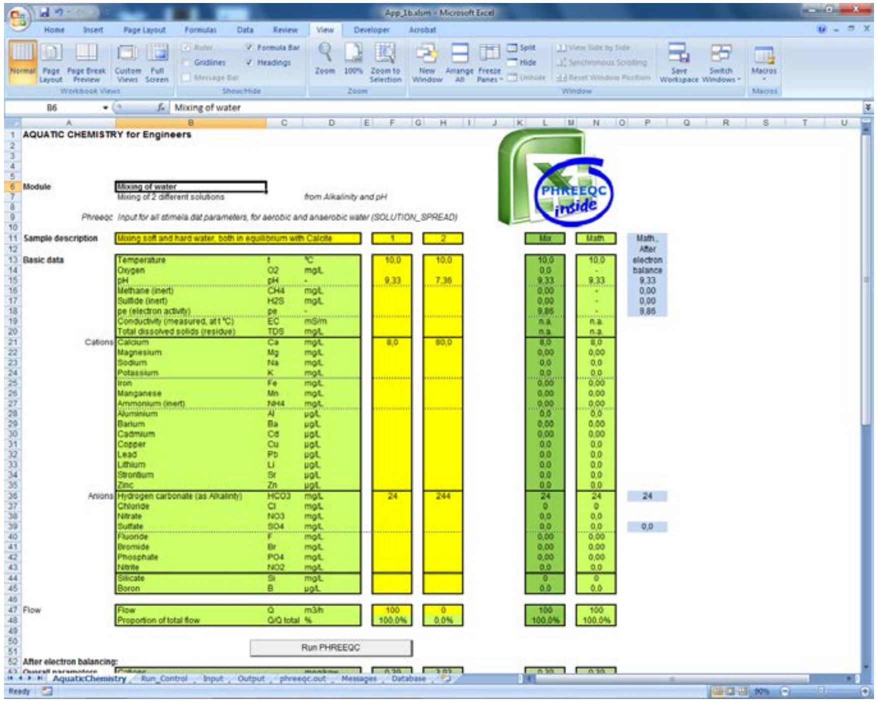
- What is the pH of mixed water ?
    - pH : 9.3 + 7.4 = ???
    - SI : 0 + 0 = < 0



- Application
    - Drinking water : hard water + soft water
    - Sewerage / wastewater: rain water + domestic wastewater

App 1b – Mixing of water

- Open App_1b.xlsm:



Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

Module : Mixing of water

- 1: Soft water
  - Ca = 8 mg/L = 0.2 mmol/kgw
  - pH = 9.33 / Alk = 0.4 meq/kgw
- 2.: Hard water
  - Ca = 80 mg/L = 2 mmol/kgw
  - pH = 7.36 / Alk = 4 meq/kgw

- Calculate pH and SI:
  - A: 1 = 100%
  - B: 2 = 100 %
  - C: 1 = 2 = 50%

- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module — Mixing of water
Mixing of 2 different solutions — *from Alkalinity and pH*

Phreeqc Input for all stimela.dat parameters, for aerobic and anaerobic water (SOLUTION_SPREAD)

Sample description	Mixing soft and hard water, both in equilibrium with Calcite			1	2	Mix	Math.	Math., After electron balance
Basic data	Temperature	t	°C	10,0	10,0	10,0	10,0	
	Oxygen	O2	mg/L			0,0	-	
	pH	pH	-	9,33	7,36	9,33	9,33	9,33
	Methane (inert)	CH4	mg/L			0,00	-	0,00
	Sulfide (inert)	H2S	mg/L			0,00	-	0,00
	pe (electron activity)	pe	-			9,86	-	9,86
	Conductivity (measured, at t °C)	EC	mS/m			n.a.	n.a.	
	Total dissolved solids (residue)	TDS	mg/L			n.a.	n.a.	
Cations	Calcium	Ca	mg/L	8,0	80,0	8,0	8,0	
	Magnesium	Mg	mg/L			0,00	0,00	
	Sodium	Na	mg/L			0,0	0,0	
	Potassium	K	mg/L			0,0	0,0	
	Iron	Fe	mg/L			0,00	0,00	
	Manganese	Mn	mg/L			0,00	0,00	
	Ammonium (inert)	NH4	mg/L			0,00	0,00	
	Aluminium	Al	µg/L			0,0	0,0	
	Barium	Ba	µg/L			0,00	0,00	
	Cadmium	Cd	µg/L			0,00	0,00	
	Copper	Cu	µg/L			0,0	0,0	
	Lead	Pb	µg/L			0,0	0,0	
	Lithium	Li	µg/L			0,0	0,0	
	Strontium	Sr	µg/L			0,0	0,0	
	Zinc	Zn	µg/L			0,0	0,0	
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	24	244	24	24	24
	Chloride	Cl	mg/L			0	0	
	Nitrate	NO3	mg/L			0,0	0,0	
	Sulfate	SO4	mg/L			0,0	0,0	0,0
	Fluoride	F	mg/L			0,00	0,00	
	Bromide	Br	mg/L			0,00	0,00	
	Phosphate	PO4	mg/L			0,00	0,00	
	Nitrite	NO2	mg/L			0,0	0,0	
	Silicate	Si	mg/L			0	0	
	Boron	B	µg/L			0,0	0,0	
Flow	Flow	Q	m3/h	100	0	100	100	
	Proportion of total flow	Q/Q total	%	100,0%	0,0%	100,0%	100,0%	

Run PHREEQC

Aquatic Chemistry for engineers

Module : Mixing of water

Answers:

AQUATIC CHEMISTRY for Engineers

Module Mixing of water
Mixing of 2 different solutions *from Alkalinity and pH*

Phreeqc Input for all stimela.dat parameters, for aerobic and anaerobic water (SOLUTION_SPREAD)

Sample description	Mixing soft and hard water, both in equilibrium with Calcite			1	2	Mix	Math.	Math., After electron balance
Basic data	Temperature	t	°C	10,0	10,0	10,0	10,0	
	Oxygen	O2	mg/L			0,0	-	
	pH	pH	-	9,33	7,36	9,33	9,33	9,33
	Methane (inert)	CH4	mg/L			0,00	-	0,00
	Sulfide (inert)	H2S	mg/L			0,00	-	0,00
	pe (electron activity)	pe	-			9,86	-	9,86
	Conductivity (measured, at t °C)	EC	mS/m			n.a.	n.a.	
	Total dissolved solids (residue)	TDS	mg/L			n.a.	n.a.	
Cations	Calcium	Ca	mg/L	8,0	80,0	8,0	8,0	
	Magnesium	Mg	mg/L			0,00	0,00	
	Sodium	Na	mg/L			0,0	0,0	
	Potassium	K	mg/L			0,0	0,0	
	Iron	Fe	mg/L			0,00	0,00	
	Manganese	Mn	mg/L			0,00	0,00	
	Ammonium (inert)	NH4	mg/L			0,00	0,00	
	Aluminium	Al	µg/L			0,0	0,0	
	Barium	Ba	µg/L			0,00	0,00	
	Cadmium	Cd	µg/L			0,00	0,00	
	Copper	Cu	µg/L			0,0	0,0	
	Lead	Pb	µg/L			0,0	0,0	
	Lithium	Li	µg/L			0,0	0,0	
	Strontium	Sr	µg/L			0,0	0,0	
	Zinc	Zn	µg/L			0,0	0,0	
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	24	244	24	24	24
	Chloride	Cl	mg/L			0	0	
	Nitrate	NO3	mg/L			0,0	0,0	
	Sulfate	SO4	mg/L			0,0	0,0	0,0
	Fluoride	F	mg/L			0,00	0,00	
	Bromide	Br	mg/L			0,00	0,00	
	Phosphate	PO4	mg/L			0,00	0,00	
	Nitrite	NO2	mg/L			0,0	0,0	
	Silicate	Si	mg/L			0	0	
	Boron	B	µg/L			0,0	0,0	
Flow	Flow	Q	m3/h	100	0	100	100	
	Proportion of total flow	Q/Q total	%	100,0%	0,0%	100,0%	100,0%	

Run PHREEQC

Aquatic Chemistry for engineers

Module : Mixing of water

Answers:

- A:
  - pH = 9.33 / SI = 0 (input 1)
- B:
  - pH = 7.36 / SI = 0 (input 2)
- C:
  - pH = 7.45 (not 8.35)
  - SI = - 0.39 (aggressive)
  - CCPP = - 0.11 mmol/kgw
  - CCPP = - aggressive CO_2
  - aggressive CO_2 = 0.11 mmol/kgw
  - pe not reliable (no redox elements)

Flow	Flow	Q	m3/h	50	50	100	100
	Proportion of total flow	Q/Q total	%	50,0%	50,0%	100,0%	100,0%
	Run PHREEQC						
After electron balancing:							
Overall parameters	Cations		meq/kgw	0,39	3,93	2,17	2,15
	Anions		meq/kgw	0,39	3,94	2,18	2,15
	Conductivity (calculated, at t °C)	EC	mS/m	2,8	25,3	14,3	14,2
	Total dissolved solids	TDS	mg/L	32	324	178	178
	Ionic strength	IS	mmol/kgw	0,6	5,9	3,3	3,2
	Total hardness	TH	mmol/kgw	0,2	2,0	1,1	1,1
	Vapor pressure water	pa	atm	0,01	0,01	0,01	0,01
	Density	rho	kg/L	1,000	1,000	1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,00	0,00	0,00	0,00
	pe (electron activity)	pe	-	9,86	-1,79	11,67	10,91
	Redox potential	Eh	mV	553	-101	655	612
Correctness checks	Charge difference		meq/kgw	0,00	-0,01	0,00	0,00
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%	-0,1%	-0,1%	-0,1%
	EC ratio, calculated/measured		-	-	-	-	-
	TDS ratio, measured/calculated		-	-	-	-	-
	Oxygen saturation (with air at sea level)		atm/atm	0,0%	0,0%	0,0%	0,0%
	pH change by electron balancing (Phreeqc)		-	0,00	0,00	-	0,00
	pe change by electron balancing (Phreeqc)		-	-	-	-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	9,33	7,36	7,45	8,35
	Alkalinity	m	meq/kgw	0,40	4,00	2,20	2,20
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	0,36	4,45	2,41	2,19
	CO2	CO2	mmol/kgw	0,00	0,46	0,21	0,03
	HCO3 -	HCO3	mmol/kgw	0,33	3,93	2,17	2,11
	CO3 2-	CO3	mmol/kgw	0,03	0,00	0,00	0,02
Calcite equilibrium	SI (calcite)	SI-c	-	0,00	0,00	-0,39	0,50
	Calcite Precipitation Potential	CPP	mmol/kgw	0,00	0,00	-0,11	0,07

Aquatic Chemistry for engineers

Module : Mixing of water - PHREEQC code

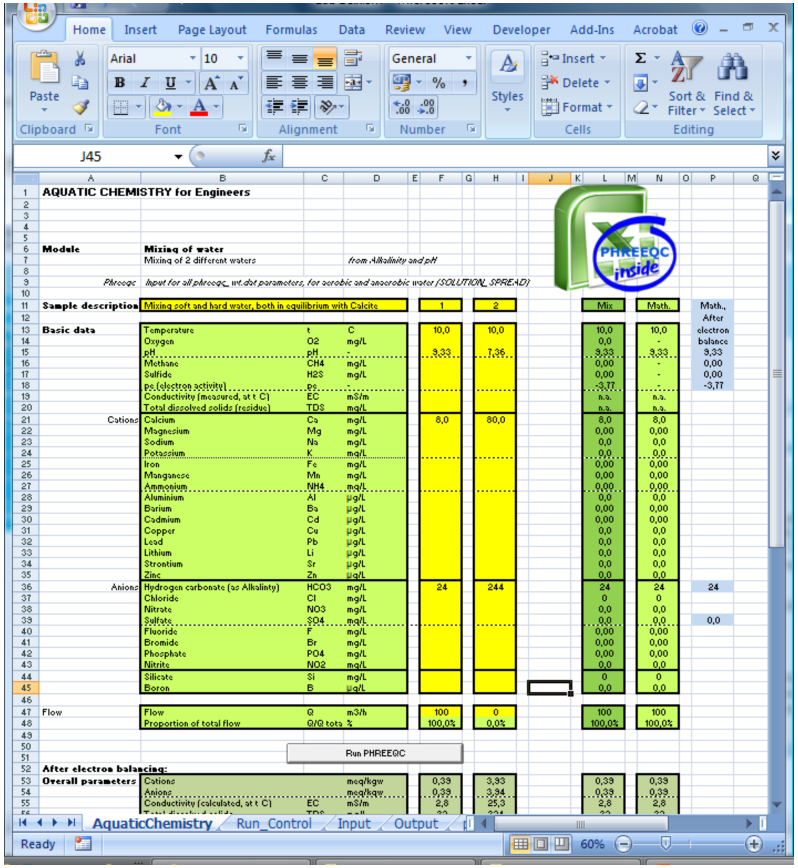
- Code for output
  - PRINT
  - SELECTED OUTPUT
  - USER PUNCH
  - CALCULATE_VALUES
- SOLUTION_SPREAD
  - 1 / 2 / 3 (= math)
  - electron balance
- MIX
  - 1 0.5 # 0.5 of Solution 1 (= mass)
  - 2 0.5 # 0.5 of Solution 2 (= mass)
- EQUILIBRIUM_PHASES (for CCPP)

```
            60      PUNCH CALC_VALUE("Anion") + TOT("charge")     # Cation = Anion + ChargeBalans
            70      PUNCH CALC_VALUE("Anion")
      -end

CALCULATE_VALUES    # declaration of procedures (functions)
Anion               # Calculate Anion concentration from Charge Balance (=Cat-An) and Error (=(Cat-An)/(Cat+An))
      -start
            10      DELTA = TOT("charge")            # Charge Balance as Concentration (equal to CHARGE_BALANCE / TOT("water") )
            20      ERROR = PERCENT_ERROR/100        # Error as Fraction
            30      AN = (DELTA/ERROR - DELTA)/2     # Calculate by substitution
            40      SAVE AN                          # Algorithm less reliable at very small ERROR value
      -end

# END   # with an END statement the declarations above are regarded as "Simulation 1"


SOLUTION_SPREAD
      -units        mg/kgs
      -redox        pe          # if O2>0 then "O(-2)/O(0)" else if CH4>0 then "C(-4)/C(4)" else "pe"
      -density         1
      -water           1
# Simulation 1 with water quality data from sheet AquaticChemistry
Number  Temperatu O(0)  pH    [C-4]   [S-2]   pe    Ca     Mg    Na    K     Fe    Mn    [N-3]  Al     Ba     Cd
                              as CH4  as H2S                                                   ug/kgs ug/kgs ug/kgs
1       10.0      0.0   9.33  0.00    0.00    4.00  8.00   0.00  0.00  0.00  0.00  0.00  0.00   0.00   0.00   0.00
2       10.0      0.0   7.36  0.00    0.00    4.00  80.00  0.00  0.00  0.00  0.00  0.00  0.00   0.00   0.00   0.00
3       10.0      0.0   8.35  0.00    0.00    4.00  44.00  0.00  0.00  0.00  0.00  0.00  0.00   0.00   0.00   0.00
END     # Simulation 1


# calculate pe (with electron balancing) for analyse check
# for all solutions
USE SOLUTION  1;    EQUILIBRIUM_PHASES ;   END   # simulation 2
USE SOLUTION  2;    EQUILIBRIUM_PHASES ;   END   # simulation 3
USE SOLUTION  3;    EQUILIBRIUM_PHASES ;   END   # simulation 4

# mix , values from initial solution
MIX
1       0.50    # fraction x of SOLUTION 1 (= mass) is mixed with
2       0.50    # fraction y of SOLUTION 2 (= mass)
SAVE Solution 4
END  # Simulation 5

# calculate CCPP for all solutions
USE SOLUTION  1;    EQUILIBRIUM_PHASES ;   Calcite ;    END   # simulation 6
USE SOLUTION  2;    EQUILIBRIUM_PHASES ;   Calcite ;    END   # simulation 7
USE SOLUTION  3;    EQUILIBRIUM_PHASES ;   Calcite ;    END   # simulation 8
USE SOLUTION  4;    EQUILIBRIUM_PHASES ;   Calcite ;    END   # simulation 9
```

Conclusions - Lessons learned

Oxidation state (Redox)

- ‘Funny’ pe results
- PHREEQC and REDOX
  - change in water quality
  - reactions to redox equilibrium
- To do
  - include a redox couple
  - O_2 for aerobic water
  - CH_4 for anaerobic water
- Check your PHREEQC results
  - What happened ?

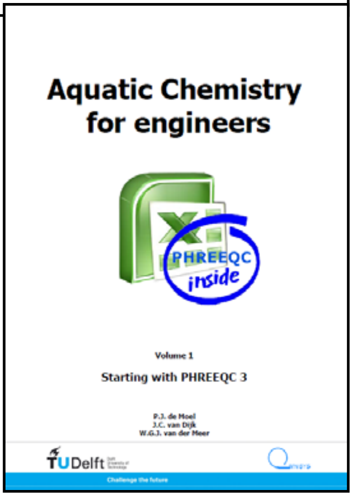


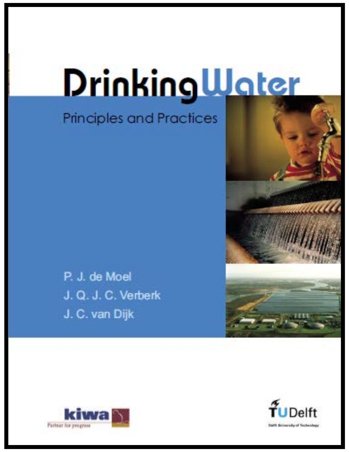
Questions?

Course program

Aquatic Chemistry for engineers

- Introduction (lecture + Starting with PHREEQC 3)
  - PHREEQC – PHREEQC Interactive – PHREEQC-COM
- Drinking water (App 1a+b)
  - Chemistry: SI / CCPP / Buffercapacity / Corrosion
  - Engineering: Ionic balance / Conductivity / Mixing
- Gases in water (App 2a+b+c)
  - Chemistry: solubility O_2, N_2, CO_2 , CH_4 etc
  - Engineering: P*V/T = R   / Biodegradation wastewater
- Hardness and pH (App 3a+b)
  - Chemistry: acid/base, solubility $CaCO_3$, $FeCO_3$, etc
  - Engineering: pH control / Neutralization / Softening





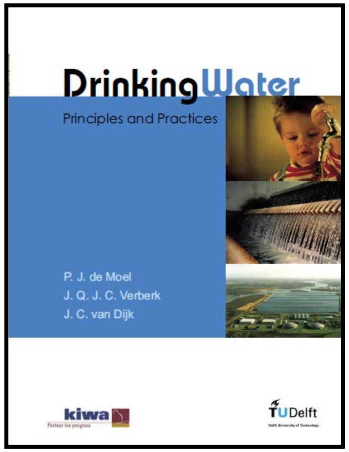
Aquatic Chemistry for engineers

Module : Gases in water (App 2a)

- Solubility of O_2
  - Drinking water: aeration of groundwater
  - Aerobic wastewater treatment
  - Influences of temperature and ionic strength

- Solublility of other gases
  - Carbon dioxide - CO_2
  - Methane – CH_4
  - Anaerobic wastewater treatment

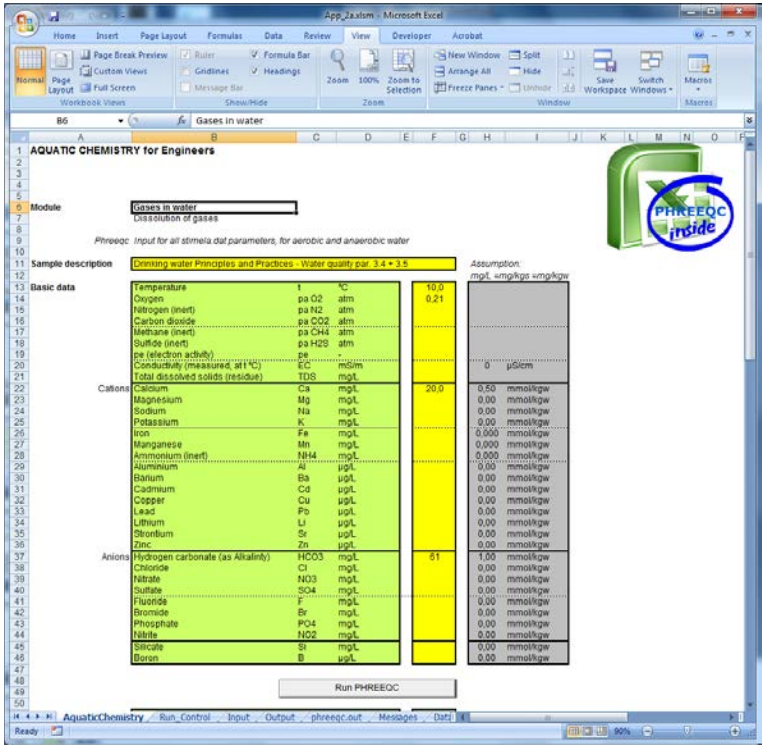
- Application
  - Drinking water : aeration / stripping (gas exchange)
  - Sewerage / wastewater: aerobic and anaerobic treatment, digisters



Water quality
3.4 + 3.5

App 2a - Gases in water

- Open App_2a.xlsm:



Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

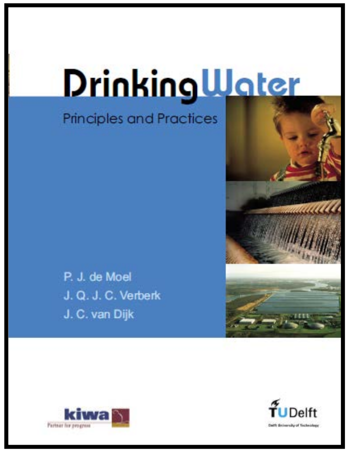
Item : Solubility of gases in water

Computation of gas concentration in water

Compute the oxygen concentration in water, which is in free exchange to open air (at 10°C, 1 bar = 101,325 Pa).

At sea level, air contains approximately 21 volume percent of oxygen.
The molar fraction of oxygen amounts to 0.21.
The partial pressure is 0.21 bar or (101,325 · 0.21 =) 21,300 Pa.

The oxygen concentration in air is: (21,300 / (8.3143 · (273+10)) =) 9.05 mol/m³.
Having a Henry coefficient of 0.041 for oxygen, the oxygen concentration in water will be: (0.041 · 9.05 =) 0.37 mol/m³.
At a molar mass of 32 g this amounts to (0.37 · 32 =) 12 g/m³ (mg/l).



- Henry's law: $H = \frac{c_w}{c_g}$ with : $c_g = \frac{p_a}{RT}$ for each gas

$$c_w = \frac{p_a}{RT} H$$

Aquatic Chemistry for engineers

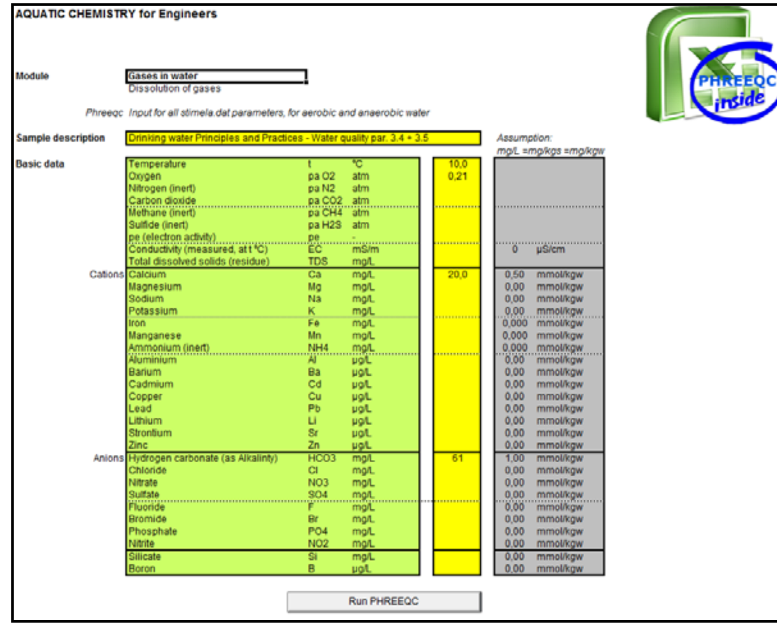
Item : Solubility of gases in water - oxygen

- Atmospheric (dry) air
  - O_2 21% p_a = 0.21 atm
- Water
  - Ca= 20 mg/L Alk=61 mg/L HCO_3
- Calculate O_2 content in water:
  - A: at 10 ^{0}C
  - B: at 25 ^{0}C
  - C: at 90 ^{0}C
  - D: at 10 ^{0}C in seawater

    assume for seawater extra NaCl:

    Na = 0.47 mol/kgw =10,800 mg/L

    Cl = 0.55 mol/kgw = 19,500 mg/L
- I give you 3 minutes….



AQUATIC CHEMISTRY for Engineers

Module: Gases in water
Dissolution of gases

Phreeqc: *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description: Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption: mg/L =mg/kgs =mg/kgw

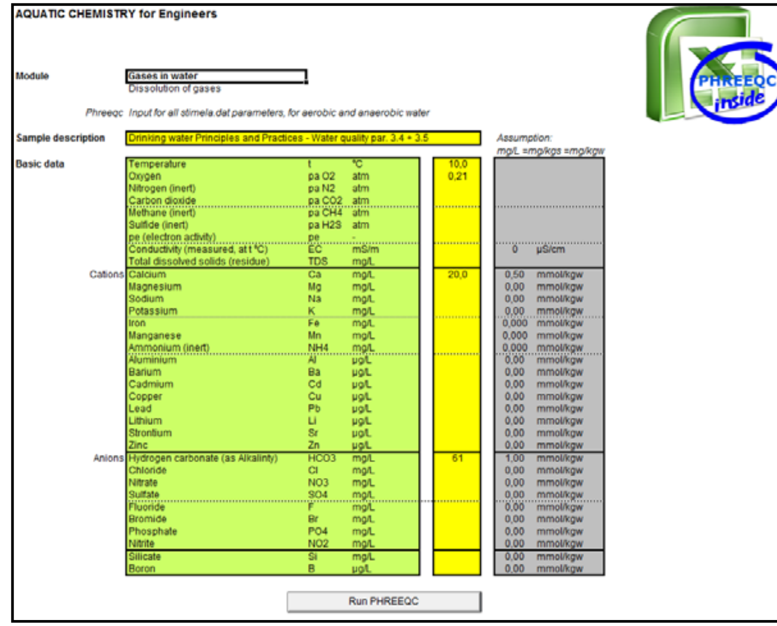
Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm			
	Carbon dioxide	pa CO2	atm			
	Methane (inert)	pa CH4	atm			
	Sulfide (inert)	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	20,0	0,50	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	61	1,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

Run PHREEQC

Aquatic Chemistry for engineers

Item : Solubility of gases in water - oxygen

Answers:



AQUATIC CHEMISTRY for Engineers

Module Gases in water
Dissolution of gases

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption:
mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm			
	Carbon dioxide	pa CO2	atm			
	Methane (inert)	pa CH4	atm			
	Sulfide (inert)	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	20,0	0,50	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	61	1,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

Run PHREEQC

Aquatic Chemistry for engineers

Item : Solubility of gases in water - oxygen

Answers:

- O_2 content mmol/kgw mg/L
  - A: 10 ^{0}C 0.36 11.5
  - B: 25 ^{0}C 0.27 8.6
  - C: 90 ^{0}C 0.16 5.2
  - D: 10 ^{0}C seawater 0.32 10.2
- Higher temperature (phreeqc.out)
  - 10 ^{0}C: $H=K=10^{-2.77} = 0.00170$
  - 90 ^{0}C: $H=K=10^{-3.11} = 0.00079$
- Higher salt content (phreeqc.out)
  - "Salting out" $\{O_2\} = \text{gamma}\,[O_2]$
  - Seawater: $\text{gamma} = 10^{0.053} = 1.13$

Run PHREEQC

Overall parameters	Cations		meq/kgw	0,99		
	Anions		meq/kgw	1,00		
	Conductivity (calculated, at t °C)	EC	mS/m	6,7	1	μS/cm
	Total dissolved solids	TDS	mg/L	81		
	Ionic strength	IS	mmol/kgw	1,5		
	Total hardness	TH	mmol/kgw	0,50	2,8	°D
	Vapor pressure water	pa	atm	0,01		
	Density	rho	kg/L	1,000		
Redox conditions	Oxygen	O2	mmol/kgw	0,36	11,5	mg/L
	pe (electron activity)	pe	-	14,97		
	Redox potential	Eh	mV	840		
Correctness checks	Charge difference		meq/kgw	0,00		
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			0,0%		
	EC ratio, calculated/measured		-	-		
	TDS ratio, measured/calculated		-	-		
	Oxygen saturation (with air at sea level)		atm/atm	102,2%		
	pH change by electron balancing (Phreeqc)		-	0,00		
	pe change by electron balancing (Phreeqc)		-	-		
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,00		
	Alkalinity	m	meq/kgw	1,00		
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	1,28	15	mg/L C
	CO2	CO2	mmol/kgw	0,28	12,21	mg/L
	HCO3 -	HCO3	mmol/kgw	0,99	61	mg/L
	CO3 2-	CO3	mmol/kgw	0,00	0	mg/L
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,18		
	Buffer capacity	BI	mmol/kgw /pH	0,51		
Calcite equilibrium	SI (calcite)	SI-c	-	-1,48		
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	8,48		
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,26	11	mg/L CO2
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,21	9	mg/L CO2
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	-0,14	6	mg/L CO2
Gases in water	Oxygen	O2	mmol/kgw	0,36	11,5	mg/L
	Nitrogen	N2	mmol/kgw	0,00	0,0	mg/L
	Carbon dioxide	CO2	mmol/kgw	0,28	12,21	mg/L
	Methane	CH4	mmol/kgw	0,00	0,00	mg/L
	Sulfide	H2S	mmol/kgw	0,00	0,00	mg/L
	Ammonia	NH3	mmol/kgw	0,00	0,00	mg/L
Gases in gas						
Elements / Species	C		mmol/kgw	1,28		
	CO2			21,7%	12	mg/L

Aquatic Chemistry for engineers

Module : Solubility of gases in water - PHREEQC code

- Code for output
  - PRINT / SELECTED OUTPUT etc

- SOLUTION 1
  - O(0) 1 O2(g) -0.6778

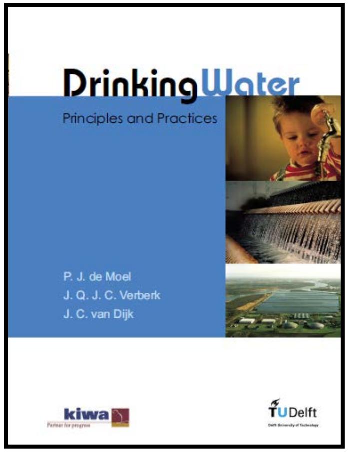
  element dummy phase SI = log(p_a)

- Others
  - electron balance
  - CCPP
  - Buffer capacity
  - CCPP at 60 / 90 ^{0}C

```
                70      PUNCH CALC_VALUE("Anion")
        -end

CALCULATE_VALUES        # declaration of procedures (functions)
Anion                   # Calculate Anion concentration from Charge Balance (=Cat-An) and
        -start
                10      DELTA = TOT("charge")                  # Charge Bal
                20      ERROR = PERCENT_ERROR/100              # Error as Fra
                30      AN = (DELTA/ERROR - DELTA)/2           # Calculate b
                40      SAVE AN                                # Algorithm le
        -end

# END   # with an END statement the declarations above are regarded as "Simulation 1"


SOLUTION                1
        -units          mg/kgs
        -redox          O(-2)/O(0)                 #  if O2>0 then "O(-2)/O(0)" else if C
        -density        1
        -water          1
        -pe             4.00                       #  if pe = empty then pe = 4
        temp    10.0
        O(0)    1       O2(g)       -0.6778        # SI = log(pa)
#       N(0)    1       N2(g)       #NUM!          # SI = log(pa)
#       Ntg     1       Ntg(g)      #NUM!          # SI = log(pa)
#       C(4)    1       CO2(g)      #NUM!          # SI = log(pa)
#       [C-4]   1       [C-4]H4(g)  #NUM!          # SI = log(pa)
#       [S-2]   1       H2[S-2](g)  #NUM!          # SI = log(pa)
        Ca      20.00
        Mg      0.00
        Na      10800.00
        K       0.00
        Fe      0.00
        Mn      0.00
```

Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases



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At sea level, air contains 78% nitrogen, 21% oxygen, 1% argon and 0.032% carbon dioxide. The volume fractions of the other gases (methane, hydrogen sulfide) are even lower. From this information one can compute that water, when it is in equilibrium with air at 10°C and 1 bar, contains 11.9 mg/l of oxygen (O_2), 17.9 mg/l of nitrogen (N_2) and 0.75 mg/l of carbon dioxide (CO_2).

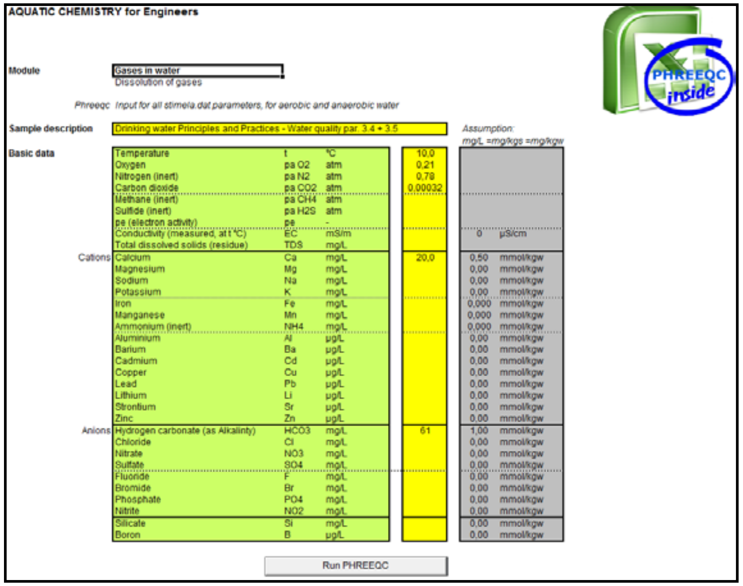
- Henry's law: $H = \frac{c_w}{c_g}$ with : $c_g = \frac{p_a}{RT}$ for each gas

$$c_w = \frac{p_a}{RT} H$$

Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases

- Atmospheric (dry) air
  - N_2 78% $p_a = 0.78$ atm
  - O_2 21% $p_a = 0.21$ atm
  - Ar 1% $p_a = 0.01$ atm
  - CO_2 0.032% $p_a = 0.00032$ atm
  - Argon is not in stimela.dat
- Water
  - Ca= 20 mg/L Alk=61 mg/L HCO_3
- Calculate gas contents in water:
  - A: at 10 ^{0}C
- I give you 3 minutes....


AQUATIC CHEMISTRY for Engineers

Module: Gases in water
Dissolution of gases

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption: mg/L =mg/kgs =mg/kgw

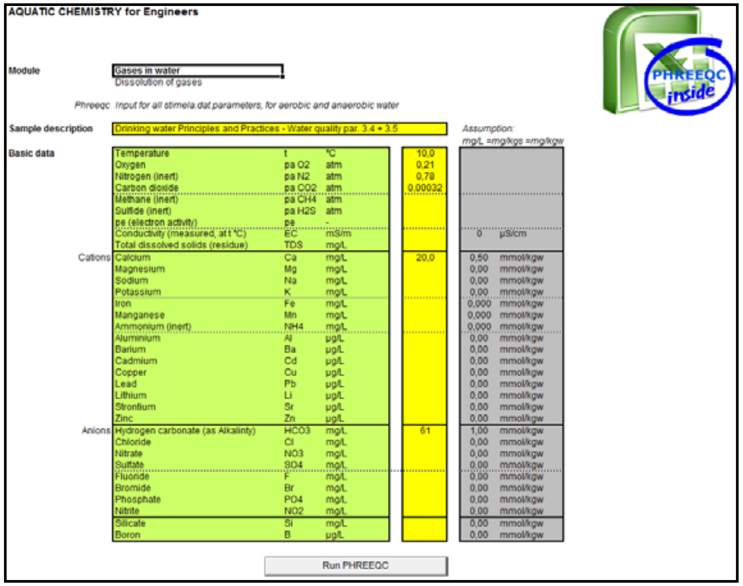
Basic data	Temperature	t	°C	10,0	
	Oxygen	pa O2	atm	0,21	
	Nitrogen (inert)	pa N2	atm	0,78	
	Carbon dioxide	pa CO2	atm	0,00032	
	Methane (inert)	pa CH4	atm		
	Sulfide (inert)	pa H2S	atm		
	pe (electron activity)	pe	-		
	Conductivity (measured, at t °C)	EC	mS/m		0 µS/cm
	Total dissolved solids (residue)	TDS	mg/L		
Cations	Calcium	Ca	mg/L	20,0	0,50 mmol/kgw
	Magnesium	Mg	mg/L		0,00 mmol/kgw
	Sodium	Na	mg/L		0,00 mmol/kgw
	Potassium	K	mg/L		0,00 mmol/kgw
	Iron	Fe	mg/L		0,000 mmol/kgw
	Manganese	Mn	mg/L		0,000 mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000 mmol/kgw
	Aluminium	Al	µg/L		0,00 mmol/kgw
	Barium	Ba	µg/L		0,00 mmol/kgw
	Cadmium	Cd	µg/L		0,00 mmol/kgw
	Copper	Cu	µg/L		0,00 mmol/kgw
	Lead	Pb	µg/L		0,00 mmol/kgw
	Lithium	Li	µg/L		0,00 mmol/kgw
	Strontium	Sr	µg/L		0,00 mmol/kgw
	Zinc	Zn	µg/L		0,00 mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	61	1,00 mmol/kgw
	Chloride	Cl	mg/L		0,00 mmol/kgw
	Nitrate	NO3	mg/L		0,00 mmol/kgw
	Sulfate	SO4	mg/L		0,00 mmol/kgw
	Fluoride	F	mg/L		0,00 mmol/kgw
	Bromide	Br	mg/L		0,00 mmol/kgw
	Phosphate	PO4	mg/L		0,00 mmol/kgw
	Nitrite	NO2	mg/L		0,00 mmol/kgw
	Silicate	Si	mg/L		0,00 mmol/kgw
	Boron	B	µg/L		0,00 mmol/kgw

Run PHREEQC

Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases

Answers:



AQUATIC CHEMISTRY for Engineers

Module Gases in water
Dissolution of gases

Phreeqc Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm	0,78		
	Carbon dioxide	pa CO2	atm	0,00032		
	Methane (inert)	pa CH4	atm			
	Sulfide (inert)	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	20,0	0,50	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	61	1,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

Run PHREEQC

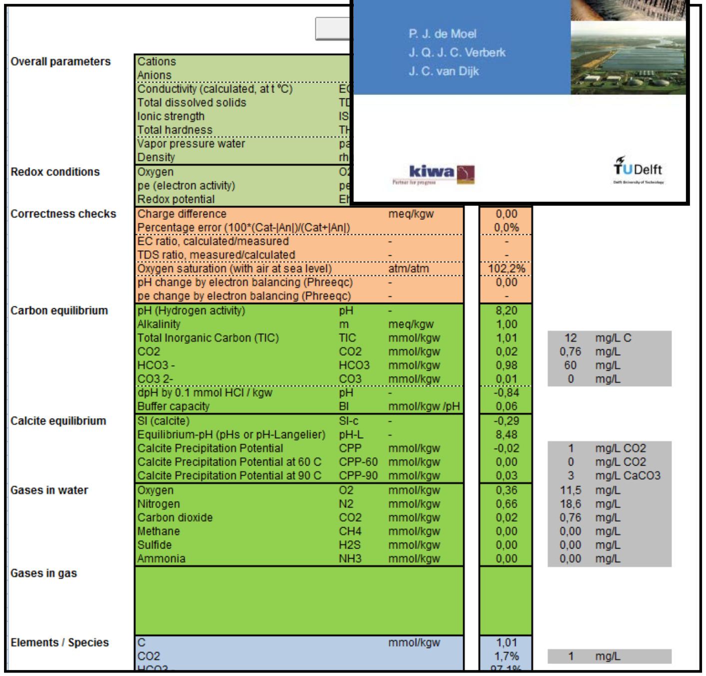
Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases

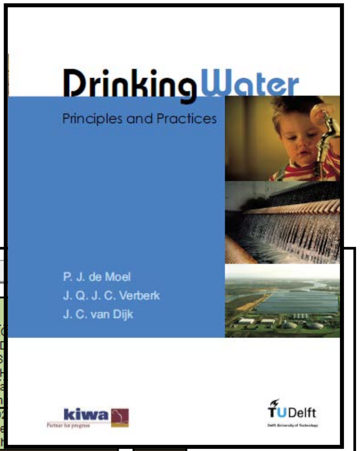
Answers:

Content	PHREEQC mmol/kgw	PHREEQC mg/L	DW P&P mg/L
• O_2:	0.36	11.5	11.9
• N_2:	0.66	18.6	17.9
• Ar:	-	-	-
• CO_2	0.02	0.76	0.75

- O_2 more soluble than N_2
  - $p_a\ N_2 = 4 * p_a\ O_2$
- CO_2 is very soluble
  - $p_a\ O_2 = 650 * p_a\ CO_2$ $[O_2] = 18 * [CO_2]$
  - CO_2 stripping > 1 mg/L



Overall parameters	Cations					
	Anions					
	Conductivity (calculated, at t °C)	EC				
	Total dissolved solids	TD				
	Ionic strength	IS				
	Total hardness	TH				
	Vapor pressure water	pa				
	Density	rh				
Redox conditions	Oxygen	O2				
	pe (electron activity)	pe				
	Redox potential	Eh				
Correctness checks	Charge difference		meq/kgw	0,00		
	Percentage error (100*(Cat-|An|)/(Cat+|An|))			0,0%		
	EC ratio, calculated/measured		-	-		
	TDS ratio, measured/calculated		-	-		
	Oxygen saturation (with air at sea level)		atm/atm	102,2%		
	pH change by electron balancing (Phreeqc)		-	0,00		
	pe change by electron balancing (Phreeqc)		-	-		
Carbon equilibrium	pH (Hydrogen activity)	pH	-	8,20		
	Alkalinity	m	meq/kgw	1,00		
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	1,01	12	mg/L C
	CO2	CO2	mmol/kgw	0,02	0,76	mg/L
	HCO3 -	HCO3	mmol/kgw	0,98	60	mg/L
	CO3 2-	CO3	mmol/kgw	0,01	0	mg/L
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,84		
	Buffer capacity	BI	mmol/kgw /pH	0,06		
Calcite equilibrium	SI (calcite)	SI-c	-	-0,29		
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	8,48		
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,02	1	mg/L CO2
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,00	0	mg/L CO2
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,03	3	mg/L CaCO3
Gases in water	Oxygen	O2	mmol/kgw	0,36	11,5	mg/L
	Nitrogen	N2	mmol/kgw	0,66	18,6	mg/L
	Carbon dioxide	CO2	mmol/kgw	0,02	0,76	mg/L
	Methane	CH4	mmol/kgw	0,00	0,00	mg/L
	Sulfide	H2S	mmol/kgw	0,00	0,00	mg/L
	Ammonia	NH3	mmol/kgw	0,00	0,00	mg/L
Gases in gas						
Elements / Species	C		mmol/kgw	1,01		
	CO2			1,7%	1	mg/L



Aquatic Chemistry for engineers

Module : Solubility of gases in water - PHREEQC code

- Code for output
  - PRINT / SELECTED OUTPUT etc
- SOLUTION 1
  - O(0) 1 O2(g) -0.6778

  element dummy phase SI = log(p_a)
  - Other gases
- Others
  - electron balance
  - CCPP
  - Buffer capacity
  - CCPP at 60 / 90 ^{0}C

SOLUTION		1			
	-units		mg/kgs		
	-redox		O(-2)/O(0)		# if O2>0 then "O(-2)/O(0)" else if CH
	-density		1		
	-water		1		
	-pe		4.00		# if pe = empty then pe = 4
	temp	10.0			
	O(0)	1	O2(g)	-0.6778	# SI = log(pa)
#	N(0)	1	N2(g)	-0.1079	# SI = log(pa)
	Ntg	1	Ntg(g)	-0.1079	# SI = log(pa)
	C(4)	1	CO2(g)	-3.4949	# SI = log(pa)
#	[C-4]	1	[C-4]H4(g)	#NUM!	# SI = log(pa)
#	[S-2]	1	H2[S-2](g)	#NUM!	# SI = log(pa)
	Ca	20.00			
	Mg	0.00			
	Na	0.00			
	K	0.00			
	Fe	0.00			
	Mn	0.00			
	[N-3]	0.00	as NH4		
#	N(-3)	0.00	as NH4		
	Al	0.00	ug/kgs		
	Ba	0.00	ug/kgs		
	Cd	0.00	ug/kgs		
	Cu	0.00	ug/kgs		
	Pb	0.00	ug/kgs		

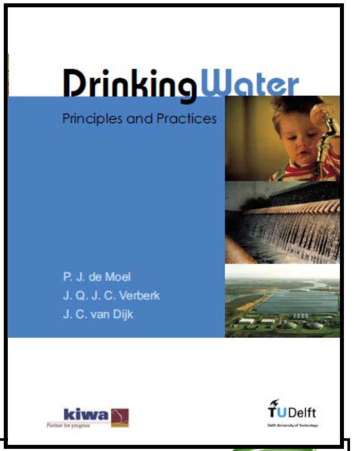
Conclusions - Lessons learned

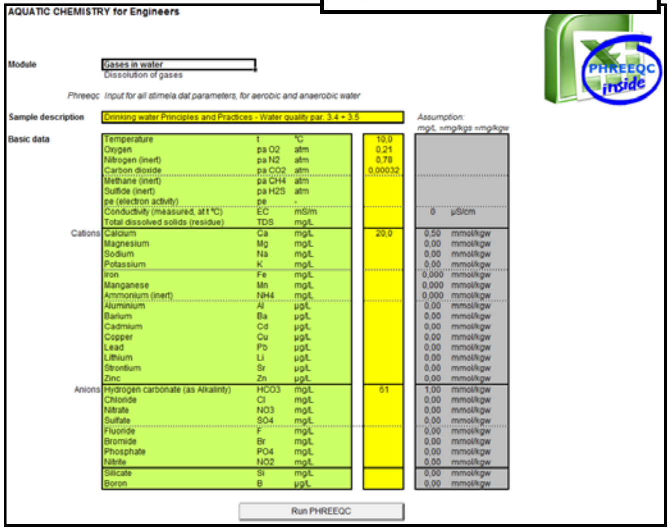
Solubility of gases in water

- Content of gases in water:
  - Can also be expressed as p_a of gas
  - Henry's law = equilibrium

- PHREEQC gives H_2O also as gas
  - p_a H_2O = vapor pressure

- PHREEQC is more exact:
  - Influence gamma (ionic strength)





Questions?

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO_2 and pH

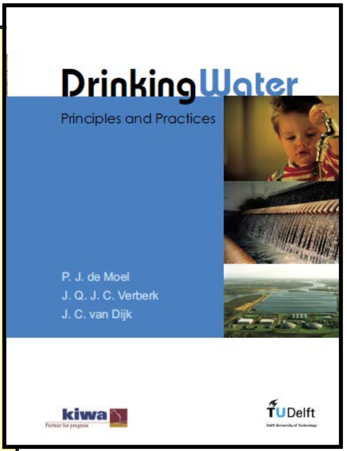
Dissociation of carbon dioxide

A spring water factory puts 4.4 g CO_2 in 1 liter of demineralized water.
What will be the pH value of this water?
What amount of true CO_2 will be in the water?
What will be the pH value when 1 mmol/l HCO_3^- is added?

The inserted amount of CO_2 (or H_2CO_3) is 4.4 / 44 = 0.1 mol.
When x mol of CO_2 dissociates, x mol H^+, x mol HCO_3^- and 1 - x mol CO_2 will be formed (neglecting the amount of HCO_3^- that is transformed into CO_3^{2-}).
From $K_1 = x \cdot x / (0.1 - x) = 4.5\ 10^{-7}$ it follows that $x = 0.00021$ mol/l or 0.21 mmol/l.
Thus, the pH value will be $pH = -\log(0.00021) = 3.68$.

From $K_2 = 4.7 \cdot 10^{-11} = [H^+]\,[CO_3^{2-}] / [HCO_3^-]$ and after entering the known values for H^+ and HCO_3^- it follows that $CO_3^{2-} = 4.7 \cdot 10^{-11}$. This can indeed be neglected, so that:
$[CO_2] = 100 - 0.21 = 99.79$ mmol/l and $[HCO_3^-] = 0.21$ mmol/l
(meaning that 0.2% has dissociated)

After adding 1 mmol/l HCO_3^- the pH value will be:
$pH = 6.35 - \log\{99.79 / (0.21+1.00)\} = 6.35 - 1.92 = 4.43$

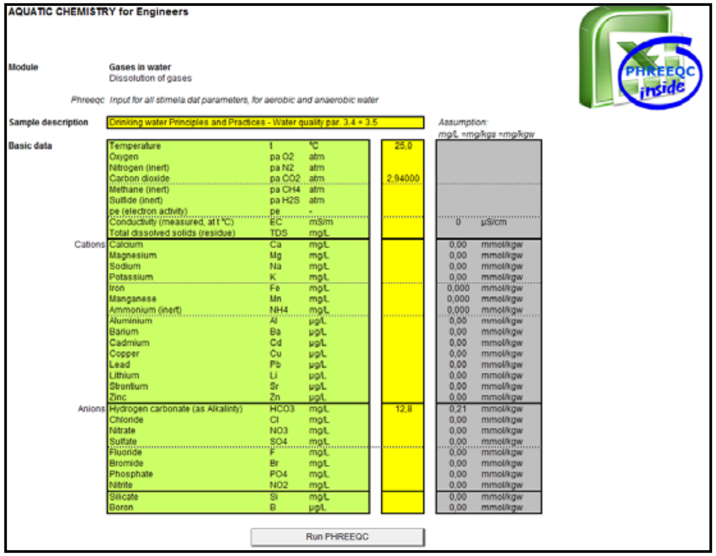


CO_2 = 4.4 g/L = 4,400 mg/L : $p_a\ CO_2$ = 2.94 atm at 25 ^{0}C

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO_2 and pH

- CO_2 in water
  - CO_2 — p_a = 2.94 atm
  - Temperature — 25 ^{0}C
- Calculate pH:
  - A: Alkalinity — 12.8 mg/L HCO_3 (=0.21 meq/L)
  - B: Alkalinity — 73.8 mg/L HCO_3 (= 1.21 meq/L)



AQUATIC CHEMISTRY for Engineers

Module: **Gases in water** — Dissolution of gases

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption: mg/L =mg/kgs =mg/kgw

	Parameter	Symbol	Unit	Input	Calc.	Unit
Basic data	Temperature	t	°C	25,0		
	Oxygen	pa O2	atm			
	Nitrogen (inert)	pa N2	atm			
	Carbon dioxide	pa CO2	atm	2,94000		
	Methane (inert)	pa CH4	atm			
	Sulfide (inert)	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	12,8	0,21	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

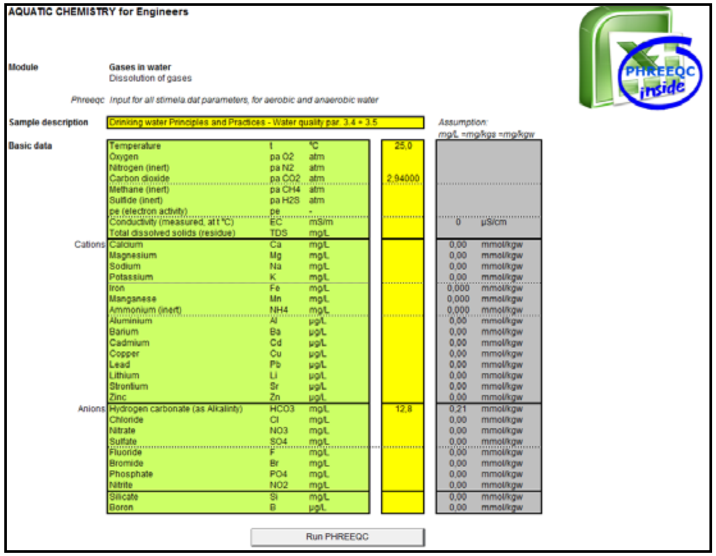
Run PHREEQC

- I give you 3 minutes….

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO_2 and pH

Answers:



AQUATIC CHEMISTRY for Engineers

Module — **Gases in water**
Dissolution of gases

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Water quality par. 3.4 + 3.5

Assumption:
mg/L =mg/kgs =mg/kgw

Basic data

	Temperature	t	°C	25,0		
	Oxygen	pa O2	atm			
	Nitrogen (inert)	pa N2	atm			
	Carbon dioxide	pa CO2	atm	2,94000		
	Methane (inert)	pa CH4	atm			
	Sulfide (inert)	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	12,8	0,21	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

Run PHREEQC

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO_2 and pH

Answers:

pH	PHREEQC pH	DW P&P pH
• A: Alk = 0.21	3.88	3.68
• B: Alk= 1.21	4.44	4.43

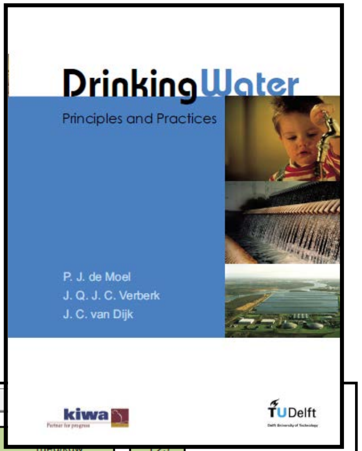
(Alk in meq/kgw)

- PHREEQC calculates pH from $HCO_3^- + CO_2$:

  $$pH = pK_1 - \log(\{CO_2\} / \{HCO_3^-\})$$

- DW P&P calculates pH from $HCO_3^- + CO_2$:

  $$pH = pK_1 - \log([CO_2] / [HCO_3^-])$$



Overall parameters	Cations					
	Anions		meq/kgw	1,25		
	Conductivity (calculated, at t °C)	EC	mS/m	6,7	1	µS/cm
	Total dissolved solids	TDS	mg/L	74		
	Ionic strength	IS	mmol/kgw	0,6		
	Total hardness	TH	mmol/kgw	0,00	0,0	°D
	Vapor pressure water	pa	atm	0,03		
	Density	rho	kg/L	0,999		
Redox conditions	Oxygen	O2	mmol/kgw	1,28	41,0	mg/L
	pe (electron activity)	pe	-	16,36		
	Redox potential	Eh	mV	967		
Correctness checks	Charge difference		meq/kgw	-1,21		
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			0,0%		
	EC ratio, calculated/measured		-	-		
	TDS ratio, measured/calculated		-	-		
	Oxygen saturation (with air at sea level)		atm/atm	0,0%		
	pH change by electron balancing (Phreeqc)		-	0,00		
	pe change by electron balancing (Phreeqc)		-	-		
Carbon equilibrium	pH (Hydrogen activity)	pH	-	4,44		
	Alkalinity	m	meq/kgw	1,21		
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	101,19	1215	mg/L C
	CO2	CO2	mmol/kgw	99,95	4398,70	mg/L
	HCO3 -	HCO3	mmol/kgw	1,25	76	mg/L
	CO3 2-	CO3	mmol/kgw	0,00	0	mg/L
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,04		
	Buffer capacity	BI	mmol/kgw /pH	2,91		
Calcite equilibrium	SI (calcite)	SI-c	-	-		
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	-		
	Calcite Precipitation Potential	CPP	mmol/kgw	-13,21	581	mg/L CO2
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-9,55	420	mg/L CO2
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	-6,42	283	mg/L CO2
Gases in water	Oxygen	O2	mmol/kgw	1,28	41,0	mg/L
	Nitrogen	N2	mmol/kgw	0,00	0,0	mg/L
	Carbon dioxide	CO2	mmol/kgw	99,95	4398,70	mg/L
	Methane	CH4	mmol/kgw	0,00	0,00	mg/L
	Sulfide	H2S	mmol/kgw	0,00	0,00	mg/L
	Ammonia	NH3	mmol/kgw	0,00	0,00	mg/L

Aquatic Chemistry for engineers

Module : Solubility of gases in water - PHREEQC code

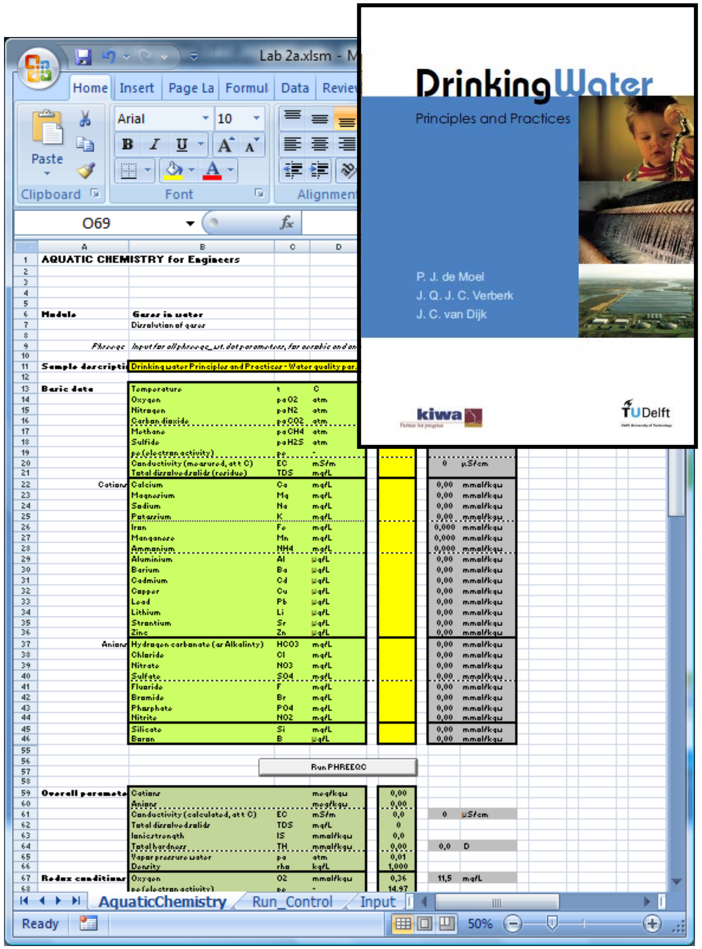
- Code for output
  - PRINT / SELECTED OUTPUT etc
- SOLUTION 1
  - C(4) 1 CO2(g) 0.4683
    Input as phase SI = log(p_a)
  - Similar for other gases
  - Alkalinity >= 0.001 mg/L HCO3
    To get pH calculation from CO_2 + Alk
- Others
  - electron balance
  - CCPP + Buffer capacity + CCPP at 60 / 90 ^{0}C

```
                10      DELTA = TOT("charge")                       # Charge Balance as Concentration (equal to CHARGE_BAL
                20      ERROR = PERCENT_ERROR/100                   # Error as Fraction
                30      AN = (DELTA/ERROR - DELTA)/2                # Calculate by substitution
                40      SAVE AN                                     # Algorithm less reliable at very small ERROR value
        -end

# END   # with an END statement the declarations above are regarded as "Simulation 1"



SOLUTION                1
        -units          mg/kgs
        -redox          pe                      #  if O2>0 then "O(-2)/O(0)" else if CH4>0 then "C(-4)/C(4)" else "pe"
        -density        1
        -water          1
        -pe             4.00                    #  if pe = empty then pe = 4
        temp    25.0
        O(0)    1       O2(g)       #NUM!       # SI = log(pa)
#       N(0)    1       N2(g)       #NUM!       # SI = log(pa)
#       Ntg     1       Ntg(g)      #NUM!       # SI = log(pa)
        C(4)    1       CO2(g)      0.4683      # SI = log(pa)
#       [C-4]   1       [C-4]H4(g)  #NUM!       # SI = log(pa)
#       [S-2]   1       H2[S-2](g)  #NUM!       # SI = log(pa)
        Ca      0.00
        Mg      0.00
        Na      0.00
        K       0.00
        Fe      0.00
        Mn      0.00
        [N-3]   0.00    as NH4
#       N(-3)   0.00    as NH4
        Al      0.00    ug/kgs
        Ba      0.00    ug/kgs
        Cd      0.00    ug/kgs
        Cu      0.00    ug/kgs
        Pb      0.00    ug/kgs
        Li      0.00    ug/kgs
        Sr      0.00    ug/kgs
        Zn      0.00    ug/kgs
        Alkalinity 0.001 as HCO3                # default Alkalinity = 0.001 to avoid pH=7 (default of PHREEQC ) with given CO2
        Cl      0.00
        N(+5)   0.00    as NO3
```

Conclusions - Lessons learned

Solubility of gases in water

- Content of gases in water:
  - Can also be expressed as p_a of gas
  - Henry's law = equilibrium
- Carbonated drinks:
  - Soda (= $NaCO_3$) water = CO_2 in water
  - pH < 3 - 5
  - At 25 ^{0}C and 1 atm: CO_2 = 1,500 mg/L
  - Pressure bottles if CO_2 > 1,500 mg/L
- PHREEQC brings more:
  - Influence gamma (ionic strength)
  - Combined water quality CO_2 - HCO_3



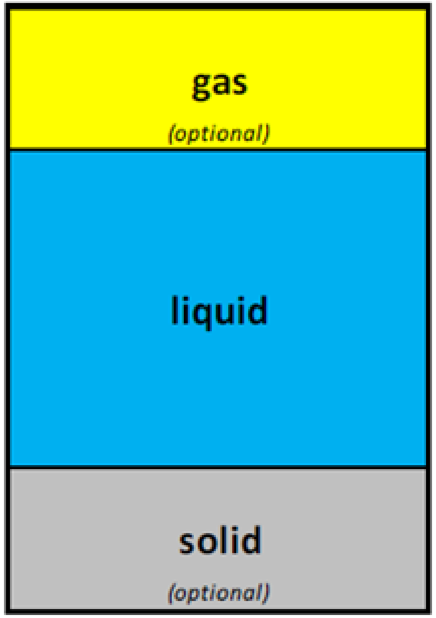
Questions?

Aquatic Chemistry for engineers

Module : Gases in water and gas (App 2b)

- Solubility of gases
  - Drinking water: aeration of groundwater
  - Wastewater: Aerobic and anaerobic treatment

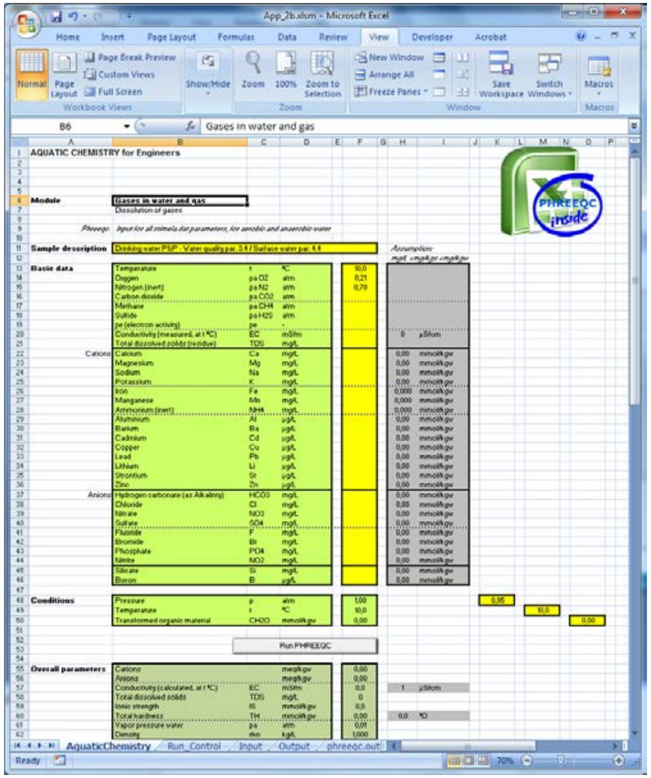
- Mass balance between water and gas phase
  - Gas saturation (p total = sum pa > water pressure)
  - Anaerobic wastewater treatment
  - Temperature (heating / boiling of water)



- Application
  - Drinking water : gas bubbles in warmer and hot water
  - Sewerage / wastewater: anaerobic treatment, digisters

App 2b - Gases in water and gas

- Open App_2b.xlsm:



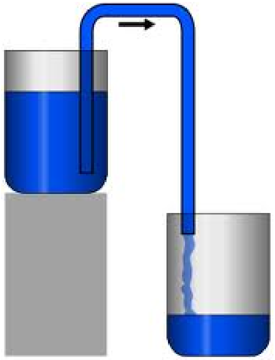
Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

Item : Gas bubbles formed in water

- Bubbles from pressure reduction
  - (Warm) water from the tap
  - Under-pressure in pipelines (siphon)
  - Under-pressure in sand filters
  - Vacuum degasifier

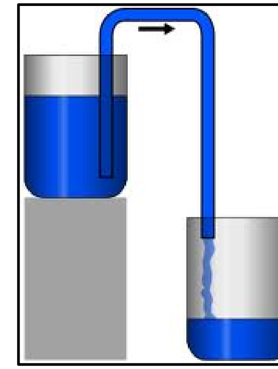


- Bubbles from temperature increase
  - Cold water in a warm kitchen

- Bubbles from rotting
  - Organic decomposition forms CO_2 and CH_4
  - Gas production in digister
  - Anaerobic water treatment

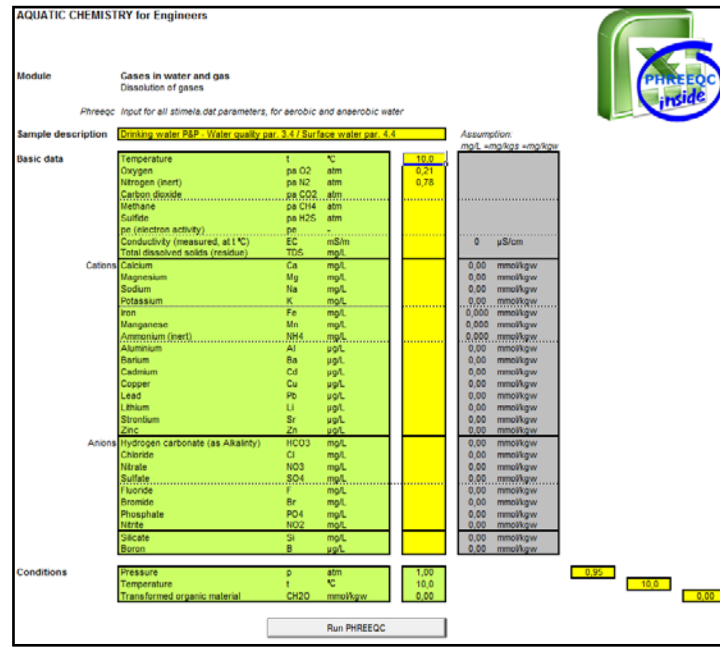
Aquatic Chemistry for engineers

Item : Bubbles from pressure reduction



- Water
  - Temperature 10 ^{0}C
  - p_a O_2 = 0.21 atm
  - p_a N_2 = 0.78 atm
  - No gas bubbles (gas volume = 0 mL)

- Calculate gas volume at pressure:
  - A: p = 0.95 atm (filter -0.5 mwc)
  - B: p = 0.50 atm (siphon)
  - C: p = 0.05 atm (vacuum degasifier)



AQUATIC CHEMISTRY for Engineers

Module: Gases in water and gas — Dissolution of gases

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water P&P - Water quality par. 3.4 / Surface water par. 4.4

Assumption: mg/L =mg/kgs =mg/kgw

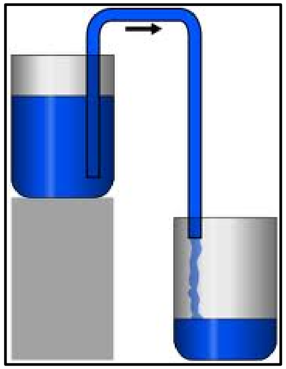
Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm	0,78		
	Carbon dioxide	pa CO2	atm			
	Methane	pa CH4	atm			
	Sulfide	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L		0,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Conditions	Pressure	p	atm	1,00	0,95	
	Temperature	t	°C	10,0	10,0	
	Transformed organic material	CH2O	mmol/kgw	0,00	0,00	

Run PHREEQC

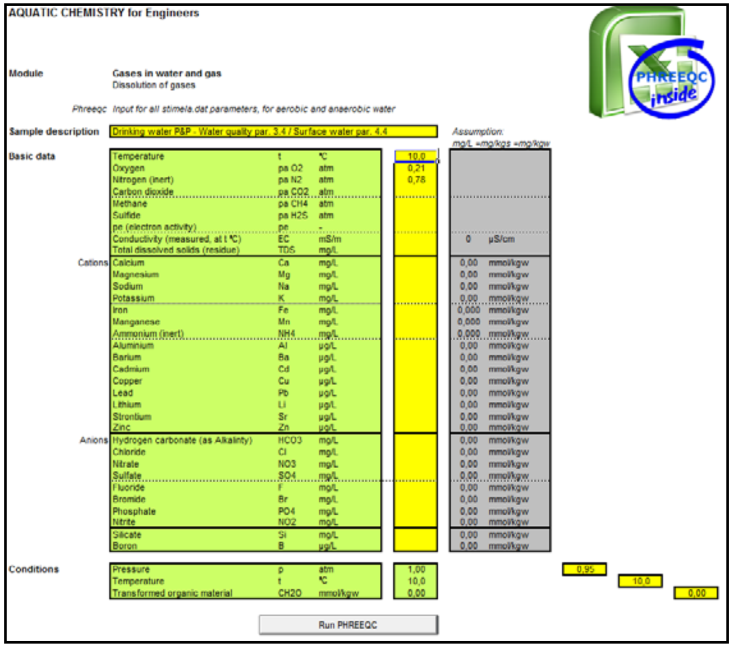
- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : Bubbles from pressure reduction



Answers:



AQUATIC CHEMISTRY for Engineers

Module: **Gases in water and gas**
Dissolution of gases

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description: Drinking water P&P - Water quality par. 3.4 / Surface water par. 4.4

Assumption: mg/L =mg/kgs =mg/kgw

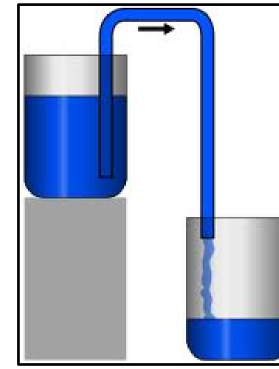
Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm	0,78		
	Carbon dioxide	pa CO2	atm			
	Methane	pa CH4	atm			
	Sulfide	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L		0,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw

Conditions	Pressure	p	atm	1,00	0,95
	Temperature	t	°C	10,0	10,0
	Transformed organic material	CH2O	mmol/kgw	0,00	0,00

Run PHREEQC

Aquatic Chemistry for engineers

Item : Bubbles from pressure reduction



Answers:

- Volume of gas bubbles
  - A: p = 0.95 atm 0.93 mL
  - B: p = 0.50 atm 23.6 mL
  - C: p = 0.05 atm 604 mL
- Bubble diameter 1 mm:
  - Volume per bubble = $5.3 * 10^{-4}$ mL
  - So 1 mL gas = 1,900 bubbles
- Gas phase volume:
  - 23.6 mL = 2.4 % of water volume (1 L)
  - 604 mL= 60 % of water volume (1 L)

Conditions	Pressure	p	atm	1,00			0,95
	Temperature	t	°C	10,0			
	Transformed organic material	CH2O	mmol/kgw	0,00			
	Run PHREEQC						
Overall parameters	Cations		meq/kgw	0,00			
	Anions		meq/kgw	0,00			
	Conductivity (calculated, at t °C)	EC	mS/m	0,0	1	µS/cm	
	Total dissolved solids	TDS	mg/L	0			
	Ionic strength	IS	mmol/kgw	0,0			
	Total hardness	TH	mmol/kgw	0,00	0,0	°D	
	Vapor pressure water	pa	atm	0,01			
	Density	rho	kg/L	1,000			
Redox conditions	Oxygen	O2	mmol/kgw	0,36	11,5	mg/L	
	pe (electron activity)	pe	-	14,97			
	Redox potential	Eh	mV	840			
Correctness checks	Charge difference		meq/kgw	0,00			
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			0,0%			
	EC ratio, calculated/measured		-	-			
	TDS ratio, measured/calculated		-	-			
	Oxygen saturation (with air at sea level)		atm/atm	102,2%			
	pH change by electron balancing (Phreeqc)		-	0,00			
	pe change by electron balancing (Phreeqc)		-	-			
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,00			
	Alkalinity	m	meq/kgw	0,00			
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	0,00	0	mg/L C	
	CO2	CO2	mmol/kgw	0,00	0,00	mg/L	
	HCO3 -	HCO3	mmol/kgw	0,00	0	mg/L	
	CO3 2-	CO3	mmol/kgw	0,00	0	mg/L	
	dpH by 0.1 mmol HCl / kgw	pH	-	-3,00			
	Buffer capacity	BI	mmol/kgw /pH	0,01			
Calcite equilibrium	SI (calcite)	SI-c	-	-			
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	-			
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,11	5	mg/L CO2	
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,16	7	mg/L CO2	
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	-0,18	8	mg/L CO2	
Gases in water	Oxygen	O2	mmol/kgw	0,36	11,5	mg/L	0,35
	Nitrogen (inert)	Ntg	mmol/kgw	0,66	18,6	mg/L	0,62
	Carbon dioxide	CO2	mmol/kgw	0,00	0,00	mg/L	0,00
	Methane	CH4	mmol/kgw	0,00	0,00	mg/L	0,00
	Sulfide	H2S	mmol/kgw	0,00	0,00	mg/L	0,00
	Ammonia	NH3	mmol/kgw	0,00	0,00	mg/L	0,00
Gases in gas	Total gas volume		mL/kgw	0,00			1,25
	Total gas pressure		atm	1,00			0,95
	Oxygen	O2	atm	0,21			0,20
	Nitrogen	N2	atm	0,78			0,73
	Carbon dioxide	CO2	atm	0,00			0,00
	Methane	CH4	atm	0,00			0,00
	Sulfide	H2S	atm	0,00			0,00
	Ammonia	NH3	atm	0,00			0,00
	Water (vapour)	H2O	atm	0,01			0,01
Elements / Species	C		mmol/kgw	0,00			

Aquatic Chemistry for engineers

Module : Gases in water and gas - PHREEQC code

- Code for output :
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc
- Gas phase simulations:
  - GAS_PHASE
    - -fixed_pressure (gas type)
    - -pressure 0.05 (fixed, atm)
    - -temperature 10 (initial Moles)
    - -volume 1e-8 (initial Moles)
    - $O_2(g)$ 0.0 (initial Moles)
    - Other gases in gas phase

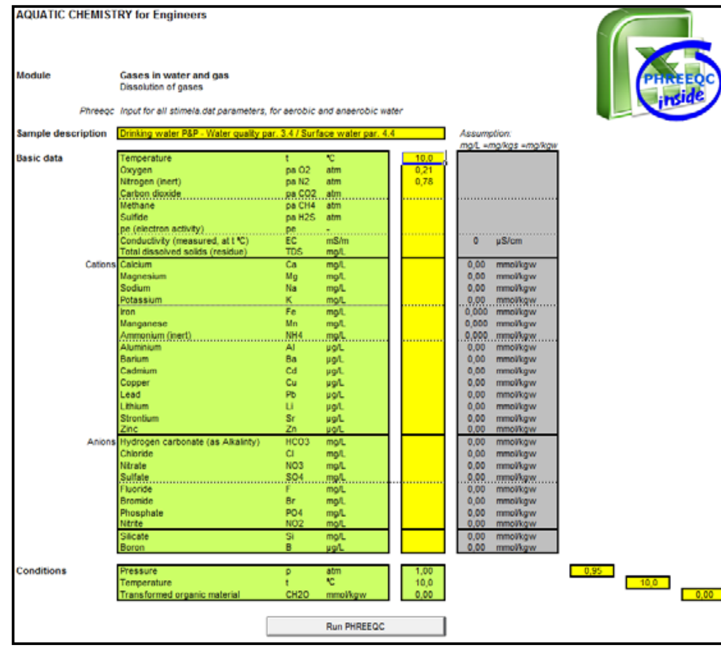
```
REACTION_TEMPERATURE
          60  90                                   # solution
EQUILIBRIUM_PHASE
          Calcite
END       # Simulation 5


TITLE     Gas phase , for pressure
USE solution 1
GAS_PHASE 1                                        # Defines
          -fixed_pressure                          # Gas pha
          -pressure          0.05                  # Gas pre
          -temperature       10                    # Initial ga
          -volume            1e-8                  # Initial vo
          O2(g)              0.0                   # Gas nar
#         N2(g)              0.0
          Ntg(g)             0.0
          H2O(g)             0.0
          CO2(g)             0.0
          CH4(g)             0.0
#         NH3(g)             0.0
          H2S(g)             0.0
END       # Simulation 6
```

Questions?

Aquatic Chemistry for engineers

Item : Bubbles from temperature increase

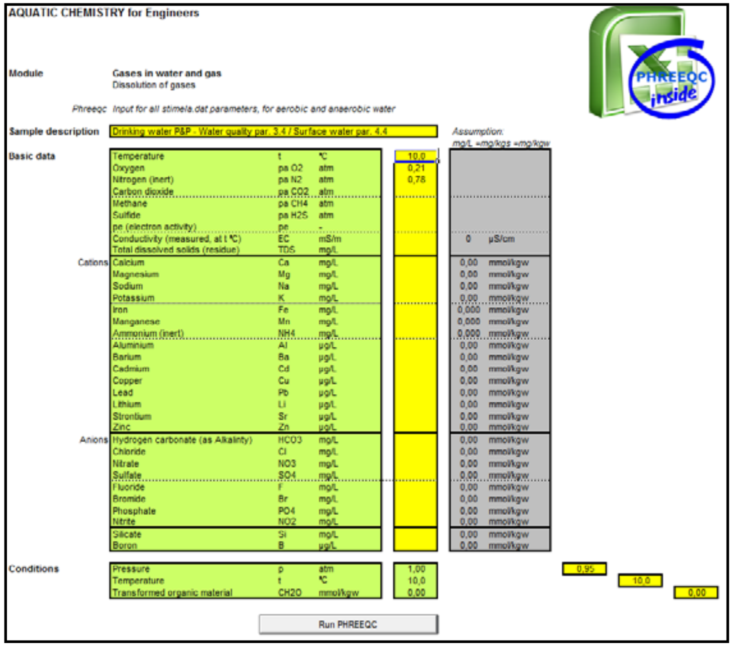
- Water
  - Temperature 10 ^{0}C
  - $p_a\ O_2$ = 0.21 atm
  - $p_a\ N_2$ = 0.78 atm
  - No gas bubbles (gas volume = 0 mL)
- Calculate gas volume at temperature:
  - A: 25 ^{0}C (cold water in the kitchen)
  - B: 70 ^{0}C (heating water, noice)
- I give you 3 minutes....



Aquatic Chemistry for engineers

Item : Bubbles from temperature increase

Answers:


AQUATIC CHEMISTRY for Engineers

Module: **Gases in water and gas**
Dissolution of gases

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water P&P - Water quality par. 3.4 / Surface water par. 4.4

Assumption: mg/L =mg/kgs =mg/kgw

	Parameter	Symbol	Unit	Value		
Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm	0,78		
	Carbon dioxide	pa CO2	atm			
	Methane	pa CH4	atm			
	Sulfide	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L		0,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Conditions	Pressure	p	atm	1,00	0,95	
	Temperature	t	°C	10,0	10,0	
	Transformed organic material	CH2O	mmol/kgw	0,00	0,00	

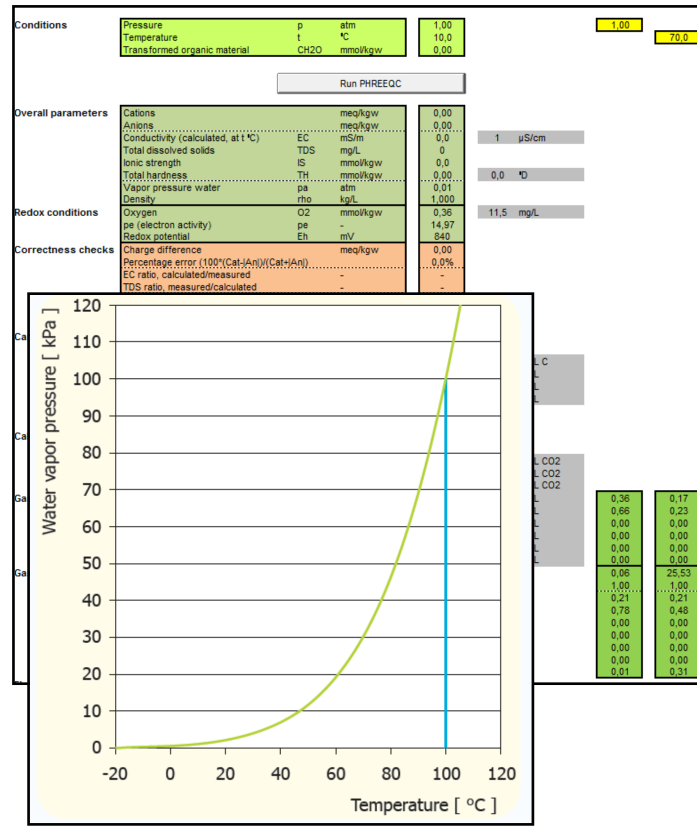
Run PHREEQC

Aquatic Chemistry for engineers

Item : Bubbles from temperature increase

Answers:

- Volume of gas bubbles
  - A: 25 ^{0}C 3.15 mL
  - B: 70 ^{0}C 25.5 mL
- Bubble diameter 1 mm
  - Volume per bubble = 5.3 * 10^{-4} mL
  - So 1 mL gas = 1,900 bubbles
- Higher temperature
  - Gases less soluble
  - Vapour pressure (p_a 70 ^{0}C = 0.31 atm)



Aquatic Chemistry for engineers

Module : Gases in water and gas - PHREEQC code

- Code for output :
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

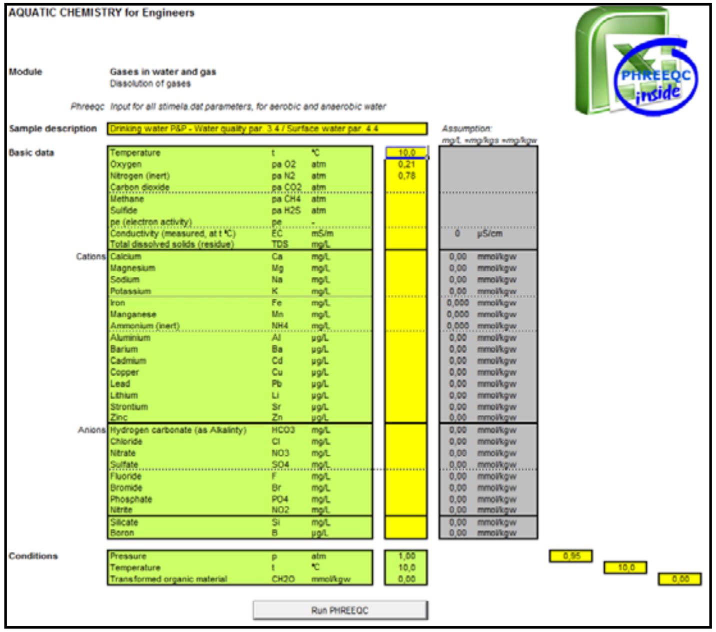
- Gas phase simulations:
  - GAS_PHASE
    - -fixed_pressure (gas type)
    - -pressure 1.00 (fixed, atm)
    - other settings
  - REACTION_TEMPERATURE
    - 70.0 (reaction temp)

```
        H2S(g)              0.0
END     # Simulation 6


TITLE   Gas phase , for temperature
USE solution 1
GAS_PHASE 1                                   # Defines a gas p
        -fixed_pressure                       # Gas phase with
        -pressure           1.00              # Gas pressure in
        -temperature        10                # Initial gas tempe
        -volume             1e-8              # Initial volume in
        O2(g)               0.0               # Gas name from
#       N2(g)               0.0
        Ntg(g)              0.0
        H2O(g)              0.0
#       CO2(g)              0.0
#       CH4(g)              0.0
#       NH3(g)              0.0
#       H2S(g)              0.0
REACTION_TEMPERATURE
        70.0
END     # Simulation 7
```

Questions?

Aquatic Chemistry for engineers

Item : Bubbles from rotting

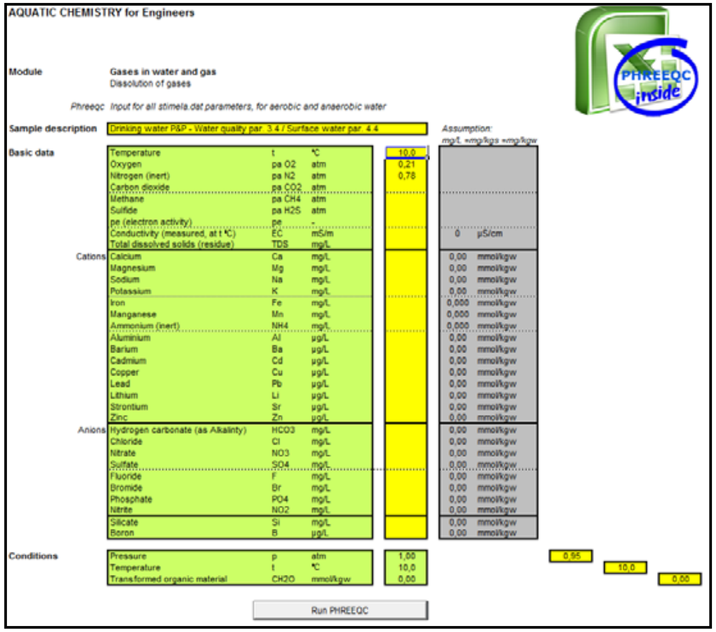


- Water (t = 10 ^{0}C, gas volume = 0 mL):
  - p_a O_2 = 0.21 atm
  - p_a N_2 = 0.78 atm
- Calculate gas volume after biodegradation of organic material
  CH_2O + O_2 into CO_2 + H_2O (+CH_4)
  - A: 0.3 mmol/kgw (water)
  - B: 0.6 mmol/kgw (water)
  - C: 300 mmol/kgw (sludge, 9 g/L, 0.9%)
  - D: 3000 mmol/kgw (digister, 90 g/L)
- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : Bubbles from rotting

Answers:



AQUATIC CHEMISTRY for Engineers

Module — **Gases in water and gas**
Dissolution of gases

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water P&P - Water quality par. 3.4 / Surface water par. 4.4

Assumption:
mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	pa O2	atm	0,21		
	Nitrogen (inert)	pa N2	atm	0,78		
	Carbon dioxide	pa CO2	atm			
	Methane	pa CH4	atm			
	Sulfide	pa H2S	atm			
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L		0,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L		0,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Conditions	Pressure	p	atm	1,00	0,95	
	Temperature	t	°C	10,0	10,0	
	Transformed organic material	CH2O	mmol/kgw	0,00	0,00	

Run PHREEQC

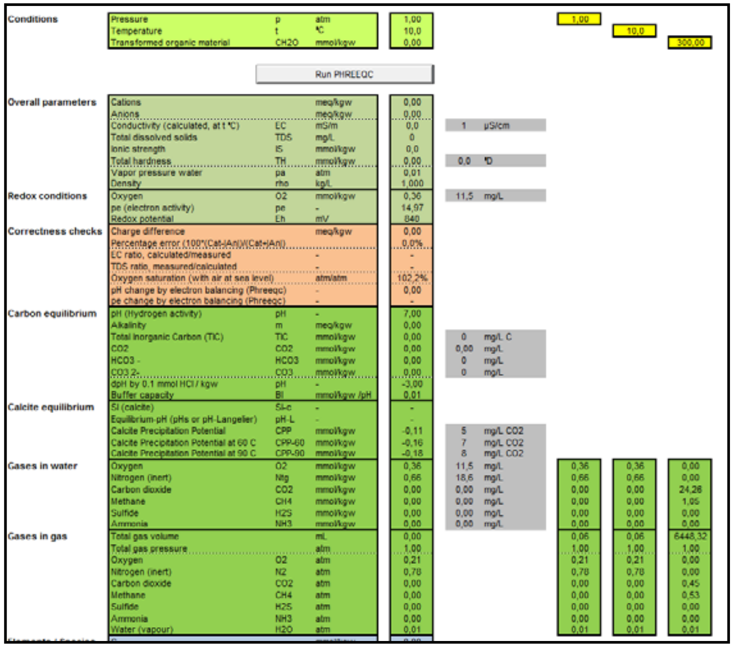
Aquatic Chemistry for engineers

Item : Bubbles from rotting

Answers:

- Biodegradation into water and gas

OM mmol/kgw	O_2 w id	CH_4 w id	gas L/kgw
• Initial	0.36	0.00	0
• A: 0.3	0.06	0.00	0
• B: 0.6	0.00	0.12	0
• C: 300	0.00	1.05	6.45
• D: 3000	0.00	0.98	69.9



Conditions	Pressure	p	atm	1,00		1,00		
	Temperature	t	°C	10,0			10,0	
	Transformed organic material	CH2O	mmol/kgw	0,00				300,00
	Run PHREEQC							
Overall parameters	Cations		meq/kgw	0,00				
	Anions		meq/kgw	0,00				
	Conductivity (calculated, at t °C)	EC	mS/m	0,0	1 µS/cm			
	Total dissolved solids	TDS	mg/L	0				
	Ionic strength	IS	mmol/kgw	0,0				
	Total hardness	TH	mmol/kgw	0,00	0,0 °D			
	Vapor pressure water	pa	atm	0,01				
	Density	rho	kg/L	1,000				
Redox conditions	Oxygen	O2	mmol/kgw	0,36	11,5 mg/L			
	pe (electron activity)	pe	-	14,97				
	Redox potential	Eh	mV	840				
Correctness checks	Charge difference		meq/kgw	0,00				
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			0,0%				
	EC ratio, calculated/measured		-	-				
	TDS ratio, measured/calculated		-	-				
	Oxygen saturation (with air at sea level)		atm/atm	102,2%				
	pH change by electron balancing (Phreeqc)		-	0,00				
	pe change by electron balancing (Phreeqc)		-	-				
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,00				
	Alkalinity	m	meq/kgw	0,00				
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	0,00	0 mg/L C			
	CO2	CO2	mmol/kgw	0,00	0,00 mg/L			
	HCO3 -	HCO3	mmol/kgw	0,00	0 mg/L			
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L			
	dpH by 0.1 mmol HCl / kgw	pH	-	-3,00				
	Buffer capacity	BI	mmol/kgw /pH	0,01				
Calcite equilibrium	SI (calcite)	SI-c	-	-				
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	-				
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,11	5 mg/L CO2			
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,16	7 mg/L CO2			
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	-0,18	8 mg/L CO2			
Gases in water	Oxygen	O2	mmol/kgw	0,36	11,5 mg/L	0,36	0,36	0,00
	Nitrogen (inert)	Ntg	mmol/kgw	0,66	18,6 mg/L	0,66	0,66	0,00
	Carbon dioxide	CO2	mmol/kgw	0,00	0,00 mg/L	0,00	0,00	24,26
	Methane	CH4	mmol/kgw	0,00	0,00 mg/L	0,00	0,00	1,05
	Sulfide	H2S	mmol/kgw	0,00	0,00 mg/L	0,00	0,00	0,00
	Ammonia	NH3	mmol/kgw	0,00	0,00 mg/L	0,00	0,00	0,00
Gases in gas	Total gas volume		mL	0,00		0,06	0,06	6448,32
	Total gas pressure		atm	1,00		1,00	1,00	1,00
	Oxygen	O2	atm	0,21		0,21	0,21	0,00
	Nitrogen (inert)	N2	atm	0,78		0,78	0,78	0,00
	Carbon dioxide	CO2	atm	0,00		0,00	0,00	0,45
	Methane	CH4	atm	0,00		0,00	0,00	0,53
	Sulfide	H2S	atm	0,00		0,00	0,00	0,00
	Ammonia	NH3	atm	0,00		0,00	0,00	0,00
	Water (vapour)	H2O	atm	0,01		0,01	0,01	0,01

- Initial phase: Oxygen consumption
- Second phase: Anaerobic conversion
- Third phase: Gas formation, increasing CO_2 content in water (low pH)

Aquatic Chemistry for engineers

Module : Gases in water and gas - PHREEQC code

- Code for output :
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

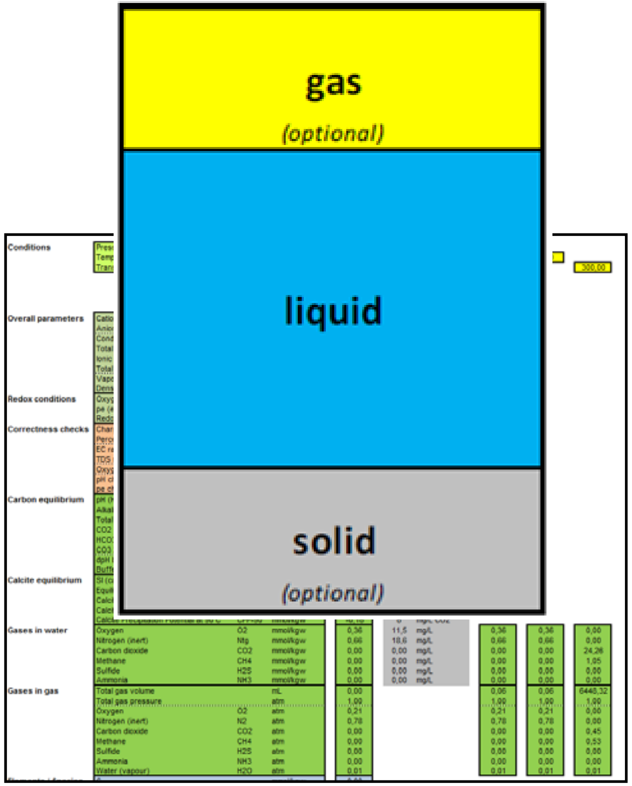
- Gas phase simulations:
  - GAS_PHASE
    - -fixed_pressure (gas type)
    - -pressure 1.00 (fixed, atm)
    - other settings
  - REACTION
    - CH2O 1.0 (Reactant formula, stoichiometric coefficient)
    - 3000 mmol (mass)

```
#       NH3(g)          0.0
#       H2S(g)          0.0
REACTION_TEMPERATURE
        10.0
END     # Simulation 7


TITLE   Gas phase , for biodegradation
USE solution 1
GAS_PHASE 1                                     # Defines a gas phase
        -fixed_pressure                         # Gas phase with fixed tota
        -pressure       1.0                     # Gas pressure in atm
        -temperature    10                      # Initial gas temperature in
        -volume         1e-8                    # Initial volume in Liter (neg
        O2(g)           0.0                     # Gas name from PHASES
#       N2(g)           0.0
        Ntg(g)          0.0
        H2O(g)          0.0
        CO2(g)          0.0
        CH4(g)          0.0
#       NH3(g)          0.0
        H2S(g)          0.0
REACTION
        CH2O    1.0                             #  Reactant formula, stoich
        300.00  mmol                            # Adds 1.0 * x =  x mmol C
END     # Simulation 8                          # last END is optional (End
```

Conclusions - Lessons learned

Solubility of gases in water and gas

- Initial gas phase (optional) specified as:
  - Total gas pressure
  - Total gas volume
  - Temperature
  - Partial pressure for each component
- Gas phase defined as:
  - Moles per component
  - Pressure
- PHREEQC keeps mass balance:
  - Mass transfer between water and gas
  - Caused by reactions and tempertaure change



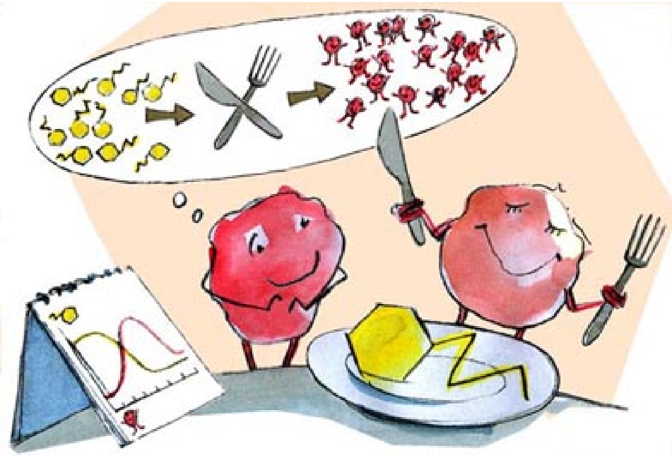
Questions?

Aquatic Chemistry for engineers

Module : Biodegradation - Monod kinetics (Lab 2c)

- Organic C (oxydation)
  - Additive Monod kinetics
  - Rate = f (O_2 NO_3 SO_4)
  - dMass = Rate x Mass x Timestep

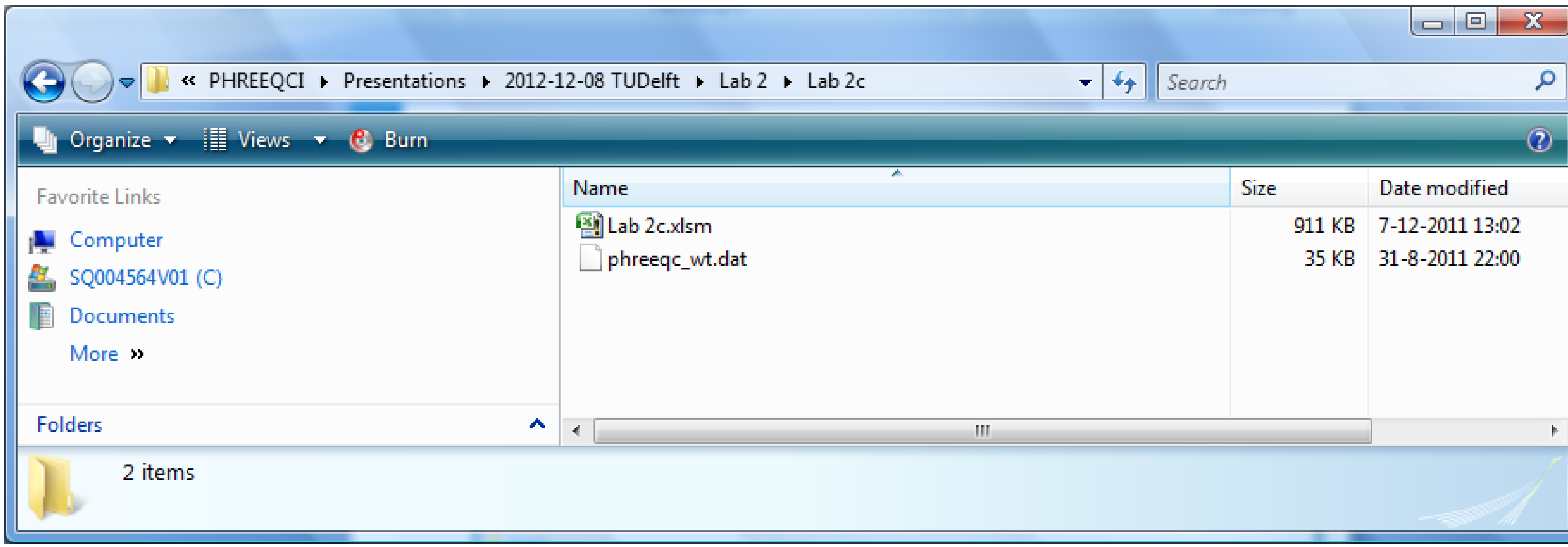
$$\frac{dX}{dt} = \mu \cdot X \qquad \mu = \mu_{max} \cdot \frac{S}{K_s + S}$$



- Application
  - Drinking water : O_2 in slow sand or carbon filters
  - Sewerage / wastewater: O_2 / NO_3 reduction in aerobic treatment

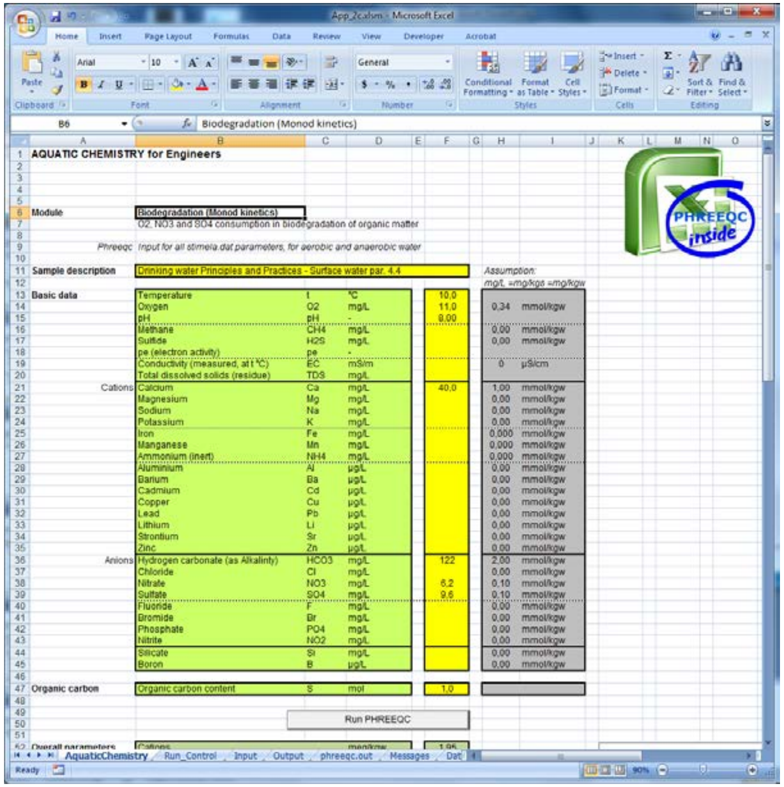
Folder App 2c

- Double click App_2c.xlsm



App 2c - Biodegradation (Monod)

- Open App_2c.xlsm:



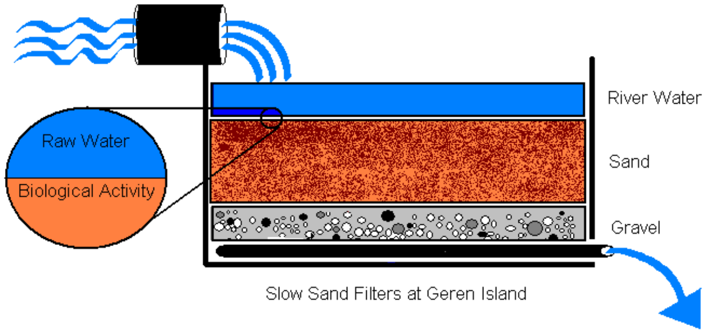
Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

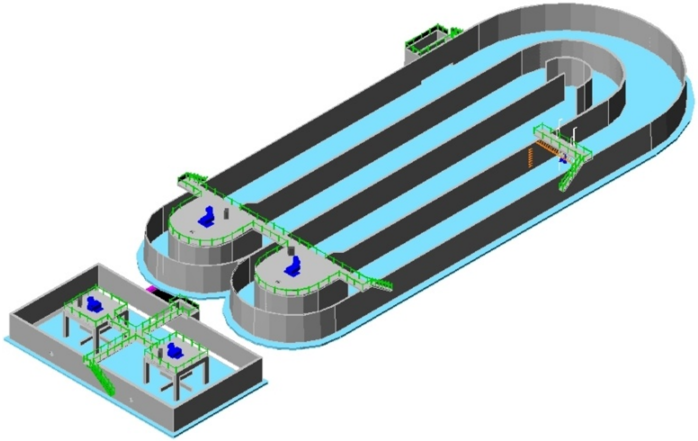
Aquatic Chemistry for engineers

Item : O_2 and NO_3 reduction

- Organic matter use oxygen if present
  - High rate



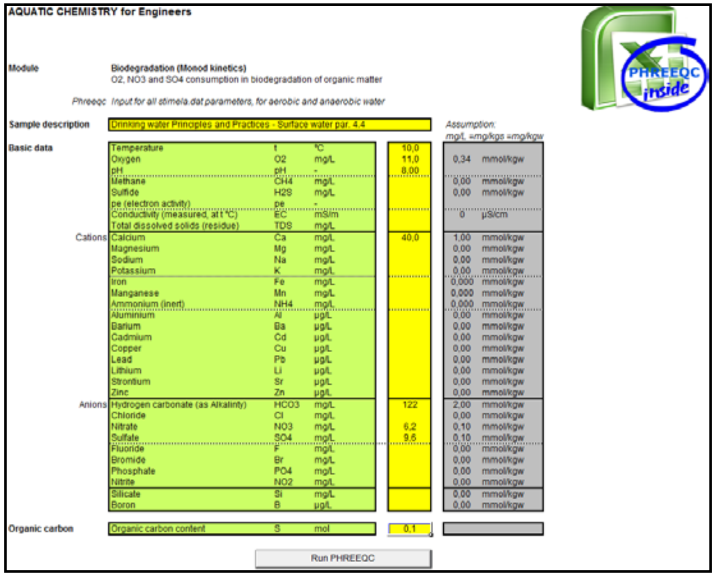
- Organic matter uses nitrate after oxygen
  - Low rate



Aquatic Chemistry for engineers

Item : O_2 and NO_3 reduction

- Water
  - Temperature 10 ^{0}C
  - O_2 = 11 mg/L pH = 8.0
  - Ca = 40 mg/L HCO_3 = 122 mg/L
  - NO_3 = 6.2 mg/L SO_4 = 9.6 mg/L



AQUATIC CHEMISTRY for Engineers

Module: **Biodegradation (Monod kinetics)**
O2, NO3 and SO4 consumption in biodegradation of organic matter

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description: Drinking water Principles and Practices - Surface water par. 4.4

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	8,00		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	40,0	1,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	122	2,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L	6,2	0,10	mmol/kgw
	Sulfate	SO4	mg/L	9,6	0,10	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Organic carbon	Organic carbon content	S	mol	0,1		

Run PHREEQC

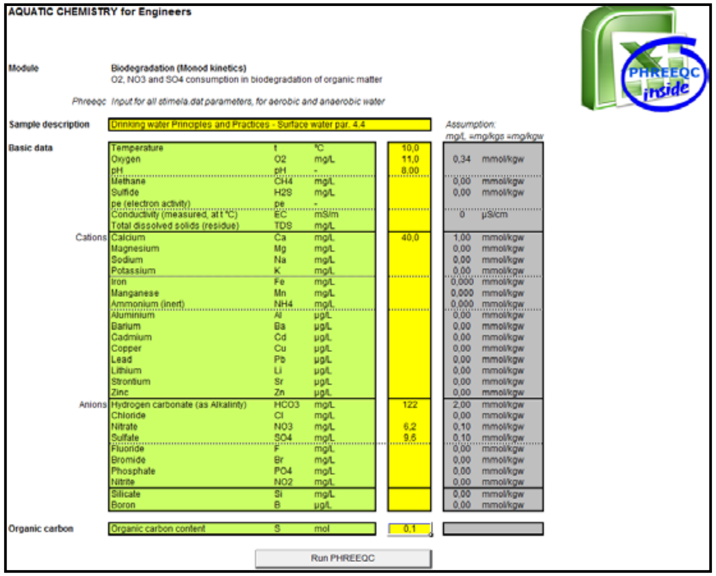
- Calculate depletion time of O_2:
  - A: organic C: 0.1 mol
  - B: organic C: 1.0 mol

- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : O_2 and NO_3 reduction

Answers:



AQUATIC CHEMISTRY for Engineers

PHREEQC inside

Module — **Biodegradation (Monod kinetics)**
O2, NO3 and SO4 consumption in biodegradation of organic matter

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Surface water par. 4.4

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	8,00		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	40,0	1,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
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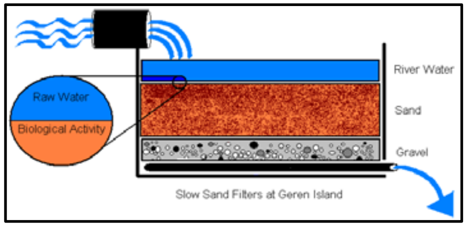
	Sulfate	SO4	mg/L	9,6	0,10	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Organic carbon	Organic carbon content	S	mol	0,1		

Run PHREEQC

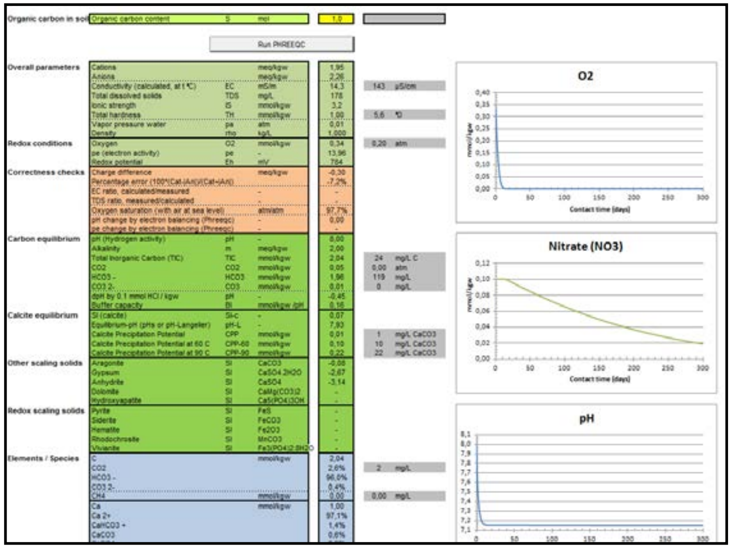
Aquatic Chemistry for engineers

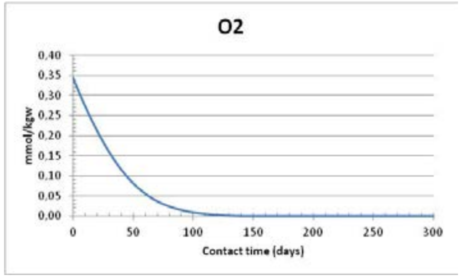
Item : O_2 and NO_3 reduction

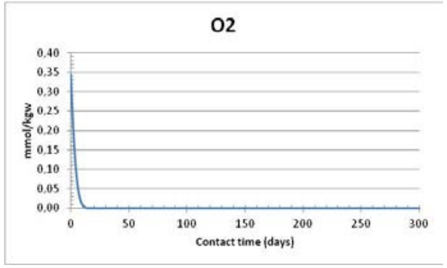


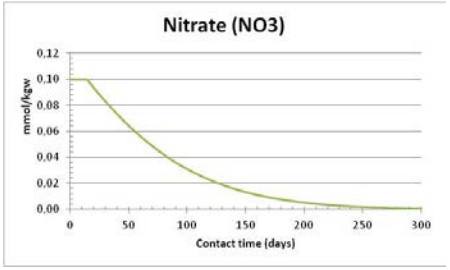
Answers:

- Depletion time O_2:
  - A: 0.1 mol 112 days
  - B: 1.0 mol 12 days
    - NO_3 depleted in ca. 400 days









Aquatic Chemistry for engineers

Module : Biodegradation-Monod - PHREEQC code

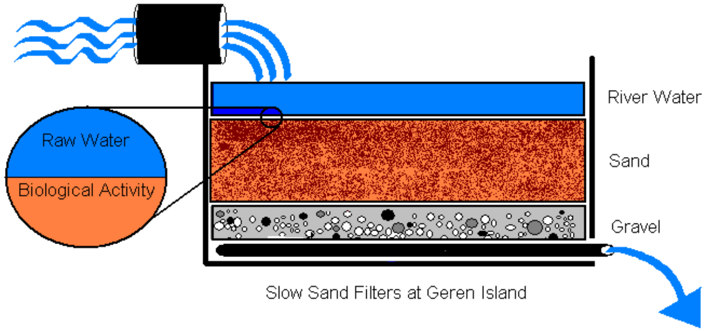
- Code for output :
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc
- Kinetic simulations:
  - KINETICS
    - Organic_C (RATES in .dat)
    - -formula CH2O 1.0 (stoich)
    - -m0 0.1 (initial mass)
    - -m 0.1 (mass)
    - -tol 1e-8 (integration tollerance)
    - -step 0 300*86400 (sec)
  - INCREMENTAL_REACTIONS true

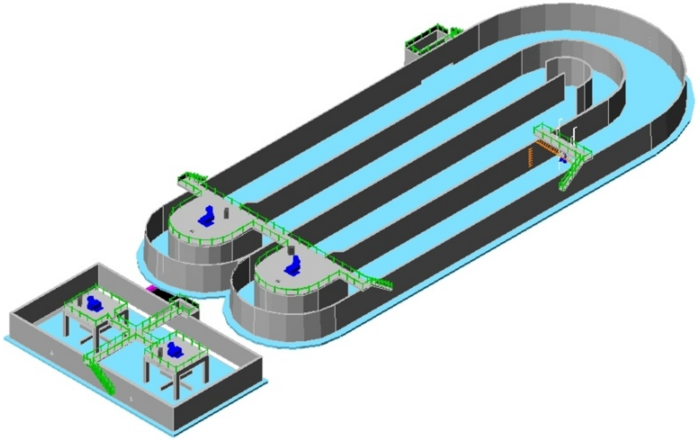
```
EQUILIBRIUM_PHASE
        Calcite
END     # Simulation 5


# Kinetics Organic_C


USE solution 1;
KINETICS 1
        Organic_C                                   # rate name (must be defined in RATES)
         -formula CH2O 1.0                          # reactant's elements and stoichiometric
         -m0       0.10                             # initial reactant moles (constant). Defaul
         -m        0.10                             # reactant moles at the start (changes wi
         -tol 1e-8                                  # Tolerance for integration procedure (mol
         -step              0  300*86400            # Time steps over which to integrate the r
INCREMENTAL_REACTIONS     TRUE
END     # Simulation 6                                      # last END is optional (EndOfF
```

Conclusions - Lessons learned

Item : O_2 and NO_3 reduction

- PHREEQC allows for kinetics
  - Based on species concentration





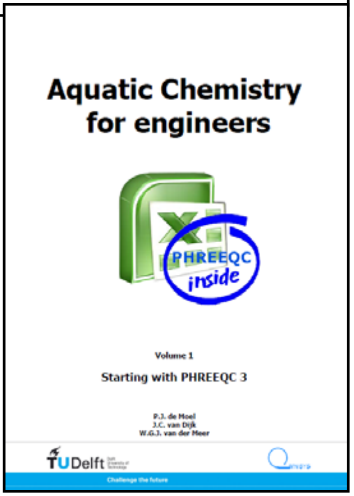
- Kinetic models to be improved:
  - For water treatment conditions
  - For short detention time in water treatment

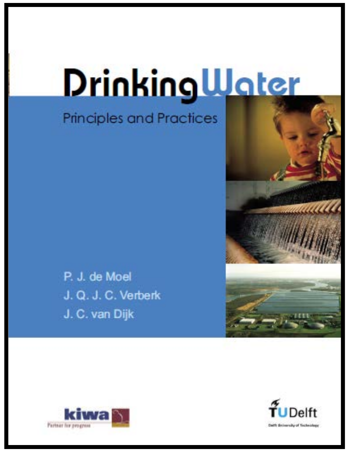
Questions?

Course program

Aquatic Chemistry for engineers

- Introduction (lecture + Starting with PHREEQC 3)
  - PHREEQC – PHREEQC Interactive – PHREEQC-COM
- Drinking water (App 1a+b)
  - Chemistry: SI / CCPP / Buffercapacity / Corrosion
  - Engineering: Ionic balance / Conductivity / Mixing
- Gases in water (App 2a+b+c)
  - Chemistry: solubility O_2, N_2, CO_2 , CH_4 etc
  - Engineering: P*V/T = R / Biodegradation wastewater
- Hardness and pH (App 3a+b)
  - Chemistry: acid/base, solubility $CaCO_3$, $FeCO_3$, etc
  - Engineering: pH control / Neutralization / Softening





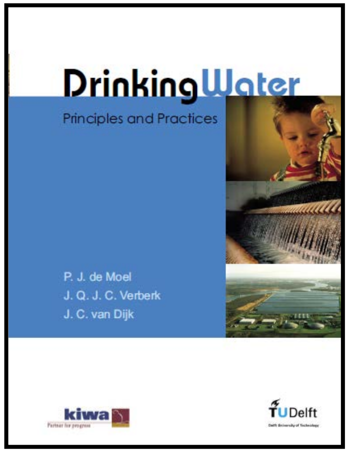
Aquatic Chemistry for engineers

Module : Chemical softening (App 3a)

- Neutralization
  - Aeration
  - Limestone filtration
  - Caustic soda

- Softening
  - Sodium hydroxide - $Ca(OH)_2$
  - Caustic soda – NaOH
  - Split-treatment

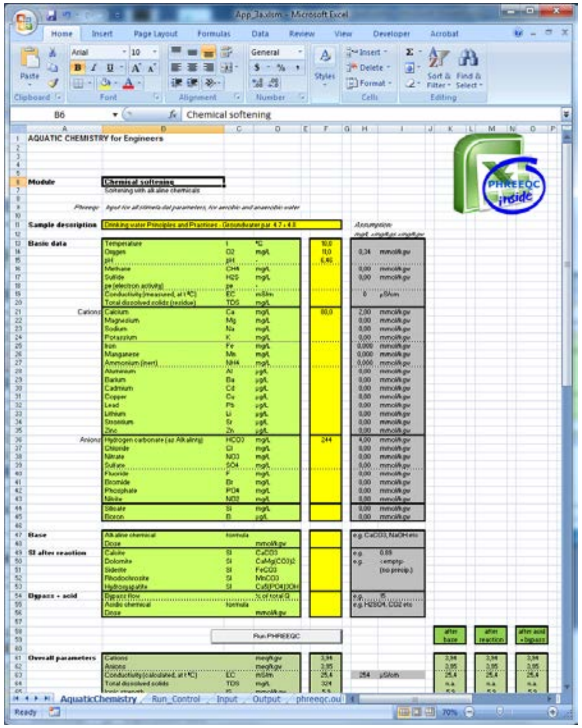
- Application
  - Drinking water : pH control + neutralization + softening
  - Sewerage / wastewater: pH control + precipitation



Groundwater
4.7 + 4.8

App 3a - Chemical softening

- Open App_3a.xlsm:



Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

Item : Neutralization by aeration

Neutralization by aeration/gas transfer

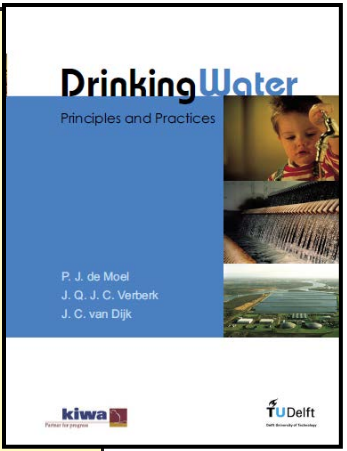
The raw water (10°C) of a pumping station has the following composition:
Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, pH = 6.46.
What is the pH in equilibrium after aeration, and how much CO_2 has to be removed?

From $pK_1 = pH + \log \{ [CO_2] / [HCO_3^-] \}$ results that
$\log \{ [CO_2] / [HCO_3^-] \} = 6.46 - 6.46 = 0$, that is $[CO_2] / [HCO_3^-] = 10^0 = 1$
so $[CO_2] = 4.0$ mmol/l $= 4.0 \cdot 44 = 176$ mg/l.

From $pH_s = pK_2 - pK_s - \log \{ [Ca^{2+}] \cdot [HCO_3^-] \}$ results that
$pH_s = 10.49 - 8.36 - \log (2.0\ 10^{-3} \cdot 4.0\ 10^{-3}) = 2.13 + 4.80 = 7.23$ and
$SI = pH - pH_s = 6.46 - 7.23 = -0.77$, so the raw water is limestone aggressive.

When removing CO_2, $[Ca^{2+}]$ and $[HCO_3^-]$ remain equal and thus pH_s remains equal.
Therefore, in equilibrium $pH = pH_s = 7.23$.

With pK_1: $\log \{ [CO_2] / [4.0\ 10^{-3}] \} = pK_1 - pH = 6.46 - 7.23 = -0.77$ so
$[CO_2] = 10^{-0.77} \cdot 4.0\ 10^{-3} = 0.34 \cdot 4.0\ 10^{-3} = 0.68\ 10^{-3}$ mol/l = 0.68 mmol/l
During aeration 4.0 - 0.68= 3.32 mmol/l CO_2 is removed, that is $3.32 \cdot 44 = 146$ mg/l.
Therefore, the required efficiency is (146 - 1 / 176 - 1 =) 83%.



Aquatic Chemistry for engineers

Item : Neutralization by aeration

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - pH = 6.46
- Calculate raw water:
  - A: CO_2 content
  - B: SI
- Calculate at equilibrium (SI=0):
  - C: pH
  - D: CO_2 removed
- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module — **Chemical softening**
Softening with alkaline chemicals

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption:
mg/L = mg/kgs = mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
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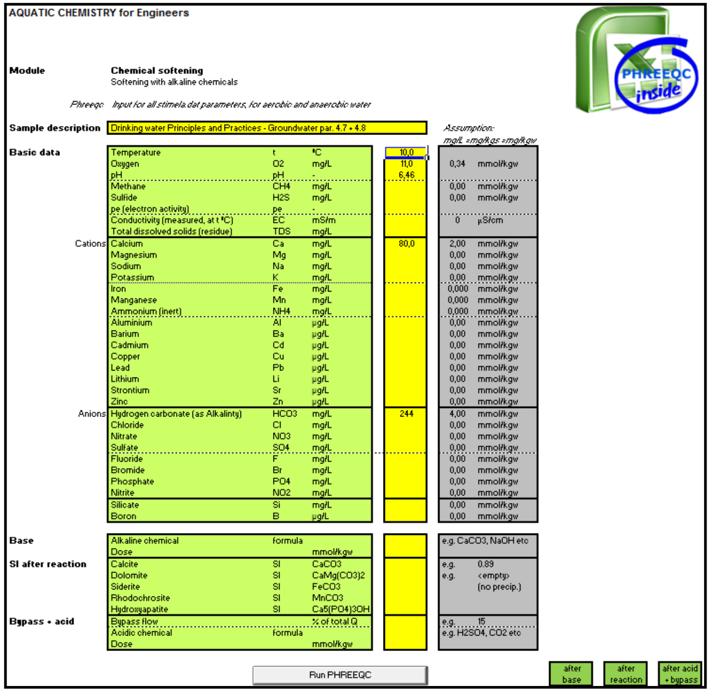
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC — after base — after reaction — after acid + bypass

Aquatic Chemistry for engineers

Item : Neutralization by aeration

Answers:



AQUATIC CHEMISTRY for Engineers

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	Conductivity (measured, at t °C)	EC	mS/m		0	μS/cm
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	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	μg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC — after base — after reaction — after acid + bypass

Aquatic Chemistry for engineers

Item : Neutralization by aeration

Answers:

- A : CO_2 = 3.68 mmol/kgw
- B : SI = -0.90

- C : pH = 7.36 (= pH_s = pH_L raw water)
  - Aeration will only change pH
  - SI = 0
- D : CO_2 = 0.46 mmol/kgw (at pH=7.36)
  - Removed 3.68 - 0.46 = 3.22 mmol/kgw

- Aeration = Gas exchange with air
- Aeration = Stripping CO_2

<table>
<tr><td>Base</td><td>Alkaline chemical</td><td>formula</td><td></td><td></td><td colspan="2">e.g. CaCO3, NaOH etc</td></tr>
<tr><td></td><td>Dose</td><td></td><td>mmol/kgw</td><td></td><td></td><td></td></tr>
<tr><td>SI after reaction</td><td>Calcite</td><td>SI</td><td>CaCO3</td><td></td><td>e.g.</td><td>0.89</td></tr>
<tr><td></td><td>Dolomite</td><td>SI</td><td>CaMg(CO3)2</td><td></td><td>e.g.</td><td><empty></td></tr>
<tr><td></td><td>Siderite</td><td>SI</td><td>FeCO3</td><td></td><td></td><td>(no precip.)</td></tr>
<tr><td></td><td>Rhodochrosite</td><td>SI</td><td>MnCO3</td><td></td><td></td><td></td></tr>
<tr><td></td><td>Hydroxyapatite</td><td>SI</td><td>Ca5(PO4)3OH</td><td></td><td></td><td></td></tr>
<tr><td>Bypass + acid</td><td>Bypass flow</td><td></td><td>% of total Q</td><td></td><td>e.g.</td><td>15</td></tr>
<tr><td></td><td>Acidic chemical</td><td>formula</td><td></td><td></td><td colspan="2">e.g. H2SO4, CO2 etc</td></tr>
<tr><td></td><td>Dose</td><td></td><td>mmol/kgw</td><td></td><td></td><td></td></tr>
<tr><td></td><td colspan="4">Run PHREEQC</td><td></td><td></td></tr>
<tr><td>Overall parameters</td><td>Cations</td><td></td><td>meq/kgw</td><td>3,94</td><td></td><td></td></tr>
<tr><td></td><td>Anions</td><td></td><td>meq/kgw</td><td>3,95</td><td></td><td></td></tr>
<tr><td></td><td>Conductivity (calculated, at t °C)</td><td>EC</td><td>mS/m</td><td>25,4</td><td>254</td><td>µS/cm</td></tr>
<tr><td></td><td>Total dissolved solids</td><td>TDS</td><td>mg/L</td><td>324</td><td></td><td></td></tr>
<tr><td></td><td>Ionic strength</td><td>IS</td><td>mmol/kgw</td><td>5,9</td><td></td><td></td></tr>
<tr><td></td><td>Total hardness</td><td>TH</td><td>mmol/kgw</td><td>2,00</td><td>11,2</td><td>°D</td></tr>
<tr><td></td><td>Vapor pressure water</td><td>pa</td><td>atm</td><td>0,01</td><td></td><td></td></tr>
<tr><td></td><td>Density</td><td>rho</td><td>kg/L</td><td>1,000</td><td></td><td></td></tr>
<tr><td>Redox conditions</td><td>Oxygen</td><td>O2</td><td>mmol/kgw</td><td>0,34</td><td>0,20</td><td>atm</td></tr>
<tr><td></td><td>pe (electron activity)</td><td>pe</td><td>-</td><td>15,50</td><td></td><td></td></tr>
<tr><td></td><td>Redox potential</td><td>Eh</td><td>mV</td><td>870</td><td></td><td></td></tr>
<tr><td>Correctness checks</td><td>Charge difference</td><td></td><td>meq/kgw</td><td>-0,01</td><td></td><td></td></tr>
<tr><td></td><td>Percentage error (100*(Cat-|An|)/(Cat+|An|)</td><td></td><td></td><td>-0,1%</td><td></td><td></td></tr>
<tr><td></td><td>EC ratio, calculated/measured</td><td></td><td>-</td><td>-</td><td></td><td></td></tr>
<tr><td></td><td>TDS ratio, measured/calculated</td><td></td><td>-</td><td>-</td><td></td><td></td></tr>
<tr><td></td><td>Oxygen saturation (with air at sea level)</td><td></td><td>atm/atm</td><td>97,7%</td><td></td><td></td></tr>
<tr><td></td><td>pH change by electron balancing (Phreeqc)</td><td></td><td>-</td><td>0,00</td><td></td><td></td></tr>
<tr><td></td><td>pe change by electron balancing (Phreeqc)</td><td></td><td>-</td><td>-</td><td></td><td></td></tr>
<tr><td>Carbon equilibrium</td><td>pH (Hydrogen activity)</td><td>pH</td><td>-</td><td>6,46</td><td></td><td></td></tr>
<tr><td></td><td>Alkalinity</td><td>m</td><td>meq/kgw</td><td>4,00</td><td></td><td></td></tr>
<tr><td></td><td>Total Inorganic Carbon (TIC)</td><td>TIC</td><td>mmol/kgw</td><td>7,67</td><td>92</td><td>mg/L C</td></tr>
<tr><td></td><td>CO2</td><td>CO2</td><td>mmol/kgw</td><td>3,68</td><td>0,07</td><td>atm</td></tr>
<tr><td></td><td>HCO3 -</td><td>HCO3</td><td>mmol/kgw</td><td>3,95</td><td>241</td><td>mg/L</td></tr>
<tr><td></td><td>CO3 2-</td><td>CO3</td><td>mmol/kgw</td><td>0,00</td><td>0</td><td>mg/L</td></tr>
<tr><td></td><td>dpH by 0.1 mmol HCl / kgw</td><td>pH</td><td>-</td><td>-0,02</td><td></td><td></td></tr>
<tr><td></td><td>Buffer capacity</td><td>BI</td><td>mmol/kgw /pH</td><td>4,41</td><td></td><td></td></tr>
<tr><td>Calcite equilibrium</td><td>SI (calcite)</td><td>SI-c</td><td>-</td><td>-0,90</td><td></td><td></td></tr>
<tr><td></td><td>Equilibrium-pH (pHs or pH-Langelier)</td><td>pH-L</td><td>-</td><td>7,36</td><td></td><td></td></tr>
<tr><td></td><td>Calcite Precipitation Potential</td><td>CPP</td><td>mmol/kgw</td><td>-1,53</td><td>67</td><td>mg/L CO2</td></tr>
<tr><td></td><td>Calcite Precipitation Potential at 60 C</td><td>CPP-60</td><td>mmol/kgw</td><td>-0,66</td><td>29</td><td>mg/L CO2</td></tr>
<tr><td></td><td>Calcite Precipitation Potential at 90 C</td><td>CPP-90</td><td>mmol/kgw</td><td>0,02</td><td>2</td><td>mg/L CaCO3</td></tr>
<tr><td>Other scaling solids</td><td>Aragonite</td><td>SI</td><td>CaCO3</td><td>-1,06</td><td></td><td></td></tr>
</table>

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output
  - PRINT / SELECTED OUTPUT etc
- SOLUTION
  - 1
  - electron balance
  - CCPP
  - Buffer capacity
  - CCPP at 60 / 90 ^{0}C
- Dosing/softening part

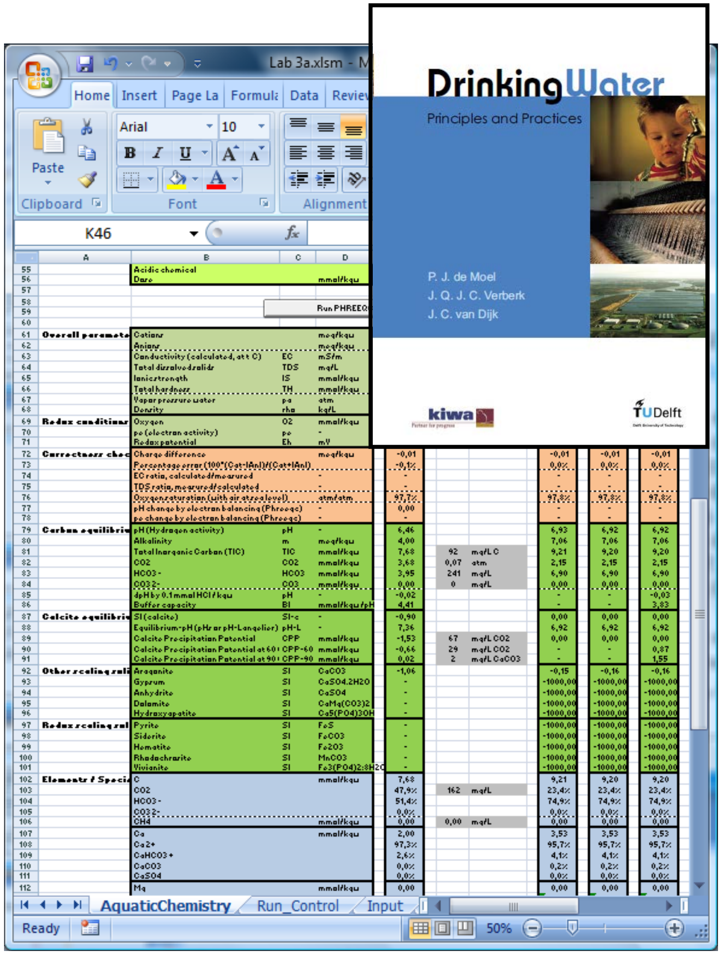
```
SOLUTION                1
        -units              mg/kgs
        -redox              O(-2)/O(0)          # if O2>0 then "O(-2)/O(0)" else if CH4>0 the
        -density            1
        -water              1
        -pe                 4.00                # if pe = empty then pe = 4
        temp        10.0
        O(0)        11.0
        pH          6.46
        C(-4)       0.00    as CH4
        S(-2)       0.00    as H2S
        Ca          80.00
        Mg          0.00
        Na          0.00
        K           0.00
        Fe          0.00
        Mn          0.00
        [N-3]       0.00    as NH4
#       N(-3)       0.00    as NH4
        Al          0.00    ug/kgs
        Ba          0.00    ug/kgs
        Cd          0.00    ug/kgs
        Cu          0.00    ug/kgs
        Pb          0.00    ug/kgs
        Li          0.00    ug/kgs
        Sr          0.00    ug/kgs
        Zn          0.00    ug/kgs
        Alkalinity  244.00  as HCO3
        Cl          0.00
        N(+5)       0.00    as NO3
        S(+6)       0.00    as SO4
        F           0.00
        Br          0.00
        P           0.00    as PO4
        N(+3)       0.00    as NO2
#       N(0)        1       N2(g) -0,1079       # SI[N2(g)] = log(pa) = log(0.78) = -0.1079
#       Ntg         1       Ntg(g) -0,1079      # SI[Ntg(g)] = log(pa) = log(0.78) = -0.1079
        Si          0.00    as Si
        B           0.00    ug/kgs as B
END     # Simulation 1

TITLE   Simulation for calculating pe (redox equilibrium)
USE solution 1
EQUILIBRIUM_PHASE                               # dummy to start final calculation, with identi
SAVE SOLUTION 1
END     # Simulation 2

TITLE   Simulation for calculating CalciumCarbonate Precipitation Potential
USE solution 1
EQUILIBRIUM_PHASE
```

Conclusions - Lessons learned

Neutralization by aeration - Compare results

- A : CO_2 = 3.68 vs 4.0 mmol/kgw
  - Gamma book = 0 : $[HCO_3] = [CO_2]$
  - Now: $0.925\ [HCO_3] = 1.002\ [CO_2]$
- B : SI = -0.90 vs -0.77
  - pK_s book = 8.36
  - pK_s PHREEQC = 8.41 + gamma
- C : pH = 7.36 vs 7.23
- D : CO_2 = 0.46 vs 0.68 mmol/kgw

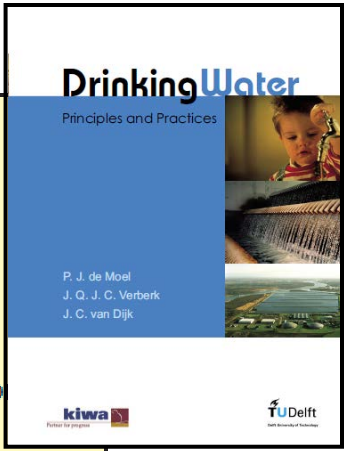
- PHREEQC is more exact:
  - Influence gamma (ionic strength)
  - Other pK_s (pK_w, pK_1, pK_2 equal)
  - Ion pairs



Questions?

Aquatic Chemistry for engineers

Item : Neutralization by limestone filtration – $CaCO_3$



Neutralization by limestone filtration

Raw water (10°C) of a pumping station has the following composition:

Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, pH = 6.46, CO_2 = 4.0 mmol/l

What is the pH in equilibrium after limestone filtration and how much $CaCO_3$ is required?

When x mol $CaCO_3$ reacts, then x mol CO_2 is removed and x mol Ca^{2+} and 2x mol HCO_3^- are fo

From K $= [Ca^{2+}] \cdot [HCO_3^-]^2 / [CO_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

$(2.0 + x) \cdot (4.0 + 2x)^2 / (4.0 - x)\ 10^{-6} = 10^{-4.33}$ so that $x = 1.20$ mmol/l

Thus in equilibrium is:

Ca^{2+} = 3.20 mmol/l, HCO_3^- = 6.40 mmol/l, CO_2 = 2.80 mmol/l.

From $pH_s = pK_2 - pK_s - \log\{[Ca^{2+}]\,[HCO_3^-]\}$ results:

$pH_s = 10.49 - 8.36 - \log\{[3.20\ 10^{-3}]\,[6.40\ 10^{-3}]\} = 2.13 + 4.69 = 6.82$

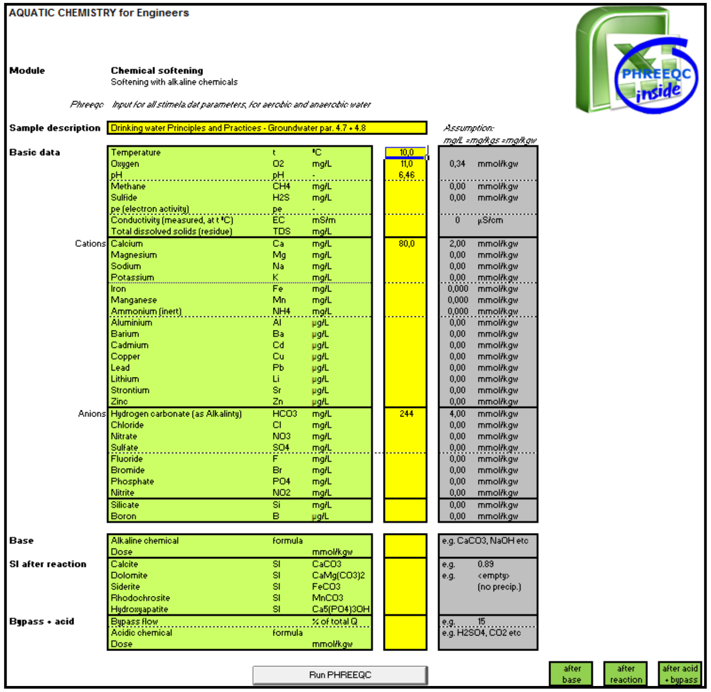
After limestone filtration the pH (or pH_s) is lower than after aeration/gas transfer.

During filtration 1.20 mmol/l CO_2 is transformed and 1.20 mmol/l $CaCO_3$ is consumed,
that is (1.20 · 100 =) 120 g/m³.
A production of 1 million m³ per year corresponds to 120 tons per year.

Aquatic Chemistry for engineers

Item : Neutralization by limestone filtration – $CaCO_3$

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - pH = 6.46
  - CO_2 = 3.68 mmol/kgw (was 4.0)
- Calculate:
  - A: pH at equilibrium with $CaCO_3$
  - B: $CaCO_3$ consumption



AQUATIC CHEMISTRY for Engineers

Module — **Chemical softening**
Softening with alkaline chemicals

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

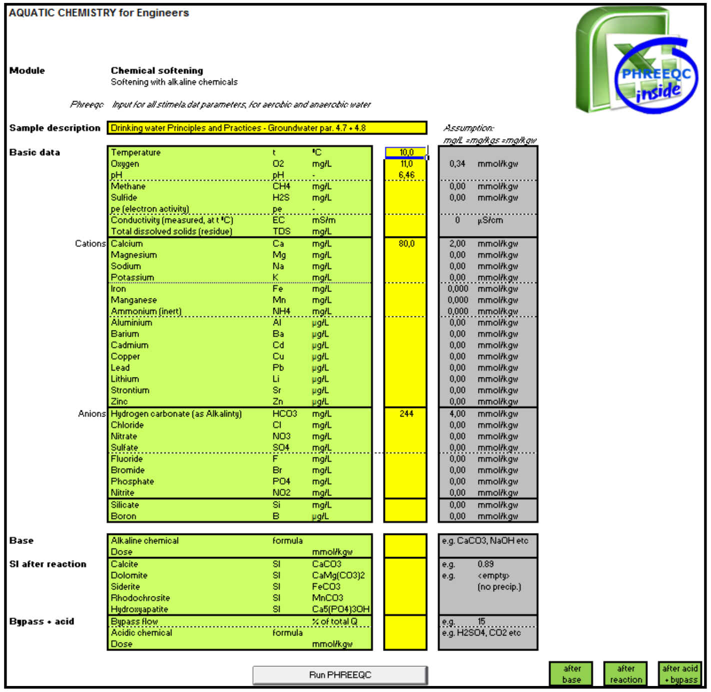
Run PHREEQC | after base | after reaction | after acid + bypass

- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : Neutralization by limestone filtration – $CaCO_3$

Answers:



AQUATIC CHEMISTRY for Engineers

Module **Chemical softening**
Softening with alkaline chemicals

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC

after base | after reaction | after acid + bypass

Aquatic Chemistry for engineers

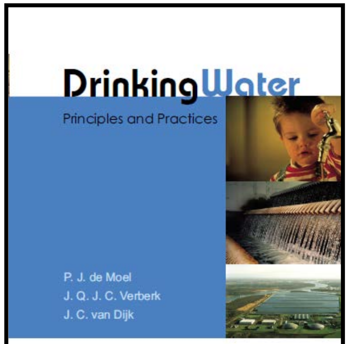
Item : Neutralization by limestone filtration – $CaCO_3$

Answers:

- Reaction to $CaCO_3$ equilibrium
  - CPP (=$CaCO_3$) = - Calcite consumption
  - Calcite dose = 1.53 mmol/kgw
  - Alternative: trial-and-error to SI = 0

- A : pH at equilibrium = 6.93
- B : Calcite = 1.53 mmol/kgw

- Book Drinking water P&P:
  - pH = 6.82
  - Calcite = 1.20 mmol/kgw
  - Other pK_s, ionic strength, ion pairs



Base	Alkaline chemical	formula		CaCO3	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw	1,53		
SI after reaction	Calcite	SI	CaCO3		e.g. 0.89	
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>	
	Siderite	SI	FeCO3		(no precip.)	
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g. 15	
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			
	Run PHREEQC					after base
Overall parameters	Cations		meq/kgw	3,94		6,90
	Anions		meq/kgw	3,95		6,90
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	43,3
	Total dissolved solids	TDS	mg/L	324		n.a.
	Ionic strength	IS	mmol/kgw	5,9		10,3
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	3,53
	Vapor pressure water	pa	atm	0,01		0,01
	Density	rho	kg/L	1,000		1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34
	pe (electron activity)	pe	-	15,50		15,04
	Redox potential	Eh	mV	870		844
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		0,0%
	EC ratio, calculated/measured		-	-		-
	TDS ratio, measured/calculated		-	-		-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%
	pH change by electron balancing (Phreeqc)		-	0,00		-
	pe change by electron balancing (Phreeqc)		-	-		-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	6,46		6,93
	Alkalinity	m	meq/kgw	4,00		7,06
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	7,67	92 mg/L C	9,21
	CO2	CO2	mmol/kgw	3,68	0,07 atm	2,15
	HCO3 -	HCO3	mmol/kgw	3,95	241 mg/L	6,90
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,02		-
	Buffer capacity	BI	mmol/kgw /pH	4,41		-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,90		0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		6,92
	Calcite Precipitation Potential	CPP	mmol/kgw	-1,53	67 mg/L CO2	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,66	29 mg/L CO2	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,02	2 mg/L CaCO3	-

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

- Dosing base simulation:
  - USE solution 1
  - REACTION
    - CaCO3
    - 1.53 millimoles (mass)
  - SAVE SOLUTION 2

```
# Dosing base

USE solution 1
REACTION 1
        CaCO3        1
        1.53     millimoles
SAVE SOLUTION 2
END  # Simulation 6

USE solution 2
EQUILIBRIUM_PHASES
        Calcite          0        # CCPP
END # Simulation 7
```

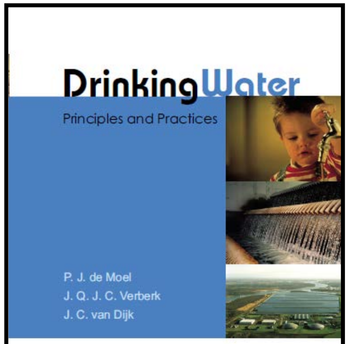
Conclusions - Lessons learned

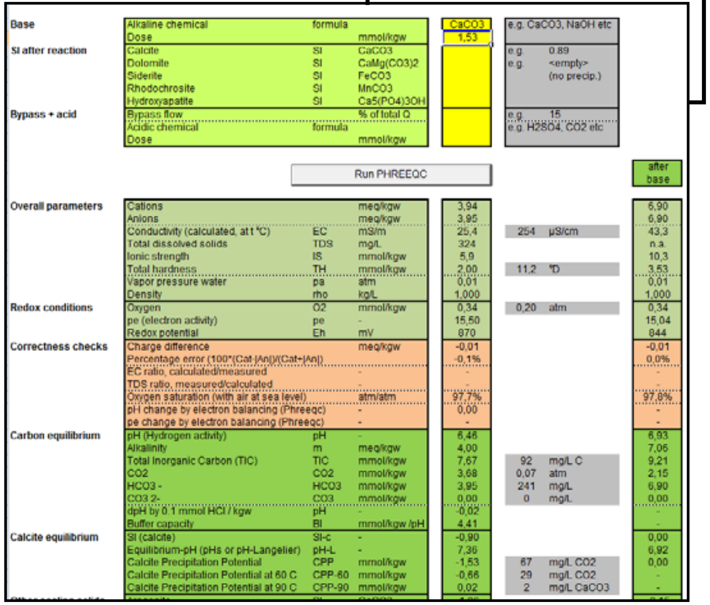
Neutralization by limestone filtration – $CaCO_3$

- In water quality $CaCO_3$ = Calcite
- Other crystal forms of $CaCO_3$:
  - Aragonite (more soluble)
  - Vaterite (more soluble)

- CPP = - Aggressive CO_2

- PHREEQC is more exact:
  - Other CO_2 content
  - Influence gamma (ionic strength)
  - Other pK_s (pK_w, pK_1, pK_2 equal)
  - Ion pairs





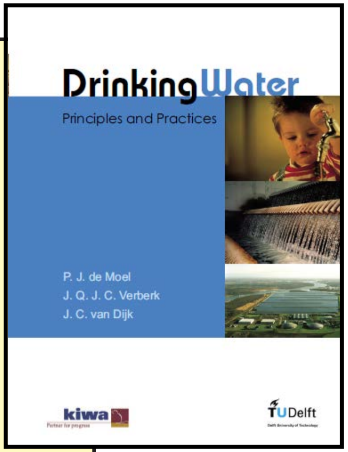
Base	Alkaline chemical	formula		CaCO3	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw	1,53		
SI after reaction	Calcite	SI	CaCO3		e.g. 0.89	
	Dolomite	SI	CaMg(CO3)2		e.g. <empty> (no precip.)	
	Siderite	SI	FeCO3			
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g. 15	
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			
	Run PHREEQC					after base
Overall parameters	Cations		meq/kgw	3,94		6,90
	Anions		meq/kgw	3,95		6,90
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	43,3
	Total dissolved solids	TDS	mg/L	324		n.a.
	Ionic strength	IS	mmol/kgw	5,9		10,3
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	3,53
	Vapor pressure water	pa	atm	0,01		0,01
	Density	rho	kg/L	1,000		1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34
	pe (electron activity)	pe	-	15,50		15,04
	Redox potential	Eh	mV	870		844
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		0,0%
	EC ratio, calculated/measured		-	-		-
	TDS ratio, measured/calculated		-	-		-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%
	pH change by electron balancing (Phreeqc)		-	0,00		-
	pe change by electron balancing (Phreeqc)		-	-		-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	6,46		6,93
	Alkalinity	m	meq/kgw	4,00		7,06
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	7,67	92 mg/L C	9,21
	CO2	CO2	mmol/kgw	3,68	0,07 atm	2,15
	HCO3 -	HCO3	mmol/kgw	3,95	241 mg/L	6,90
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,02		-
	Buffer capacity	BI	mmol/kgw /pH	4,41		-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,90		0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		6,92
	Calcite Precipitation Potential	CPP	mmol/kgw	-1,53	67 mg/L CO2	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,66	29 mg/L CO2	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,02	2 mg/L CaCO3	-

Questions?



Aquatic Chemistry for engineers

Item : Neutralization by caustic soda - NaOH



Neutralization by dosing caustic soda

Raw water (10°C) of a pumping station has the following composition:
Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, pH = 6.46, CO_2 = 4.0 mmol/l.
What is the pH in equilibrium after dosing caustic soda and how much NaOH is required?

When x mol NaOH is dosed, then x mol CO_2 is removed and x mol HCO_3^- is formed.
From $K = [Ca^{2+}]\,[HCO_3^-]^2 / [CO_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:
$(2.0) \cdot (4.0 + x)^2 / (4.0 - x) \cdot 10^{-6} = 10^{-4.33}$ so that x = 2.30 mmol/l

Thus, in equilibrium is:
Ca^{2+} = 2.00 mmol/l, HCO_3^- = 6.30 mmol/l, CO_2 = 1.70 mmol/l
From $pH_s = pK_2 - pK_s - \log\{[Ca^{2+}]\,[HCO_3^-]\}$ results:
$pH_s = 10.49 - 8.36 - \log\{[2.00\ 10^{-3}]\,[6.30\ 10^{-3}]\} = 2.13 + 4.90 = 7.03$
After dosing caustic soda, the pH is lower than after aeration/gas transfer, but higher than after lime-stone filtration.

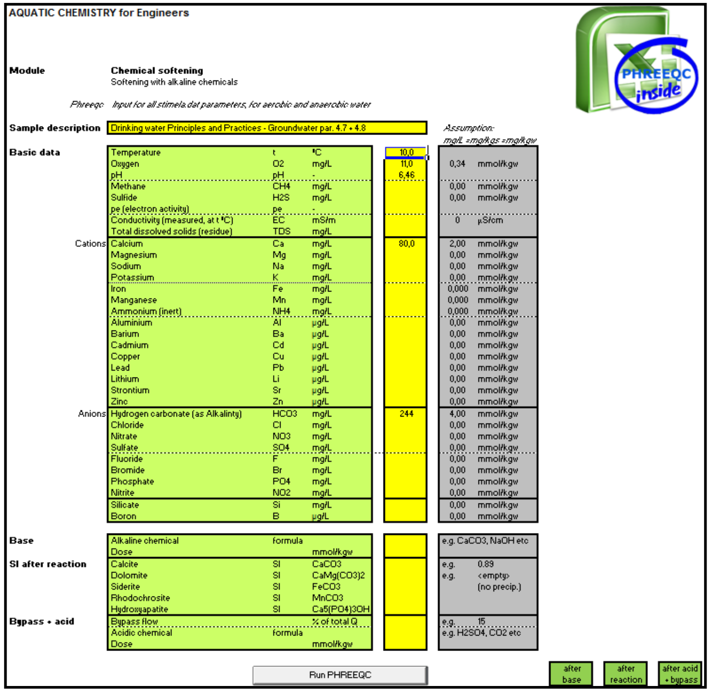
Because of dosing caustic soda, 2.30 mmol/l CO_2 is transformed and 2.30 mmol/l NaOH is consumed, that is (2,30 • 40 =) 92 g/m³.
A production of 1 million m³ per year corresponds to about 92 tons NaOH (100%) per year.

Aquatic Chemistry for engineers

Item : Neutralization by caustic soda - NaOH

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - pH = 6.46
  - CO_2 = 3.68 mmol/kgw (was 4.0)

- Calculate:
  - A: pH at equilibrium with $CaCO_3$
  - B: NaOH consumption



AQUATIC CHEMISTRY for Engineers

Module: **Chemical softening** — Softening with alkaline chemicals

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L =mg/kgs =mg/kgw

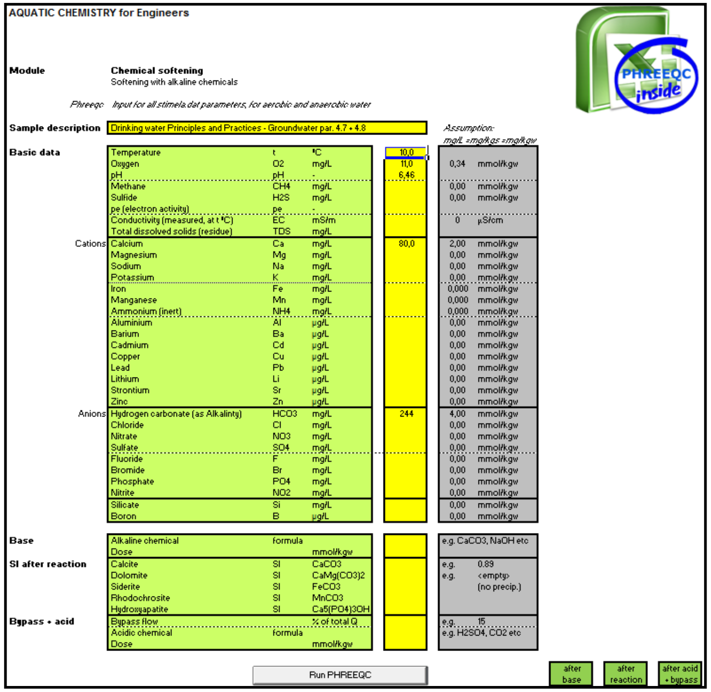
Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty> (no precip.)
	Siderite	SI	FeCO3			
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : Neutralization by caustic soda - NaOH

Answers:



Aquatic Chemistry for engineers

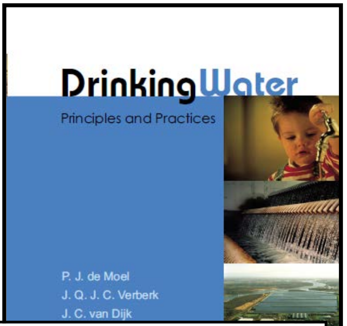
Item : Neutralization by caustic soda - NaOH

Answers:

- Reaction to $CaCO_3$ equilibrium
  - Clever trial-and-error to SI = 0
  - NaOH dose = 2.56 or 2.57 mmol/kgw

- A : pH at equilibrium = 7.18
- B : NaOH = 2.56 mmol/kgw

- Book Drinking water P&P:
  - pH = 7.03
  - NaOH = 2.30 mmol/kgw
  - Other pK_s, ionic strength, ion pairs



Base	Alkaline chemical	formula		NaOH	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw	2,56		
SI after reaction	Calcite	SI	CaCO3		e.g. 0.89	
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>	
	Siderite	SI	FeCO3		(no precip.)	
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g. 15	
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			
	Run PHREEQC					after base
Overall parameters	Cations		meq/kgw	3,94		6,45
	Anions		meq/kgw	3,95		6,46
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	40,3
	Total dissolved solids	TDS	mg/L	324		n.a.
	Ionic strength	IS	mmol/kgw	5,9		8,4
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	2,00
	Vapor pressure water	pa	atm	0,01		0,01
	Density	rho	kg/L	1,000		1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34
	pe (electron activity)	pe	-	15,50		14,78
	Redox potential	Eh	mV	870		829
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		-0,1%
	EC ratio, calculated/measured		-	-		-
	TDS ratio, measured/calculated		-	-		-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%
	pH change by electron balancing (Phreeqc)		-	0,00		-
	pe change by electron balancing (Phreeqc)		-	-		-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	6,46		7,18
	Alkalinity	m	meq/kgw	4,00		6,56
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	7,67	92 mg/L C	7,67
	CO2	CO2	mmol/kgw	3,68	0,07 atm	1,12
	HCO3 -	HCO3	mmol/kgw	3,95	241 mg/L	6,45
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,02		-
	Buffer capacity	BI	mmol/kgw /pH	4,41		-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,90		0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		7,18
	Calcite Precipitation Potential	CPP	mmol/kgw	-1,53	67 mg/L CO2	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,66	29 mg/L CO2	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,02	2 mg/L CaCO3	-

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

- Dosing base simulation:
  - USE solution 1
  - REACTION
    - NaOH
    - 2.56 millimoles (mass)
  - SAVE SOLUTION 2

```
# Dosing base

USE solution 1
REACTION 1
        NaOH        1
        2.56     millimoles
SAVE SOLUTION 2
END  # Simulation 6
```

Conclusions - Lessons learned

Neutralization – Compare the treatment options

- Option — Aeration — $CaCO_3$ — NaOH
  - Dose — -3.22 — 1.53 — 2.56
  - pH — 7.36 — 6.93 — 7.18
  - Alk — 4.00 — 7.06 — 6.56
  - Ca — 2.00 — 3.53 — 2.00

Option	Aeration	$CaCO_3$	NaOH
Dose	-3.22	1.53	2.56
pH	7.36	6.93	7.18
Alk	4.00	7.06	6.56
Ca	2.00	3.53	2.00

- Here: Aeration is best (costs, quality)

- PHREEQC (in Excel) gives more:
  - Concentration of all species
  - CPP / CCPP
  - Buffer capacity
  - SI of major solids

Base	Alkaline chemical	formula		NaOH	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw	2,56		
SI after reaction	Calcite	SI	CaCO3		e.g. 0.89	
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>	
	Siderite	SI	FeCO3		(no precip.)	
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g. 15	
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			
	Run PHREEQC					after base
Overall parameters	Cations		meq/kgw	3,94		6,45
	Anions		meq/kgw	3,95		6,46
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	40,3
	Total dissolved solids	TDS	mg/L	324		n.a.
	Ionic strength	IS	mmol/kgw	5,9		8,4
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	2,00
	Vapor pressure water	pa	atm	0,01		0,01
	Density	rho	kg/L	1,000		1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34
	pe (electron activity)	pe	-	15,50		14,78
	Redox potential	Eh	mV	870		829
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		-0,1%
	EC ratio, calculated/measured		-	-		-
	TDS ratio, measured/calculated		-	-		-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%
	pH change by electron balancing (Phreeqc)		-	0,00		-
	pe change by electron balancing (Phreeqc)		-	-		-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	6,46		7,18
	Alkalinity	m	meq/kgw	4,00		6,56
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	7,67	92 mg/L C	7,67
	CO2	CO2	mmol/kgw	3,68	0,07 atm	1,12
	HCO3 -	HCO3	mmol/kgw	3,95	241 mg/L	6,45
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,02		-
	Buffer capacity	BI	mmol/kgw /pH	4,41		-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,90		0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		7,18
	Calcite Precipitation Potential	CPP	mmol/kgw	-1,53	67 mg/L CO2	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	-0,66	29 mg/L CO2	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,02	2 mg/L CaCO3	-

Questions?

Aquatic Chemistry for engineers

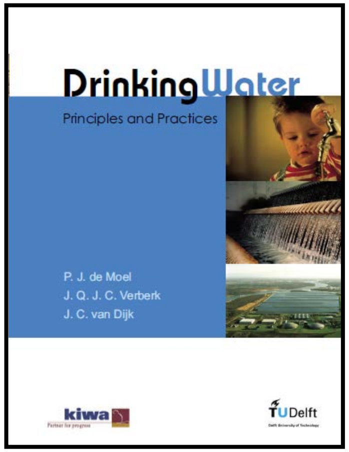
Item : Softening by caustic soda / sodium hydroxide

Softening by dosing sodium hydroxide

Raw water (10°C) of a pumping station has the following composition:
Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, CO_2 = 1.0 mmol/l
What is the required dosing with sodium hydroxide for softening down to Ca^{2+} = 1.0 mmol/l and what is the final water composition?

The content of Ca^{2+} has to be lowered with 2.0 - 1.0 = 1.0 mmol/l, for which 1.0 mmol/l NaOH is needed, then 1.0 mmol/l HCO_3^- is removed and 1.0 mmol/l $CaCO_3$ is formed.
The amount of CO_2 that has to be removed can be calculated assuming that x mol NaOH is dosed, then x mol CO_2 is removed and x mol HCO_3^- is formed.
From $K = [Ca^{2+}]\,[HCO_3^-]^2 / [CO_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:
$(1.0)\,(4.0 - 1.0 + x)^2 / (1.0 - x) \cdot 10^{-6} = 10^{-4.33}$, so x = 0.71 mmol/l
Therefore 1.0 + 0.71 = 1.71 mmol/l NaOH is needed, that is (1.71 · 40 =) 68 g/m³.
The production of 1 million m³ per year corresponds to 68 tons NaOH (100%) per year.
1.0 mmol/l $CaCO_3$ is formed, that is (1.0 • 100 =) 100 g/m³.
A production of 1 million m³ per year corresponds to 100 tons $CaCO_3$ per year.

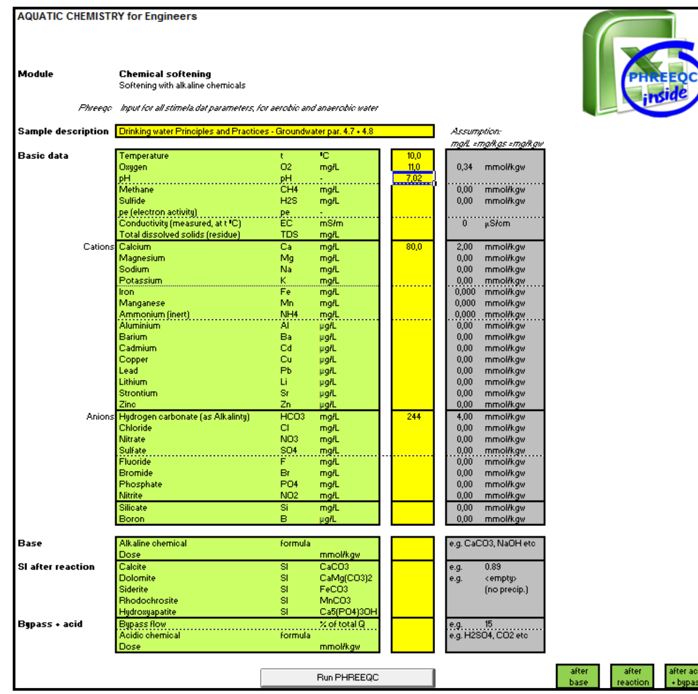
After softening:
Ca^{2+} = 1.00 mmol/l, HCO_3^- = 3.71 mmol/l, CO_2 = 0.29 mmol/l, $Na^+ = Na^+_0$ + 1.71 mmol/l, pH = pH_s (equilibrium)
From $pH_s = pK_2 - pKs - \log\{[Ca^{2+}]\,[HCO_3^-]\}$ results :
$pH_s = 10.49 - 8.36 - \log\{[1.00\ 10^{-3}]\,[3.71\ 10^{-3}]\} = 2.13 + 5.43 = 7.56$
The pH mentioned above equals pH_s. This shows that it is permissible to neglect the formation of CO_3^{2-}.



Aquatic Chemistry for engineers

Item : Softening by caustic soda - NaOH

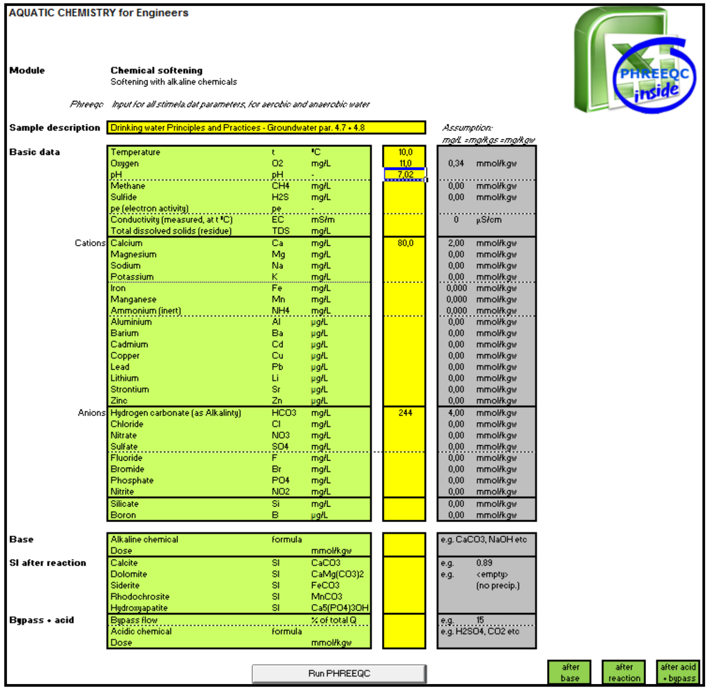
- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - CO_2 = 1.0 mmol/kgw
  - pH = 7.02
- Calculate:
  - A: NaOH dose for Ca = 1.0 mmol/kgw
  - B: pH after softening
  - Hint: assume SI calcite = 0
- I give you 3 minutes....



Aquatic Chemistry for engineers

Item : Softening by caustic soda - NaOH

Answers:



AQUATIC CHEMISTRY for Engineers

Module — **Chemical softening**
Softening with alkaline chemicals

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description: Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	7,02		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula			e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3		e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

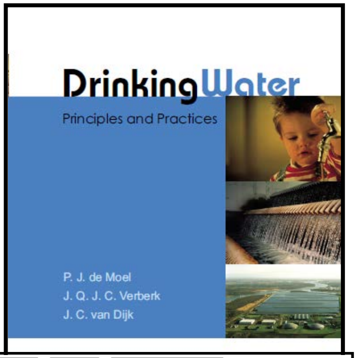
Run PHREEQC | after base | after reaction | after acid + bypass

Aquatic Chemistry for engineers

Item : Softening by caustic soda - NaOH

Answers:

- Estimate required NaOH dose
  - $NaOH = \Delta\ CO_2 + \Delta\ Ca$
  - NaOH = 1.0 + 1.0 = 2.0
  - Clever trial-and-error and SI = 0
  - NaOH dose = 1.80 mmol/kgw
- A : pH after softening = 7.67
  - CO_2 after softening = 0.22 mmol/kgw
- B : NaOH = 1.80 mmol/kgw
- Book Drinking water P&P:
  - pH = 7.56 / NaOH = 1.71 mmol/kgw
  - Other pK_s, ionic strength, ion pairs



						after base	after reaction
Base	Alkaline chemical	formula		NaOH	e.g. CaCO3, NaOH etc		
	Dose		mmol/kgw	1,80			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g. 0.89		
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>		
	Siderite	SI	FeCO3		(no precip.)		
	Rhodochrosite	SI	MnCO3				
	Hydroxyapatite	SI	Ca5(PO4)3OH				
Bypass + acid	Bypass flow		% of total Q		e.g. 15		
	Acidic chemical	formula			e.g. H2SO4, CO2 etc		
	Dose		mmol/kgw				
	Run PHREEQC						
Overall parameters	Cations		meq/kgw	3,94		4,92	3,76
	Anions		meq/kgw	3,94		4,93	3,77
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	32,1	23,9
	Total dissolved solids	TDS	mg/L	324		n.a.	n.a.
	Ionic strength	IS	mmol/kgw	5,9		6,8	4,7
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	2,00	1,00
	Vapor pressure water	pa	atm	0,01		0,01	0,01
	Density	rho	kg/L	1,000		1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34	0,34
	pe (electron activity)	pe	-	14,94		12,63	14,29
	Redox potential	Eh	mV	839		709	802
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01	-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		-0,1%	-0,1%
	EC ratio, calculated/measured		-	-		-	-
	TDS ratio, measured/calculated		-	-		-	-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%	97,7%
	pH change by electron balancing (Phreeqc)		-	0,00		-	-
	pe change by electron balancing (Phreeqc)		-	-		-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,02		9,34	7,67
	Alkalinity	m	meq/kgw	4,00		5,80	3,80
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	5,01	60 mg/L C	5,01	4,01
	CO2	CO2	mmol/kgw	1,01	0,02 atm	0,01	0,22
	HCO3 -	HCO3	mmol/kgw	3,94	240 mg/L	4,16	3,75
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	0,38	0,01
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,05		-	-
	Buffer capacity	BI	mmol/kgw /pH	1,88		-	-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,34		1,89	0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		7,45	7,67
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,32	14 mg/L CO2	1,00	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,13	14 mg/L CaCO3	-	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,56	56 mg/L CaCO3	-	-

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc
- Dosing base / precipitation simulation:
  - USE solution 1
  - REACTION
    - NaOH
    - 1.80 millimoles (mass)
  - EQUILIBRIUM_PHASES
    - Calcite 0.0 10 precipitate_only
    - Other precipitating solids

```
# Dosing base

USE solution 1
REACTION 1
        NaOH           1
        1.80      millimoles
SAVE SOLUTION 2
END  # Simulation 6

USE solution 2
EQUILIBRIUM_PHASES
        Calcite             0          # CCPP
END # Simulation 7

# Precipitation in reactor

USE solution 2
EQUILIBRIUM_PHASES
        Calcite          0.00     10 precipitate_only         # CaCO3
#       Dolomite         0.00     10 precipitate_only         # CaMgCO3
#       Siderite         0.00     10 precipitate_only         # FeCO3
#       Rhodochrosite    0.00     10 precipitate_only         # MnCO3
#       Hydroxyapatite   0.00     10 precipitate_only         # Ca5(PO4)3OH
#       Vivianite               1 10 precipitate_only         # Fe3(PO4)2:8H2O
#       Barite                  1 10 precipitate_only         # BaCO3
#       Aragonite               1 10 precipitate_only         # CaCO3
#       Pyrite                  1 10 precipitate_only         # FeS
#       Mackinawite             1 10 precipitate_only         # FeS
#       FeS(ppt)                1 10 precipitate_only         # FeS
#       Goethite                1 10 precipitate_only         # FeOOH
#       Hematite                1 10 precipitate_only         # Fe2O3
SAVE solution 3
END # Simulation 8
```

Aquatic Chemistry for engineers

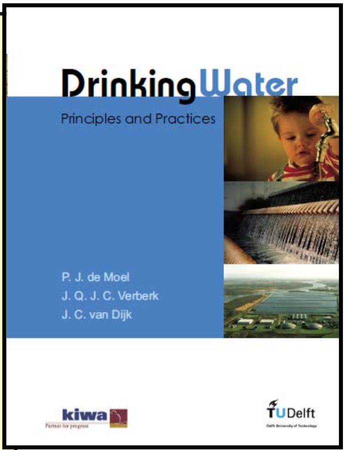
Item : Softening by (hydrated) lime - $Ca(OH)_2$

Softening by dosing lime

Raw water (10°C) of a pumping station has the following composition:
Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, CO_2 = 1.0 mmol/l
What is the required dosage of lime to soften up to Ca^{2+} = 1,0 mmol/l and what is the water composition?

The content of Ca^{2+} has to be lowered with 2.0 - 1.0 = 1.0 mmol/l, for which 1.0 mmol/l $Ca(OH)_2$ is needed, then 2.0 mmol/l HCO_3^- is removed and 2.0 mmol/l $CaCO_3$ is formed.
The amount of CO_2 that has to be removed can be calculated assuming that x mol $Ca(OH)_2$ is dosed, then x mol CO_2 is removed and x mol $CaCO_3$ is formed.
From $K = [Ca^{2+}]\,[HCO_3^-]^2 / [CO_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:
$(1.0)\,(4.0 - 2.0)^2 / (1.0 - x) \cdot 10^{-6} = 10^{-4.33}$ so that x = 0.91 mmol/l
And thus 1.0 + 0.91 = 1.91 mmol/l $Ca(OH)_2$ is needed, that is (1.91 • 77 =) 147 g/m³.
The production of 1 million m³ per year corresponds to 147 tons $Ca(OH)_2$ per year.
2.0 + 0.91 mmol/l $CaCO_3$ is formed, that is (2.91 · 100 =) 291 g/m³.
The production of 1 million m³ per year corresponds to 291 tons $CaCO_3$ per year.

After softening:
Ca^{2+} = 1.00 mmol/l, HCO_3^- = 2.00 mmol/l, CO_2 = 0.09 mmol/l, pH = pH_s (equilibrium)
From $pH_s = pK_2 - pK_s - \log\{ [Ca^{2+}]\,[HCO_3^-] \}$ results:
$pH_s = 10.49 - 8.36 - \log\{ [1.00\ 10^{-3}]\,[2.00\ 10^{-3}] \} = 2.13 + 5.70 = 7.83$
With this pH it is permissible to neglect the formation of OH^-.



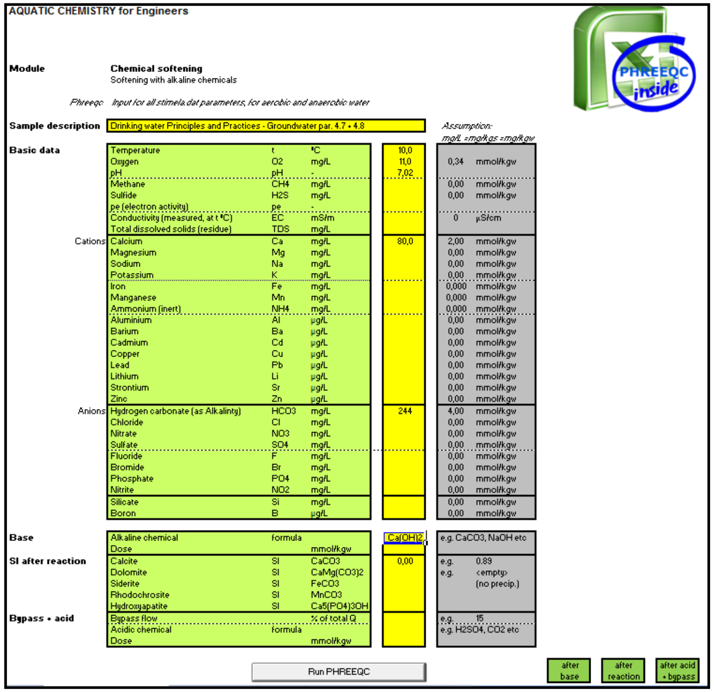
Aquatic Chemistry for engineers

Item : Softening by (hydrated) lime - $Ca(OH)_2$

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - CO_2 = 1.0 mmol/kgw
  - pH = 7.02

- Calculate:
  - A: $Ca(OH)_2$ for Ca = 1.0 mmol/kgw
  - B: pH after softening
  - Hint: assume SI calcite = 0

- I give you 3 minutes....



AQUATIC CHEMISTRY for Engineers

Module — **Chemical softening**
Softening with alkaline chemicals

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	7,02		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC — after base — after reaction — after acid + bypass

Aquatic Chemistry for engineers

Item : Softening by (hydrated) lime - $Ca(OH)_2$

Answers:

AQUATIC CHEMISTRY for Engineers

Module — **Chemical softening**
Softening with alkaline chemicals

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description: Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

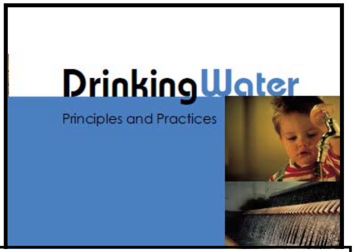
Assumption: mg/L =mg/kgs =mg/kgw

	Parameter	Symbol	Unit	Input	Value	Unit
Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	7,02		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC | after base | after reaction | after acid + bypass

Aquatic Chemistry for engineers

Item : Softening by (hydrated) lime - $Ca(OH)_2$



Answers:

- Estimate required $Ca(OH)_2$ dose
  - $Ca(OH)_2 = \Delta CO_2 + \Delta Ca$
  - $Ca(OH)_2 = 1.0 + 1.0 = 2.0$
  - Clever trial-and-error and SI = 0
  - $Ca(OH)_2$ dose = 1.95 mmol/kgw
- A : pH after softening = 7.92
  - CO_2 after softening = 0.07 mmol/kgw
- B : $Ca(OH)_2$ = 1.95 mmol/kgw

- Book Drinking water P&P:
  - pH = 7.83 / $Ca(OH)_2$ = 1.91 mmol/kgw
  - Other pK_s, ionic strength, ion pairs

						after base	after reaction
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc		
	Dose		mmol/kgw	1,95			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g. 0.89		
	Dolomite	SI	CaMg(CO3)2		e.g. <empty> (no precip.)		
	Siderite	SI	FeCO3				
	Rhodochrosite	SI	MnCO3				
	Hydroxyapatite	SI	Ca5(PO4)3OH				
Bypass + acid	Bypass flow		% of total Q		e.g. 15		
	Acidic chemical	formula			e.g. H2SO4, CO2 etc		
	Dose		mmol/kgw				
	Run PHREEQC						
Overall parameters	Cations		meq/kgw	3,94		4,45	1,97
	Anions		meq/kgw	3,94		4,45	1,98
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	31,8	13,1
	Total dissolved solids	TDS	mg/L	324		n.a.	n.a.
	Ionic strength	IS	mmol/kgw	5,9		7,8	3,0
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	3,95	1,00
	Vapor pressure water	pa	atm	0,01		0,01	0,01
	Density	rho	kg/L	1,000		1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34	0,34
	pe (electron activity)	pe	-	14,94		11,86	14,05
	Redox potential	Eh	mV	839		665	788
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01	-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		-0,1%	-0,2%
	EC ratio, calculated/measured		-	-		-	-
	TDS ratio, measured/calculated		-	-		-	-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%	97,7%
	pH change by electron balancing (Phreeqc)		-	0,00		-	-
	pe change by electron balancing (Phreeqc)		-	-		-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,02		10,10	7,92
	Alkalinity	m	meq/kgw	4,00		7,90	2,01
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	5,01	60 mg/L C	5,01	2,06
	CO2	CO2	mmol/kgw	1,01	0,02 atm	0,00	0,07
	HCO3 -	HCO3	mmol/kgw	3,94	240 mg/L	2,13	1,97
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	1,14	0,01
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,05		-	-
	Buffer capacity	BI	mmol/kgw /pH	1,88		-	-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,34		2,51	0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		7,60	7,92
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,32	14 mg/L CO2	2,95	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,13	14 mg/L CaCO3	-	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,56	56 mg/L CaCO3	-	-
Other scaling solids	Aragonite	SI	CaCO3	-0,50		2,35	-0,16
	Gypsum	SI	CaSO4.2H2O	-		-	-
	Anhydrite	SI	CaSO4	-		-	-
	Dolomite	SI	CaMg(CO3)2	-		-	-
	Hydroxyapatite	SI	Ca5(PO4)3OH	-		-	-
Redox scaling solids	Pyrite	SI	FeS	-		-	-
	Siderite	SI	FeCO3	-		-	-
	Hematite	SI	Fe2O3	-		-	-
	Rhodochrosite	SI	MnCO3	-		-	-
	Vivianite	SI	Fe3(PO4)2:8H2O	-		-	-
Elements / Species	C		mmol/kgw	5,01		5,01	2,06

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

- Dosing base / precipitation simulation:
  - USE solution 1
  - REACTION
    - Ca(OH)2
    - 1.95 millimoles (mass)
  - EQUILIBRIUM_PHASES
    - Calcite 0.0 10 precipitate_only
    - Other precipitating solids

```
# Dosing base

USE solution 1
REACTION 1
        Ca(OH)2         1
        1.95    millimoles
SAVE SOLUTION 2
END  # Simulation 6

USE solution 2
EQUILIBRIUM_PHASES
        Calcite         0       # CCPP
END # Simulation 7

# Precipitation in reactor

USE solution 2
EQUILIBRIUM_PHASES
        Calcite         0.00    10 precipitate_only     # CaCO3
#       Dolomite        0.00    10 precipitate_only     # CaMgCO3
#       Siderite        0.00    10 precipitate_only     # FeCO3
#       Rhodochrosite   0.00    10 precipitate_only     # MnCO3
#       Hydroxyapatite  0.00    10 precipitate_only     # Ca5(PO4)3OH
#       Vivianite       1       10 precipitate_only     # Fe3(PO4)2:8H2
#       Barite          1       10 precipitate_only     # BaCO3
#       Aragonite       1       10 precipitate_only     # CaCO3
#       Pyrite          1       10 precipitate_only     # FeS
#       Mackinawite     1       10 precipitate_only     # FeS
#       FeS(ppt)        1       10 precipitate_only     # FeS
#       Goethite        1       10 precipitate_only     # FeOOH
#       Hematite        1       10 precipitate_only     # Fe2O3
SAVE solution 3
END # Simulation 8

USE solution 3
EQUILIBRIUM_PHASES
        Calcite         0       # CCPP
END # Simulation 9
```

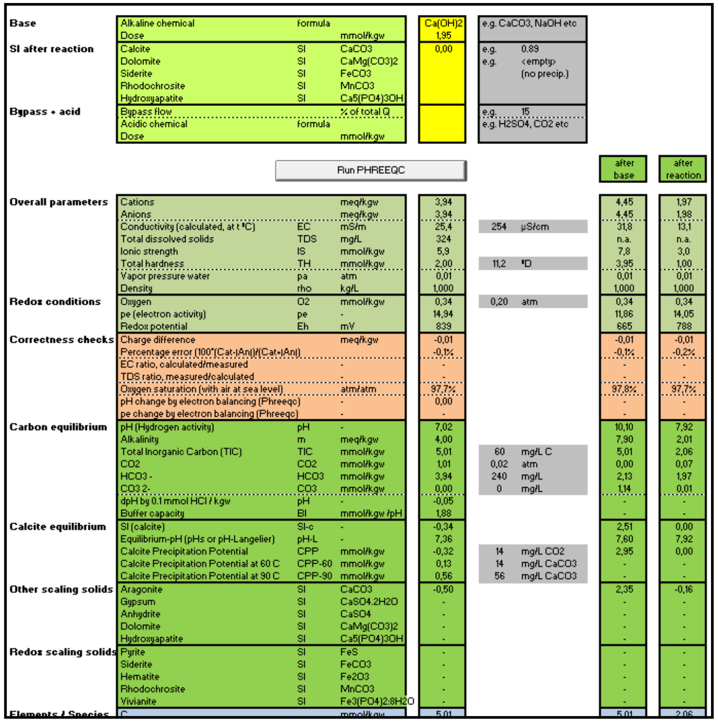
Conclusions - Lessons learned

Softening – Compare the two chemicals

- Option NaOH $Ca(OH)_2$
  - Dose 1.80 1.95
  - pH 7.67 7.92
  - Alk 3.80 2.01
  - Ca 1.00 1.00

- Here: $Ca(OH)_2$ is best (costs, quality)

- PHREEQC (in Excel) gives more:
  - Concentration of all species
  - CPP / CCPP
  - Buffer capacity
  - SI of major solids



						after base	after reaction
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc		
	Dose		mmol/kgw	1,95			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g. 0.89		
	Dolomite	SI	CaMg(CO3)2		e.g. <empty> (no precip.)		
	Siderite	SI	FeCO3				
	Rhodochrosite	SI	MnCO3				
	Hydroxyapatite	SI	Ca5(PO4)3OH				
Bypass + acid	Bypass flow		% of total Q		e.g. 15		
	Acidic chemical	formula			e.g. H2SO4, CO2 etc		
	Dose		mmol/kgw				
	Run PHREEQC						
Overall parameters	Cations		meq/kgw	3,94		4,45	1,97
	Anions		meq/kgw	3,94		4,45	1,98
	Conductivity (calculated, at t °C)	EC	mS/m	25,4	254 µS/cm	31,8	13,1
	Total dissolved solids	TDS	mg/L	324		n.a.	n.a.
	Ionic strength	IS	mmol/kgw	5,9		7,8	3,0
	Total hardness	TH	mmol/kgw	2,00	11,2 °D	3,95	1,00
	Vapor pressure water	pa	atm	0,01		0,01	0,01
	Density	rho	kg/L	1,000		1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34	0,34
	pe (electron activity)	pe	-	14,94		11,86	14,05
	Redox potential	Eh	mV	839		665	788
Correctness checks	Charge difference		meq/kgw	-0,01		-0,01	-0,01
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			-0,1%		-0,1%	-0,2%
	EC ratio, calculated/measured		-	-		-	-
	TDS ratio, measured/calculated		-	-		-	-
	Oxygen saturation (with air at sea level)		atm/atm	97,7%		97,8%	97,7%
	pH change by electron balancing (Phreeqc)		-	0,00		-	-
	pe change by electron balancing (Phreeqc)		-	-		-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,02		10,10	7,92
	Alkalinity	m	meq/kgw	4,00		7,90	2,01
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	5,01	60 mg/L C	5,01	2,06
	CO2	CO2	mmol/kgw	1,01	0,02 atm	0,00	0,07
	HCO3 -	HCO3	mmol/kgw	3,94	240 mg/L	2,13	1,97
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	1,14	0,01
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,05		-	-
	Buffer capacity	BI	mmol/kgw /pH	1,88		-	-
Calcite equilibrium	SI (calcite)	SI-c	-	-0,34		2,51	0,00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,36		7,60	7,92
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,32	14 mg/L CO2	2,95	0,00
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,13	14 mg/L CaCO3	-	-
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,56	56 mg/L CaCO3	-	-
Other scaling solids	Aragonite	SI	CaCO3	-0,50		2,35	-0,16
	Gypsum	SI	CaSO4.2H2O	-		-	-
	Anhydrite	SI	CaSO4	-		-	-
	Dolomite	SI	CaMg(CO3)2	-		-	-
	Hydroxyapatite	SI	Ca5(PO4)3OH	-		-	-
Redox scaling solids	Pyrite	SI	FeS	-		-	-
	Siderite	SI	FeCO3	-		-	-
	Hematite	SI	Fe2O3	-		-	-
	Rhodochrosite	SI	MnCO3	-		-	-
	Vivianite	SI	Fe3(PO4)2:8H2O	-		-	-
Elements / Species	C		mmol/kgw	5,01		5,01	2,06

Questions?

Aquatic Chemistry for engineers

Item : Split treatment for softening

Softening in split-treatment

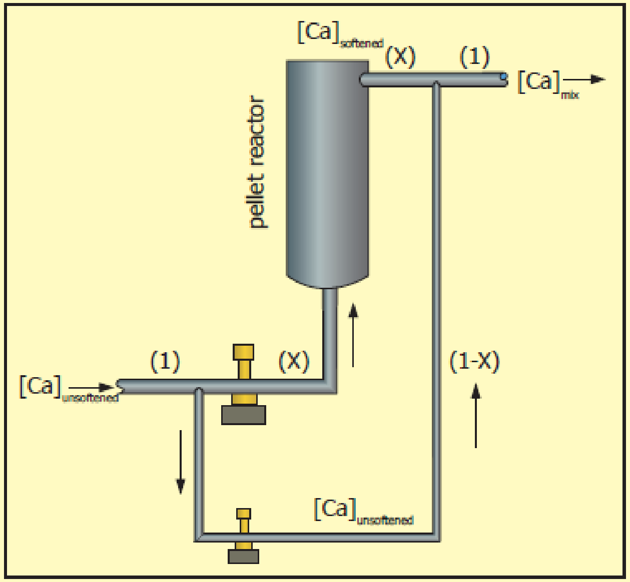
Raw water (10°C) of a pumping station has the following composition:
Ca^{2+} = 2.0 mmol/l, Mg^{2+} = 0.2 mmol/l, HCO_3^- = 4.0 mmol/l, CO_2 = 1.0 mmol/l
How much has to be removed by the softening reactors for softening down to a total hardness of 1.0 mmol/l?

With a total hardness of 1.0 mmol/l Ca^{2+} is (1.0 - 0.2 =) 0.8 mmol/l (content of Mg remains equal).
In the pellet reactor softening down to Ca^{2+} = 0.5 mmol/l (on condition that $[HCO_3^-]$ softened >1.0 mmol/l)
Assume that a fraction x is softened, then a fraction (1-x) will not be softened.
When mixing both flows, the following Ca-balance applies:

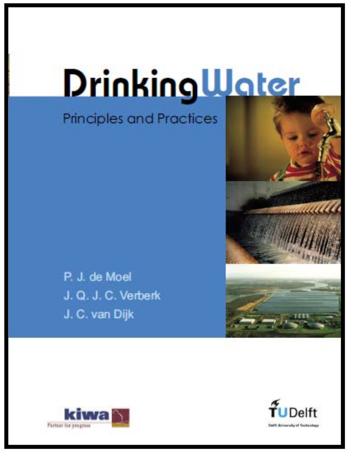
$x \cdot [Ca]_{softened} + (1-x) \cdot [Ca]_{not\ softened} = 1 \cdot [Ca]_{mixture}$

$x \cdot 0.5 + (1-x) \cdot 2.0 = 0.8$, so

$x = (2.0-0.8) / (2.0-0.5) = 1.2 / 1.5 = 0.8$



Thus, a minimum of 80% of the discharge has to be treated in the pellet reactors.



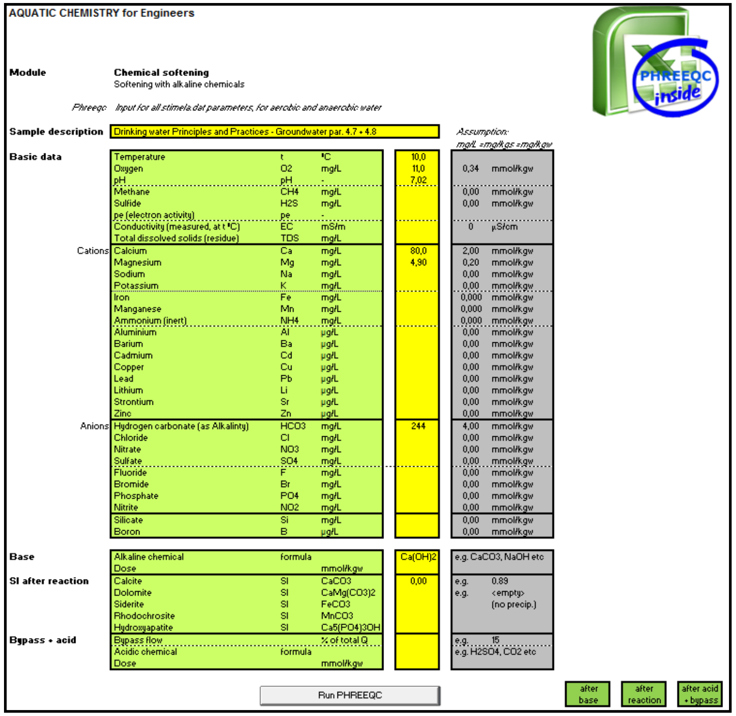
Aquatic Chemistry for engineers

Item : Split treatment for softening

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Mg = 0.2 mmol/kgw = 4.9 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - CO_2 = 1.0 mmol/kgw
  - pH = 7.02

- Calculate:
  - A: $Ca(OH)_2$ for Ca = 0.5 mmol/kgw
  - B: bypass for Ca = 0.8 mmol/kgw

- I give you 5 minutes....



AQUATIC CHEMISTRY for Engineers

Module: **Chemical softening** — Softening with alkaline chemicals

Phreeqc: Input for all stimela.dat parameters, for aerobic and anaerobic water

Sample description: Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

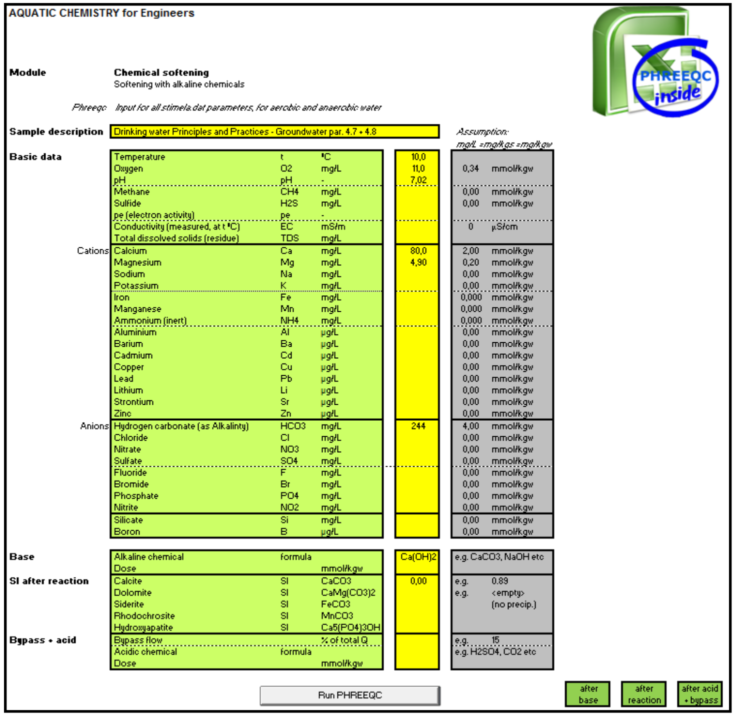
Assumption: mg/L = mg/kgs = mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	7,02		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L	4,90	0,20	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty>
	Siderite	SI	FeCO3			(no precip.)
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Aquatic Chemistry for engineers

Item : Split treatment for softening

Answers:



AQUATIC CHEMISTRY for Engineers

Module **Chemical softening**
Softening with alkaline chemicals

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8

Assumption: mg/L = mg/kgs = mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	7,02		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L	4,90	0,20	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc	
	Dose		mmol/kgw			
SI after reaction	Calcite	SI	CaCO3	0,00	e.g.	0.89
	Dolomite	SI	CaMg(CO3)2		e.g.	<empty> (no precip.)
	Siderite	SI	FeCO3			
	Rhodochrosite	SI	MnCO3			
	Hydroxyapatite	SI	Ca5(PO4)3OH			
Bypass + acid	Bypass flow		% of total Q		e.g.	15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc	
	Dose		mmol/kgw			

Run PHREEQC

after base | after reaction | after acid + bypass

Aquatic Chemistry for engineers

Item : Split treatment for softening

Answers:

- Estimate required $Ca(OH)_2$ dose
  - $Ca(OH)_2 = \Delta CO_2 + \Delta Ca$
  - $Ca(OH)_2 = 1.0 + 1.5 = 2.5$
  - Clever trial-and-error and SI = 0
  - $Ca(OH)_2$ dose = 2.51 mmol/kgw
- A : pH after softening = 8.50
  - CO_2 after softening = 0.01 mmol/kgw
  - $Ca(OH)_2$ = 2.51 mmol/kgw
- B : Bypass = 20%

- Book Drinking water P&P:
  - Same bypass flow / No equilibrium reactions

DrinkingWater

Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc			
	Dose		mmol/kgw	2,51				
SI after reaction	Calcite	SI	CaCO3	0,00	e.g. 0.89			
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>			
	Siderite	SI	FeCO3		(no precip.)			
	Rhodochrosite	SI	MnCO3					
	Hydroxyapatite	SI	Ca5(PO4)3OH					
Bypass + acid	Bypass flow		% of total Q	20	e.g. 15			
	Acidic chemical	formula			e.g. H2SO4, CO2 etc			
	Dose		mmol/kgw					
	Run PHREEQC					after base	after reaction	after acid + bypass
Overall parameters	Cations		meq/kgw	4,33		4,70	1,38	1,99
	Anions		meq/kgw	3,94		4,30	0,99	1,59
	Conductivity (calculated, at t °C)	EC	mS/m	26,5	265 µS/cm	33,8	8,0	11,8
	Total dissolved solids	TDS	mg/L	329		n.a.	n.a.	n.a.
	Ionic strength	IS	mmol/kgw	6,3		8,4	1,9	2,8
	Total hardness	TH	mmol/kgw	2,20	12,3 °D	4,71	0,70	1,00
	Vapor pressure water	pa	atm	0,01		0,01	0,01	0,01
	Density	rho	kg/L	1,000		1,000	1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34	0,34	0,34
	pe (electron activity)	pe	-	14,94		11,44	13,46	14,61
	Redox potential	Eh	mV	839		642	755	820
Correctness checks	Charge difference		meq/kgw	0,40		0,40	0,40	0,40
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			4,8%		4,4%	16,7%	11,1%
	EC ratio, calculated/measured		-	-		-	-	-
	TDS ratio, measured/calculated		-	-		-	-	-
	Oxygen saturation (with air at sea level)		atm/atm	97,8%		97,8%	97,6%	97,7%
	pH change by electron balancing (Phreeqc)		-	0,00		-	-	-
	pe change by electron balancing (Phreeqc)		-	-		-	-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,02		10,52	8,50	7,35
	Alkalinity	m	meq/kgw	4,00		9,02	1,01	1,61
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	5,00	60 mg/L C	5,00	1,00	1,80
	CO2	CO2	mmol/kgw	1,01	0,02 atm	0,00	0,01	0,19
	HCO3 -	HCO3	mmol/kgw	3,93	240 mg/L	1,09	0,96	1,59
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	1,55	0,01	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,05		-	-	-0,21
	Buffer capacity	BI	mmol/kgw /pH	1,87		-	-	0,42
Calcite equilibrium	SI (calcite)	SI-c	-	-0,35		2,63	0,00	-0,75
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,37		7,89	8,50	8,10
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,33	14 mg/L CO2	4,01	0,00	-0,15
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,13	13 mg/L CaCO3	-	-	-0,07
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,55	55 mg/L CaCO3	-	-	0,04
Other scaling solids	Aragonite	SI	CaCO3	-0,50		2,48	-0,16	-0,90
	Gypsum	SI	CaSO4.2H2O	-		-	-	-
	Anhydrite	SI	CaSO4	-		-	-	-
	Dolomite	SI	CaMg(CO3)2	-1,79		3,92	-0,49	-2,19
	Hydroxyapatite	SI	Ca5(PO4)3OH	-		-	-	-
Redox scaling solids	Pyrite	SI	FeS	-		-	-	-
	Siderite	SI	FeCO3	-		-	-	-
	Hematite	SI	Fe2O3	-		-	-	-
	Rhodochrosite	SI	MnCO3	-		-	-	-
	Vivianite	SI	Fe3(PO4)2:8H2O	-		-	-	-
Elements / Species	C		mmol/kgw	5,00		5,00	1,00	1,80
	CO2			20,1%	44 mg/L	0,0%	0,8%	10,8%
	HCO3 -			78,6%		21,8%	96,8%	88,4%
	CO3 2-			0,0%		31,1%	1,2%	0,1%
	CH4		mmol/kgw	0,00	0,00 mg/L	0,00	0,00	0,00
	Ca		mmol/kgw	2,00		4,51	0,50	0,80
	Ca 2+			97,3%		49,1%	98,2%	98,7%
	CaHCO3 +			2,6%		0,3%	0,7%	1,2%

Aquatic Chemistry for engineers

Module : Chemical softening - PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc
- Dosing base / precipitation simulation:
  - Reaction / Equilibrium_phases

- MIX softened and raw water
- REACTION acid

```
# Bypass and acid dose
MIX
1          0.20       # takes fraction 1-x of solution 1
3          0.80       # takes fraction x of solution 3
REACTION
           H2SO4            1
           0.00       millimoles
SAVE solution 4
END  # Simulation 10

USE solution 4
EQUILIBRIUM_PHASES
           Calcite              0          # CCPP
END # Simulation 11
```

Conclusions - Lessons learned

Split treatment for softening

- SI Dolomite - $CaMg(CO_3)_2 = CaCO_3.MgCO_3$
  - after $Ca(OH)_2$ = +3.92 (supersaturated)
  - Mg after reactor = 0.2 mmol/kgw
  - SI Dolomite after reactor = -0.49
  - Apparently no Mg removed
- Better: input SI Dolomite = + 5.0
- PHREEQC (in Excel) gives more:
  - Concentration of all species
  - CPP / CCPP
  - Buffer capacity
  - SI of major solids

Base	Alkaline chemical	formula		Ca(OH)2	e.g. CaCO3, NaOH etc
	Dose		mmol/kgw	2,51	
SI after reaction	Calcite	SI	CaCO3	0,00	e.g. 0.89
	Dolomite	SI	CaMg(CO3)2		e.g. <empty>
	Siderite	SI	FeCO3		(no precip.)
	Rhodochrosite	SI	MnCO3		
	Hydroxyapatite	SI	Ca5(PO4)3OH		
Bypass + acid	Bypass flow		% of total Q	20	e.g. 15
	Acidic chemical	formula			e.g. H2SO4, CO2 etc
	Dose		mmol/kgw		

Run PHREEQC

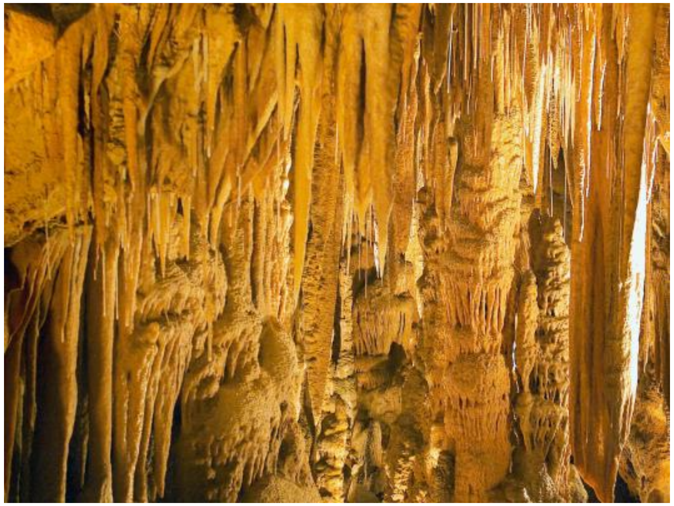
						after base	after reaction	after acid + bypass
Overall parameters	Cations		meq/kgw	4,33		4,70	1,38	1,99
	Anions		meq/kgw	3,94		4,30	0,99	1,59
	Conductivity (calculated, at t °C)	EC	mS/m	26,5	265 µS/cm	33,8	8,0	11,8
	Total dissolved solids	TDS	mg/L	329		n.a.	n.a.	n.a.
	Ionic strength	IS	mmol/kgw	6,3		8,4	1,9	2,8
	Total hardness	TH	mmol/kgw	2,20	12,3 °D	4,71	0,70	1,00
	Vapor pressure water	pa	atm	0,01		0,01	0,01	0,01
	Density	rho	kg/L	1,000		1,000	1,000	1,000
Redox conditions	Oxygen	O2	mmol/kgw	0,34	0,20 atm	0,34	0,34	0,34
	pe (electron activity)	pe	-	14,94		11,44	13,46	14,61
	Redox potential	Eh	mV	839		642	755	820
Correctness checks	Charge difference		meq/kgw	0,40		0,40	0,40	0,40
	Percentage error (100*(Cat-|An|)/(Cat+|An|)			4,8%		4,4%	16,7%	11,1%
	EC ratio, calculated/measured		-	-		-	-	-
	TDS ratio, measured/calculated		-	-		-	-	-
	Oxygen saturation (with air at sea level)		atm/atm	97,8%		97,8%	97,6%	97,7%
	pH change by electron balancing (Phreeqc)		-	0,00		-	-	-
	pe change by electron balancing (Phreeqc)		-	-		-	-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	-	7,02		10,52	8,50	7,35
	Alkalinity	m	meq/kgw	4,00		9,02	1,01	1,61
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	5,00	60 mg/L C	5,00	1,00	1,80
	CO2	CO2	mmol/kgw	1,01	0,02 atm	0,00	0,01	0,19
	HCO3 -	HCO3	mmol/kgw	3,93	240 mg/L	1,09	0,96	1,59
	CO3 2-	CO3	mmol/kgw	0,00	0 mg/L	1,55	0,01	0,00
	dpH by 0.1 mmol HCl / kgw	pH	-	-0,05		-	-	-0,21
	Buffer capacity	BI	mmol/kgw /pH	1,87		-	-	0,42
Calcite equilibrium	SI (calcite)	SI-c	-	-0,35		2,63	0,00	-0,75
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7,37		7,89	8,50	8,10
	Calcite Precipitation Potential	CPP	mmol/kgw	-0,33	14 mg/L CO2	4,01	0,00	-0,15
	Calcite Precipitation Potential at 60 C	CPP-60	mmol/kgw	0,13	13 mg/L CaCO3	-	-	-0,07
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0,55	55 mg/L CaCO3	-	-	0,04
Other scaling solids	Aragonite	SI	CaCO3	-0,50		2,48	-0,16	-0,90
	Gypsum	SI	CaSO4.2H2O	-		-	-	-
	Anhydrite	SI	CaSO4	-		-	-	-
	Dolomite	SI	CaMg(CO3)2	-1,79		3,92	-0,49	-2,19
	Hydroxyapatite	SI	Ca5(PO4)3OH	-		-	-	-
Redox scaling solids	Pyrite	SI	FeS	-		-	-	-
	Siderite	SI	FeCO3	-		-	-	-
	Hematite	SI	Fe2O3	-		-	-	-
	Rhodochrosite	SI	MnCO3	-		-	-	-
	Vivianite	SI	Fe3(PO4)2:8H2O	-		-	-	-
Elements / Species	C		mmol/kgw	5,00		5,00	1,00	1,80
	CO2			20,1%	44 mg/L	0,0%	0,8%	10,8%
	HCO3 -			78,6%		21,8%	96,8%	88,4%
	CO3 2-			0,0%		31,1%	1,2%	0,1%
	CH4		mmol/kgw	0,00	0,00 mg/L	0,00	0,00	0,00
	Ca		mmol/kgw	2,00		4,51	0,50	0,80
	Ca 2+			97,3%		49,1%	98,2%	98,7%
	CaHCO3 +			2,6%		0,3%	0,7%	1,2%

Questions?

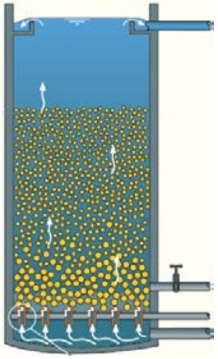
Aquatic Chemistry for engineers

Module : Kinetics of calcite – PWP model (App 3b)

- Dissolution of calcite
  - Limestone filtration



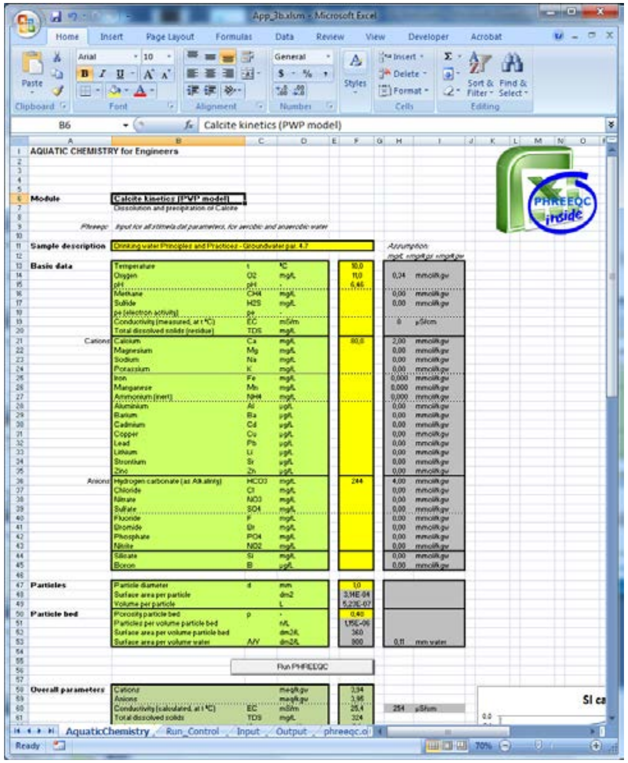
- Precipitation of calcite
  - Softening



- Application
  - Drinking water : neutralization + softening
  - Sewerage / wastewater: concrete corrosion + precipitation

App 3b - Calcite kinetics (PWP)

- Open App_3b.xlsm:

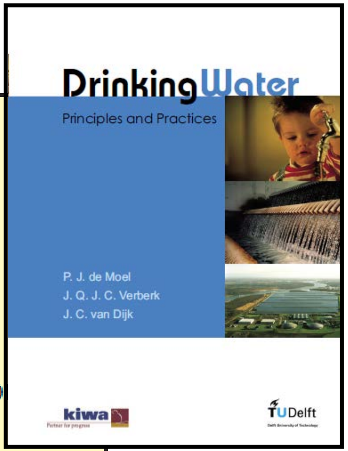


Requires:

- module IPhreeqcCOM installed (in Windows)
- macros enabled (in Excel)

Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – $CaCO_3$



Neutralization by limestone filtration

Raw water (10°C) of a pumping station has the following composition:

Ca^{2+} = 2.0 mmol/l, HCO_3^- = 4.0 mmol/l, pH = 6.46, CO_2 = 4.0 mmol/l

What is the pH in equilibrium after limestone filtration and how much $CaCO_3$ is required?

When x mol $CaCO_3$ reacts, then x mol CO_2 is removed and x mol Ca^{2+} and 2x mol HCO_3^- are fo

From $K = [Ca^{2+}] \cdot [HCO_3^-]^2 / [CO_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

$(2.0 + x) \cdot (4.0 + 2x)^2 / (4.0 - x)\ 10^{-6} = 10^{-4.33}$ so that x = 1.20 mmol/l

Thus in equilibrium is:

Ca^{2+} = 3.20 mmol/l, HCO_3^- = 6.40 mmol/l, CO_2 = 2.80 mmol/l.

From $pH_s = pK_2 - pK_s - \log\{[Ca^{2+}]\,[HCO_3^-]\}$ results:

$pH_s = 10.49 - 8.36 - \log\{[3.20\ 10^{-3}]\,[6.40\ 10^{-3}]\} = 2.13 + 4.69 = 6.82$

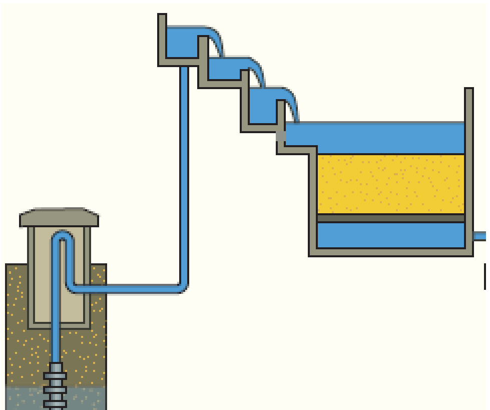
After limestone filtration the pH (or pH_s) is lower than after aeration/gas transfer.

During filtration 1.20 mmol/l CO_2 is transformed and 1.20 mmol/l $CaCO_3$ is consumed,
that is (1.20 · 100 =) 120 g/m³.
A production of 1 million m³ per year corresponds to 120 tons per year.

Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – $CaCO_3$

- 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
- Area : A/V = Area calcite / volume water
  - A = f (diameter particles, sphere)
  - V = f (porosity)

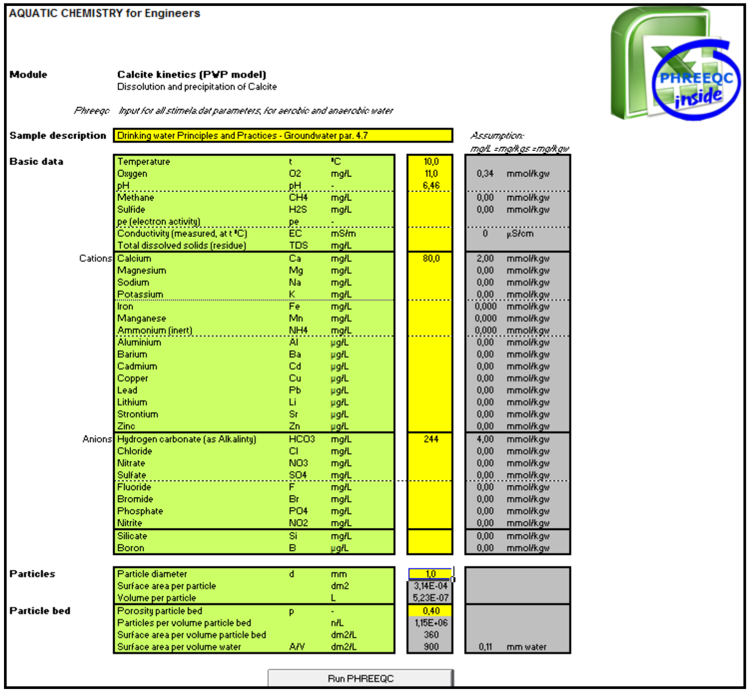


- Limestone filter/contactor
  - Diameter limestone = 1 or 2 mm
  - Porosity = 0.4
  - Empty Bed Contact Time (EBCT) = 1 m / 5 m/h = 12 minutes
  - Real contact time = 12 * 0.4 = 4.8 minutes = 288 sec

Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – $CaCO_3$

- Raw groundwater
  - Ca = 2.0 mmol/kgw = 80 mg/L
  - Alk = 4.0 meq/kgw = 244 mg/L HCO_3
  - pH = 6.46
  - CO_2 = 3.68 mmol/kgw (was 4.0)
  - Temp = 10 ^{0}C
- Calculate SI after 300 sec (p=0.4):
  - A: for d = 1 mm
  - B: for d = 2 mm
- I give you 3 minutes....



AQUATIC CHEMISTRY for Engineers

Module **Calcite kinetics (PVP model)**
Dissolution and precipitation of Calcite

Phreeqc *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description Drinking water Principles and Practices - Groundwater par. 4.7

Assumption: mg/L =mg/kgs =mg/kgw

Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Particles	Particle diameter	d	mm	1,0		
	Surface area per particle		dm2	3,14E-04		
	Volume per particle		L	5,23E-07		
Particle bed	Porosity particle bed	p	-	0,40		
	Particles per volume particle bed		n/L	1,15E+06		
	Surface area per volume particle bed		dm2/L	360		
	Surface area per volume water	A/V	dm2/L	900	0,11	mm water

Run PHREEQC

Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – $CaCO_3$

Answers:

AQUATIC CHEMISTRY for Engineers

PHREEQC inside

Module — **Calcite kinetics (PVP model)**
Dissolution and precipitation of Calcite

Phreeqc — *Input for all stimela.dat parameters, for aerobic and anaerobic water*

Sample description — Drinking water Principles and Practices - Groundwater par. 4.7

Assumption:
mg/L =mg/kgs =mg/kgw

	Parameter	Symbol	Unit	Value	Result	Unit
Basic data	Temperature	t	°C	10,0		
	Oxygen	O2	mg/L	11,0	0,34	mmol/kgw
	pH	pH	-	6,46		
	Methane	CH4	mg/L		0,00	mmol/kgw
	Sulfide	H2S	mg/L		0,00	mmol/kgw
	pe (electron activity)	pe	-			
	Conductivity (measured, at t °C)	EC	mS/m		0	µS/cm
	Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	mg/L	80,0	2,00	mmol/kgw
	Magnesium	Mg	mg/L		0,00	mmol/kgw
	Sodium	Na	mg/L		0,00	mmol/kgw
	Potassium	K	mg/L		0,00	mmol/kgw
	Iron	Fe	mg/L		0,000	mmol/kgw
	Manganese	Mn	mg/L		0,000	mmol/kgw
	Ammonium (inert)	NH4	mg/L		0,000	mmol/kgw
	Aluminium	Al	µg/L		0,00	mmol/kgw
	Barium	Ba	µg/L		0,00	mmol/kgw
	Cadmium	Cd	µg/L		0,00	mmol/kgw
	Copper	Cu	µg/L		0,00	mmol/kgw
	Lead	Pb	µg/L		0,00	mmol/kgw
	Lithium	Li	µg/L		0,00	mmol/kgw
	Strontium	Sr	µg/L		0,00	mmol/kgw
	Zinc	Zn	µg/L		0,00	mmol/kgw
Anions	Hydrogen carbonate (as Alkalinty)	HCO3	mg/L	244	4,00	mmol/kgw
	Chloride	Cl	mg/L		0,00	mmol/kgw
	Nitrate	NO3	mg/L		0,00	mmol/kgw
	Sulfate	SO4	mg/L		0,00	mmol/kgw
	Fluoride	F	mg/L		0,00	mmol/kgw
	Bromide	Br	mg/L		0,00	mmol/kgw
	Phosphate	PO4	mg/L		0,00	mmol/kgw
	Nitrite	NO2	mg/L		0,00	mmol/kgw
	Silicate	Si	mg/L		0,00	mmol/kgw
	Boron	B	µg/L		0,00	mmol/kgw
Particles	Particle diameter	d	mm	1,0		
	Surface area per particle		dm2	3,14E-04		
	Volume per particle		L	5,23E-07		
Particle bed	Porosity particle bed	p	-	0,40		
	Particles per volume particle bed		n/L	1,15E+06		
	Surface area per volume particle bed		dm2/L	360		
	Surface area per volume water	A/V	dm2/L	900	0,11	mm water

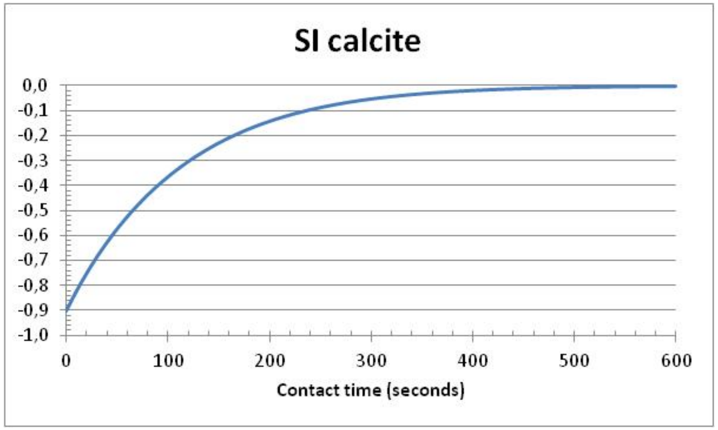
Run PHREEQC

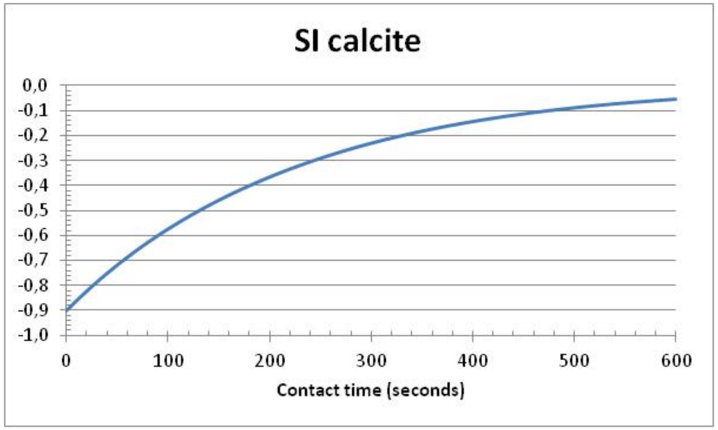
Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – $CaCO_3$

Answers:

- SI after 300 sec with p=0.4 :
  - A : d=1mm : SI (300s) = -0.05
  - B : d=2mm : SI (300s) = -0.23





Aquatic Chemistry for engineers

Module : Kinetics of calcite /PWP – PHREEQC code

- Code for output:
  - PRINT / SELECTED OUTPUT etc
- Solution simulations:
  - Sol. 1 / electron balance / CCPP etc

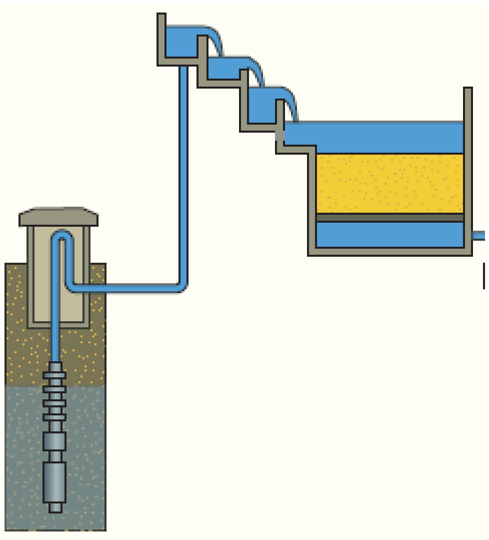
- Kinetics - Rates simulation:
  - KINETICS
    - Calcite (RATES in .dat)
    - -formula CaCO3 1.0 (stoich)
    - -m0 1.0 (initial mass)
    - -parms 900 0.67 (in RATES)
    - -step 0 300*2 (sec)

```
# Kinetics Calcite


USE solution 1
KINETICS 1
        Calcite
        -formula CaCO3 1.0
        -m0 1.0
        -parms    900       0.67
        -step             0  300*2
INCREMENTAL_REACTIONS
END      # Simulation 6
```

Conclusions - Lessons learned

Item : Kinetics of limestone filtration – $CaCO_3$

- Long contact time
  - Practice : SI -0.3 to -0.5
  - PWP: SI = 0



- Results PWP model differ from results in practice
- PWP is not OK near equilibrium (-1 < SI < 1)
- PWP is for open systems, not for closed systems

- Kinetic model to be improved:
  - For dissolution
  - For precipitation ?

Questions?

Aquatic Chemistry for engineers

PHREEQXCEL-apps for water treatment

13 September 2013

Peter de Moel – TU Delft