

Aquatic Chemistry for engineers

PHREEQXCEL-apps for water treatment

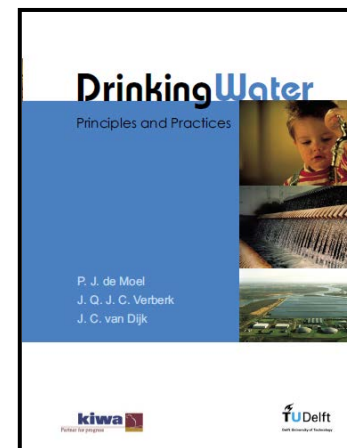
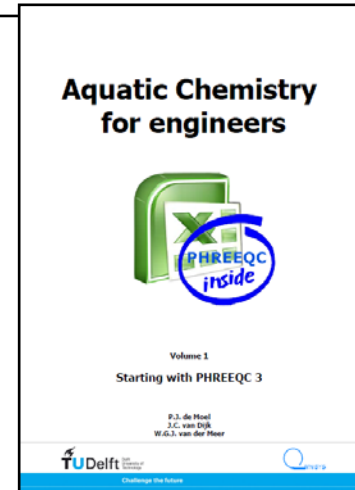
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Aquatic Chemistry for engineers

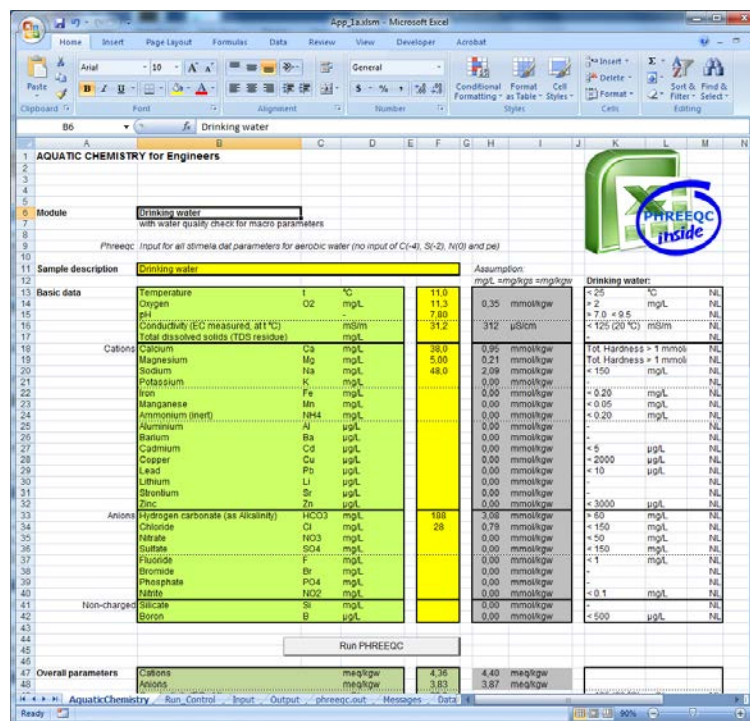
Course program

- 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 O₂, N₂, CO₂, CH₄ etc
 - Engineering: $P \cdot V / T = R$ / Biodegradation wastewater
- Hardness and pH (App 3a+b)
 - Chemistry: acid/base, solubility CaCO₃, FeCO₃, etc
 - Engineering: pH control / Neutralization / Softening



App 1a - Drinking water

- Open App_1a.xlsm:



Sample description	Drinking water	Assumption	Drinking water:
Basic data		mg/L, mmol/kgw, mmol/kgw	
Temperature	11.3 °C	0.35 mmol/kgw	+25 °C
Oxygen	7.80 mg/L		+2 mg/L
pH			+7.0 ± 0.5
Conductivity (EC measured, at 1°C)	312 µS/cm		+125 (20 °C) µS/cm
Total dissolved solids (TDS residue)			
Cations			
Calcium	88.0 mg/L	0.95 mmol/kgw	100 Hardness = 1 mmol
Magnesium	5.00 mg/L	0.21 mmol/kgw	100 Hardness = 1 mmol
Sodium	48.0 mg/L	2.09 mmol/kgw	+150 mg/L
Potassium		0.00 mmol/kgw	
Iron		0.00 mmol/kgw	+0.20 mg/L
Manganese		0.00 mmol/kgw	+0.05 mg/L
Ammonium (NH4)		0.00 mmol/kgw	+0.20 mg/L
Aluminum		0.00 mmol/kgw	
Barium		0.00 mmol/kgw	
Cadmium		0.00 mmol/kgw	+5 µg/L
Copper		0.00 mmol/kgw	+2000 µg/L
Lead		0.00 mmol/kgw	+10 µg/L
Lithium		0.00 mmol/kgw	
Strontium		0.00 mmol/kgw	
Zinc		0.00 mmol/kgw	+3000 µg/L
Anions			
Hydrogen carbonate (as Alkalinity)	108 mg/L	3.08 mmol/kgw	+50 mg/L
Chloride	28 mg/L	0.78 mmol/kgw	+150 mg/L
Nitrate		0.00 mmol/kgw	+50 mg/L
Sulfate		0.00 mmol/kgw	+150 mg/L
Fluoride		0.00 mmol/kgw	+1 mg/L
Bromide		0.00 mmol/kgw	
Phosphate		0.00 mmol/kgw	
Nitrite		0.00 mmol/kgw	+0.1 mg/L
Non-charged			
Silicate		0.00 mmol/kgw	+500 µg/L
Boron		0.00 mmol/kgw	
Overall parameters			
Cations	4.36 meq/kgw	4.40 meq/kgw	
Anions	3.83 meq/kgw	3.87 meq/kgw	

Requires:

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

Aquatic Chemistry for engineers

Module : Drinking water (aerobic water)

Water analysis report:

- Temperature 11 °C
- O₂ 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 HCO₃
- Cl 28 mg/L
- O₂ > 0.1 mg/L
- So: no CH₄, no H₂S

AQUATIC CHEMISTRY for Engineers

Module:
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:

Assumption: mg/L =mg/kgvs =mg/kgw

Basic data	Temperature	t	°C	11.0	0,35	mmol/kgw	< 25	°C	NL
	Oxygen	O2	mg/L	11,3			> 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
```

Aquatic Chemistry for engineers

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/kgw	Ca(mol/kgw	Mg(mol/kgw	Fe(mol/kgw
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
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
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
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
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
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
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
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-----
```

Species	Molality	Activity	Log Molality	Log Activity	Log Gamma	mole V 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			
Cu solvency index		Cul	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				< 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			
Redox conditions	Density	kg/L	1,000			
	Oxygen	mmol/kgw	0,35	0,21	atm	
	pe (electron activity)	pe	14,07			
Correctness checks	Redox potential	Eh	700			
	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	-				>0.9 <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.
Carbon equilibrium	pH change by electron balancing (Phreeqc)	-	0,000			< 0.01 pr.
	pH (Hydrogen activity)	pH	7,80			>7.0 <9.5 NL
	Alkalinity	m meq/kaw	3,08			>1 meq/L NL

- I give you 5 minutes....

Drinking water

What causes the charge difference?

- Answer:

Run PHREEQC						
Overall parameters	Calcium	meq/kgw	4.38	4.40	meq/kgw	
	Aluminum	meq/kgw	3.80	3.87	meq/kgw	
	Conductivity (EC at 25 °C)	ms/cm	28.3		+ 125 (20 °C) ms/cm	NL
	Total dissolved solids (TDS)	mg/L	307			
	Ionic strength	mmol/kgw	5.2	6.5	°D	+ 1 mmol/L
Redox conditions	Total hardness	mmol/kgw	1.15			
	Vapor pressure water	atm	0.01			
	Density	kg/L	1.000			
Correctness checks	Oxygen	mmol/kgw	0.35		0.21	atm
	pe (electron activity)	pe	14.07			
	Redox potential	mV	783			
	Charge difference	meq/kgw	0.52	0.52	meq/kgw	< 0.2 meq/L (n = 3) SM 1030E
	Percentage error (100*(Cat-An)/(Cat+An))	%	6.4%			< 2% (n = 3) SM 1030E
Carbon equilibrium	EC ratio, Calculated/measured	-	0.91			> 0.9 < 1.1 SM 1030E
	TDS ratio, measured/calculated	-	-			> 1.0 < 1.2 SM 1030E
	Calcium to measured EC ratio (*10)	meq.m/kgw.ms	1.54			> 0.9 < 1.1 SM 1030E
	Aluminum 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	100%			< 1.1
	pH change by electron balancing (Phreeqc)	-	0.000			< 0.05
Carbon equilibrium	pH (Hydrogen activity)	pH	7.80			> 7.0 < 9.5
	Alkalinity	m	meq/kgw	3.08		> 1 meq/L

Drinking water

What causes the charge difference?

- Answer:
- Missing anion
 - Cation > Anion 0.52 meq/kgw

Run PHREEQC					
Overall parameters	Cations	meq/kgw	4.38	4.40	meq/kgw
	Anions	meq/kgw	3.83	3.87	meq/kgw
	Conductivity (EC at 25 °C)	ms/cm	28.3		
	Total dissolved solids (TDS)	mg/L	307		
	Ionic strength	mmol/kgw	5.2	6.5	°D
	Total hardness	mmol/kgw	1.15		
Redox conditions	Vapor pressure water	atm	0.01		
	Density	kg/L	1.000		
	Oxygen	mmol/kgw	0.35		
	pe (electron activity)	pe	14.07		
Correctness checks	Redox potential	mV	783		
	Charge difference	meq/kgw	0.52	0.52	meq/kgw
Carbon equilibrium	Percentage error (100*(Cat-An)/(Cat+An))		6.4%		
	EC ratio, calculated/measured		0.91		
	TDS ratio, measured/calculated		-		
	Cations to measured EC ratio (*10)	meq/kgw/ms	1.54		
	Anions to measured EC ratio (*10)	meq/kgw/ms	1.35		
	TDS to EC ratio, measured (*10)	mg/mL/ms	-		
	TDS to EC ratio, calculated (*10)	mg/mL/ms	1.08		
	Oxygen saturation (to air at sea level)	atm/atm	100.0%		
pH change by electron balancing (Phreeqc)	pH (hydrogen activity)	pH	7.80		
	Alkalinity	m	1.08		

• 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 / p_e / 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	Caions	meq/kgw	4.36	4.40 meq/kgw	
	Naions	meq/kgw	3.83	3.87 meq/kgw	
	Conductivity (EC at 0)	µmS/cm	253		<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		
	p_e (electron activity)	pe	14.07	0.21 atm	
	Redox potential	mv	793		
Correctness checks	Charge difference	meq/kgw	0.52	0.52 meq/kgw	< 0.2 meq/L (at < 3) SM 1030E
	Percentage error (100*(Cat-An)/(Cat+An))		6.4%		< 5% (at < 3) SM 1030E
	EC ratio, calculated/measured		0.91		+0.9 < 1.1 SM 1030E
	TDS ratio, measured/calculated		-		+1.0 < 1.2 SM 1030E
	Calcium to measured EC ratio (*10)	meq meq/kgw mS	1.54		+0.9 < 1.1 SM 1030E
	Sulfate to measured EC ratio (*10)	meq meq/kgw mS	1.35		+0.9 < 1.1 SM 1030E
	TDS to EC ratio, measured (/10)	mg mL mS	-		+0.55 < 0.7 SM 1030E
	TDS to EC ratio, calculated (/10)	mg mL mS	1.08		+0.85 < 0.7 SM 1030E
	Oxygen saturation to air at sea level	atm atm	102.7%		< 1.1 pr
	pH change by electron balancing (PHEMOC)	atm atm	0.000		< 0.01 pr
Carbon equilibrium	pH (Hydrogen activity)	pH	7.80		+7.0 < 8.5 NL
	Alkalinity	m	3.88		+1 meq/L NL
	Total Inorganic Carbon (TIC)	mmol/kgw	3.19	38 mg/L C	
	CO_2	mmol/kgw	0.13	9.00 atm	
	HCO_3^-	mmol/kgw	3.02	185 mg/L	+1 mmol/L NL
	CO_3^{2-}	mmol/kgw	0.01	0 mg/L	
	pH by 0.1 mmol HCl / kgw	pH	-0.28		
Buffer capacity	mmol/kgw pH	0.32			
Calcite equilibrium	SI (calcite)	SI	0.02		+ < 0.2 NL
	Equilibrium pH (pH or pH-Langelier)	pH-L	7.70		
	Calcite Precipitation Potential	CPP	0.01		
	Calcite Precipitation Potential at 60 C	CPP-60	0.16		
	Calcite Precipitation Potential at 90 C	CPP-90	0.34		
Other scaling solids	Aragonite	SI	-0.13		+ 0.3 pr
	Gypsum	SI	-		+ 0.3 pr
	Pyrrhotite	SI	-		+ 0.3 pr
	Dolomite	SI	-0.69		+ 0.3 pr
	Hydroxapatite	SI	-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 (polarized, pitting)		0.26		+ 0.5 CEN
	Corrosion index S2 (polarized, selective)		-		+1 or +3 or N03+0.3 CEN
	Corrosion index S (copper, pitting)		-		+ 1.5 CEN
	Cl (in TIC)	mmol/kgw	3.19		
CO_2	mmol/kgw	4.0%			
HCO_3^-	mmol/kgw	94.7%			
CO_3^{2-}	mmol/kgw	0.2%			
Na	mmol/kgw	0.36			

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 additional graphs
 - developing Excel for Engineers
- Original PHREEQCI
 - only for input help / online manual

Run PHREEQC					
Overall parameters	Cations	meq/kgw	4.36	4.40 meq/kgw	
	Conductivity (EC at 0)	µS/cm	3.83	3.87 meq/kgw	
	Total dissolved solids (TDS)	mg/L	29.3		<125 (20 °C) mS/m NL
	Ionic strength	mmol/kgw	307		
	Total hardness	mmol/kgw	5.2		
Redox conditions	Vapor pressure water	atm	1.15	6.5 °D	+1 mmol/L NL
	Density	kg/L	1.000		
	Oxygen	mmol/kgw	0.35		
Correctness checks	pe (electron activity)	pe	14.07	0.21 atm	
	Redox potential	Ev	793		
Carbon equilibrium	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%		> 0.25 < 1.1 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 meq/m3	1.54		+0.9 < 1.1 SM 1030E
	Anions to measured EC ratio (*10)	meq meq/m3	1.35		+0.9 < 1.1 SM 1030E
	TDS to EC ratio, measured (/10)	mg mL/m3	-		+0.55 < 0.7 SM 1030E
Calcite equilibrium	TDS to EC ratio, calculated (/10)	mg mL/m3	1.98		+0.85 < 0.7 SM 1030E
	Oxygen saturation (to air at sea level)	atm/atm	102.7%		< 1.1 pr
	pH change by electron balancing (PHREEC)	atm/atm	0.000		< 0.01 pr
	pH (Hydrogen activity)	pH	7.80		> 7.0 < 8.5 NL
	Alkalinity	m	3.88		+1 meq/L NL
Other scaling solids	Total Inorganic Carbon (TIC)	mmol/kgw	3.19	38 mg/L C	
	CO2	mmol/kgw	0.13	0.00 atm	
	HCO3-	mmol/kgw	3.02	185 mg/L	+1 mmol/L NL
	CO3 2-	mmol/kgw	0.01	0 mg/L	
Corrosion	pH by 0.1 mmol HCl / kgw	pH	-0.28		
	Buffer capacity	Eq	0.32		
	SI (calcite)	SI	0.02		> -0.2 < 0.3 NL
	Equilibrium pH (pHs or pH-Langelier)	pH-L	7.78		
Elements / Species	Calcite Precipitation Potential	CPP	0.01	1 mg/L CaCO3	> -0.05 < 0.2 mmol/L DE + pr
	Calcite Precipitation Potential at 60 C	CPP-60	0.16	16 mg/L CaCO3	
	Calcite Precipitation Potential at 80 C	CPP-80	0.34	34 mg/L CaCO3	
	Aragonite	SI	-0.13		< 0.3 pr
Corrosion	Gypsum	SI	-		< 0.3 pr
	Hydrite	SI	-		< 0.3 pr
	Dolomite	SI	-0.69		< 0.3 pr
	Hydroxapatite	SI	-1000.00		< 0.3 pr
	Pb solvency potential	Pb	µg Pb / kgw	167	< 200 NL
Corrosion	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 N03 < 0.3 CEN
	Corrosion index S (copper, pitting)		-		< 1.5 CEN
	Cl (m TIC)	mmol/kgw	3.19		
CO2		4.0%			
HCO3-		94.7%			
CO3 2-		0.2%			
Ca	mmol/kgw	0.36			

Drinking water

What causes the charge difference?

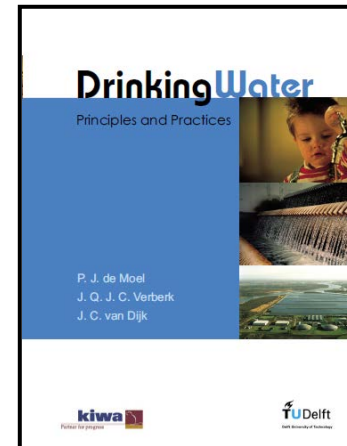
- Self study problem: Drinking water – P&P: page 225

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 SO₄²⁻ should be 1.60 meq/l (= 6.14 - 2.06 - 2.48 - 0.01).
Conclusion: SO₄²⁻ = 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?

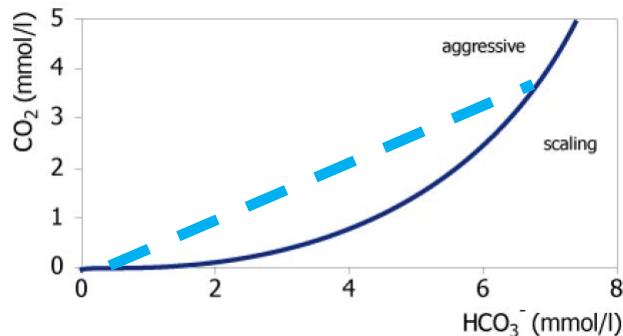


Aquatic Chemistry for engineers

Module : Mixing of water (App 1b)

- What is the pH of mixed water ?

- pH : 9.3 + 7.4 = ???
- SI : 0 + 0 = < 0

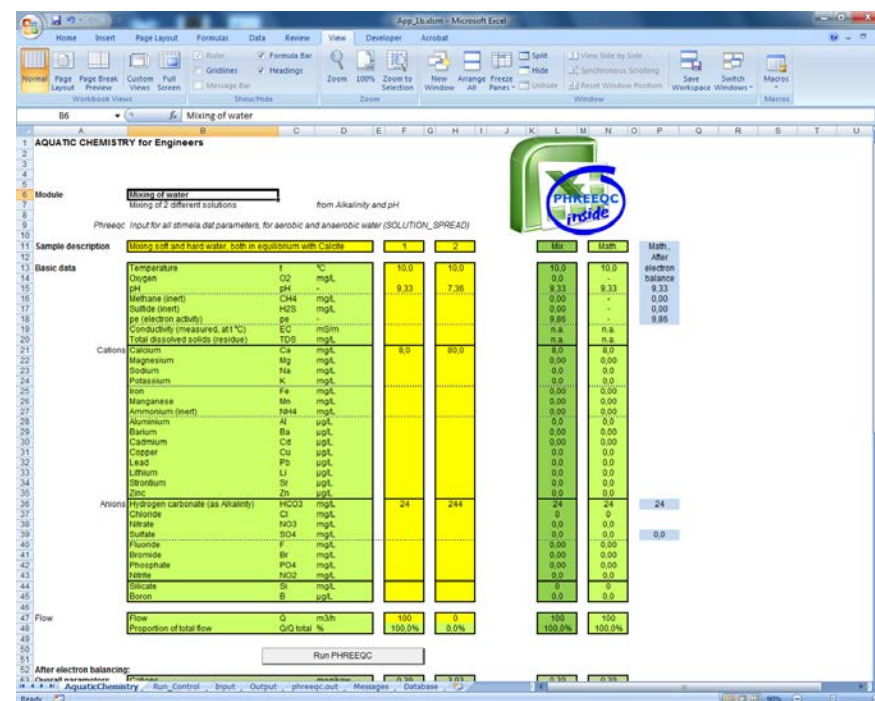


- Application

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

App 1b – Mixing of water

- Open App_1b.xlsm:



The screenshot shows the PHREEQC interface within an Excel spreadsheet. The spreadsheet is titled 'Mixing of water' and contains a table of chemical parameters and their values for two different solutions (1 and 2). The table is organized into sections: Basic data, Cations, Anions, and Flow. The 'Run PHREEQC' button is visible at the bottom of the spreadsheet.

Sample description		1	2	1st	2nd	Math	After electron balance
Temperature	t	10.0	10.0	10.0	10.0	-	-
Oxygen	O2			0.0	-		
pH		9.33	7.36	9.33	9.33		9.33
Methane (inert)	CH4			0.00	-		0.00
Sulfide (inert)	H2S			0.00	-		0.00
pe (electron activity)	pe			9.86	-		9.86
Conductivity (measured, all °C)	EC			n.a.	n.a.		n.a.
Total dissolved solids (residue)	TDS						
Calcium	Ca	8.0	80.0	8.0	80.0		
Magnesium	Mg			0.00	0.00		
Sodium	Na			0.0	0.0		
Potassium	K			0.0	0.0		
Iron	Fe			0.00	0.00		
Manganese	Mn			0.00	0.00		
Ammonium (inert)	NH4			0.00	0.00		
Aluminum	Al			0.0	0.0		
Barium	Ba			0.00	0.00		
Cadmium	Cd			0.00	0.00		
Copper	Cu			0.0	0.0		
Lead	Pb			0.0	0.0		
Lithium	Li			0.0	0.0		
Strontium	Str			0.0	0.0		
Zinc	Zn			0.0	0.0		
Hydrogen carbonate (as Alkalinity)	HCO3	24	244	24	24		24
Chloride	Cl			0	0		0
Nitrate	NO3			0.0	0.0		0.0
Sulfate	SO4			0.0	0.0		0.0
Fluoride	F			0.00	0.00		0.0
Bromide	Br			0.00	0.00		0.00
Phosphate	PO4			0.00	0.00		0.00
Nitrite	NO2			0.0	0.0		0.0
Silicate	Si			0.0	0.0		0.0
Boron	B			0.0	0.0		0.0
Flow	Q	100	0	100	100		100
Proportion of total flow	Q/Q total	100.0%	0.0%	100.0%	100.0%		100.0%

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		1	2	Mix	Math	Math. After electron balance
Basic data	Temperature	t	10.0	10.0	10.0	10.0
	Oxygen	O2	mg/L		0.0	-
	pH	pH	9.33	7.36	9.33	9.33
	Metane (inert)	CH4	mg/L		0.00	0.00
	Sulfide (inert)	H2S	mg/L		0.00	-
	pe (electron activity)	pe			9.86	9.86
	Conductivity (measured, at 1°C)	EC	mS/m		n.a.	n.a.
	Total dissolved solids (residue)	TDS	mg/L		n.a.	n.a.
Cations	Calcium	Ca	8.0	80.0	0.0	0.0
	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 Alkalinity)	HCO3	mg/L	24	244	24
	Chloride	Cl	mg/L		0	0
	Nitrate	NO3	mg/L		0.0	0.0
	Sulfate	SO4	mg/L		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
	Proportion of total flow	Q/Q total	%	100.0%	0.0%	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 1°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	0.0	0.0	
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 Alkalinity)	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 CO₂
 - aggressive CO₂ = 0.11 mmol/kgw
 - pe not reliable (no redox elements)

Flow	Q	m ³ /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 1°C)	EC	mS/m	4.8	25.3	14.3	14.2
Total dissolved solids	TDS	mg/L	32	324	178	178
Ionic strength	IS	mmol/kgw	0.5	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)	SIc		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 Temperat 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
 - O₂ for aerobic water
 - CH₄ for anaerobic water
- Check your PHREEQC results
 - What happened ?

The screenshot shows the PHREEQC software interface with a spreadsheet of data. The spreadsheet is titled 'AQUATIC CHEMISTRY for Engineers' and contains the following data:

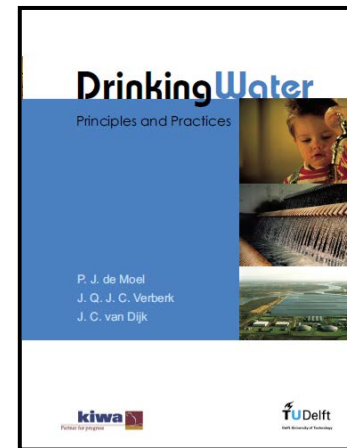
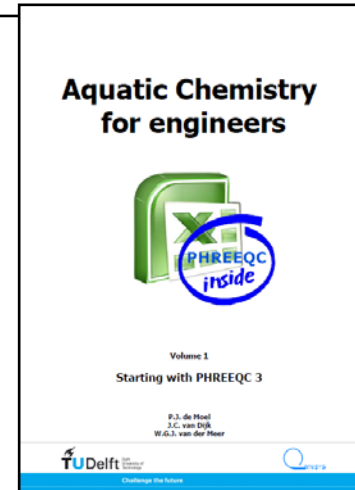
Sample description		1	2	Mix	Math	Mask
Mixing soft and hard water, both in equilibrium with Calcite						
Basic data						
Temperature	t C	10.0	10.0	10.0	10.0	
Oxygen	O2 mg/L	3.33	7.36	0.0	0.0	3.33
Methane	CH4 mg/L	0.00	0.00	0.00	0.00	0.00
Sulfide	H2S mg/L	0.00	0.00	0.00	0.00	0.00
pH (apparent solution)	pH	7.37	7.37	n.s.	n.s.	-3.17
Conductivity (measured, at t C)	EC mS/m	n.s.	n.s.	n.s.	n.s.	
Total dissolved solids (residue)	TDS mg/L	n.s.	n.s.	n.s.	n.s.	
Cations						
Calcium	Ca mg/L	8.0	8.0	8.0	8.0	
Magnesium	Mg mg/L	0.00	0.00	0.00	0.00	
Sodium	Na mg/L	0.0	0.0	0.0	0.0	
Potassium	K mg/L	0.0	0.0	0.0	0.0	
Iron	Fe mg/L	0.00	0.00	0.00	0.00	
Manganese	Mn mg/L	0.00	0.00	0.00	0.00	
Ammonium	NH4 mg/L	0.00	0.00	0.00	0.00	
Aluminum	Al mg/L	0.0	0.0	0.0	0.0	
Boron	B mg/L	0.00	0.00	0.00	0.00	
Cadmium	Cd mg/L	0.00	0.00	0.00	0.00	
Copper	Cu mg/L	0.0	0.0	0.0	0.0	
Lead	Pb mg/L	0.0	0.0	0.0	0.0	
Lithium	Li mg/L	0.0	0.0	0.0	0.0	
Strontium	Sr mg/L	0.0	0.0	0.0	0.0	
Zinc	Zn mg/L	0.0	0.0	0.0	0.0	
Anions						
Hydrogen carbonate (as Alkalinity)	HCO3 mg/L	24	244	24	24	24
Chloride	Cl mg/L	0.0	0.0	0.0	0.0	0.0
Nitrate	NO3 mg/L	0.0	0.0	0.0	0.0	0.0
Sulfate	SO4 mg/L	0.0	0.0	0.0	0.0	0.0
Fluoride	F mg/L	0.00	0.00	0.00	0.00	0.00
Bromide	Br mg/L	0.00	0.00	0.00	0.00	0.00
Phosphate	PO4 mg/L	0.00	0.00	0.00	0.00	0.00
Nitrite	NO2 mg/L	0.0	0.0	0.0	0.0	0.0
Silicate	Si mg/L	0.0	0.0	0.0	0.0	0.0
Boron	B mg/L	0.0	0.0	0.0	0.0	0.0
Flow						
Flow	Q m ³ /h	100	0	100	100	
Proportion of total flow	Q/Q tot %	100.0%	0.0%	100.0%	100.0%	
After electron balancing						
Overall parameters						
Cations	meq/lw	0.33	3.33	0.33	0.33	
Anions	meq/lw	0.33	3.34	0.33	0.33	
Conductivity (calculated, at t C)	EC mS/m	2.8	25.3	2.8	2.8	

Questions?



Course program

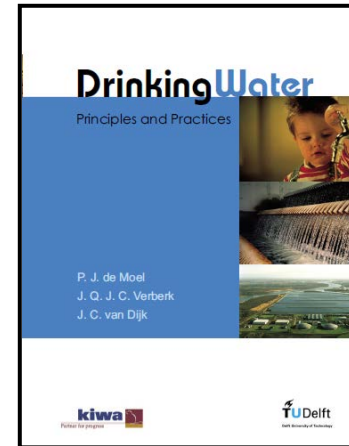
- Introduction (lecture + Starting with PHREEQC 3)
 - PHREEQC – PHREEQC Interactive – PHREEQC-COM
- Drinking water (App 1a+b)
 - Chemistry: SI / CCPP / Buffercapacity / Corrosion
 - Engineering: Ionic balance / Conductivity / Mixing
- Gases in water (App 2a+b+c)
 - Chemistry: solubility O_2 , N_2 , CO_2 , CH_4 etc
 - Engineering: $P \cdot V / T = R$ / 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)

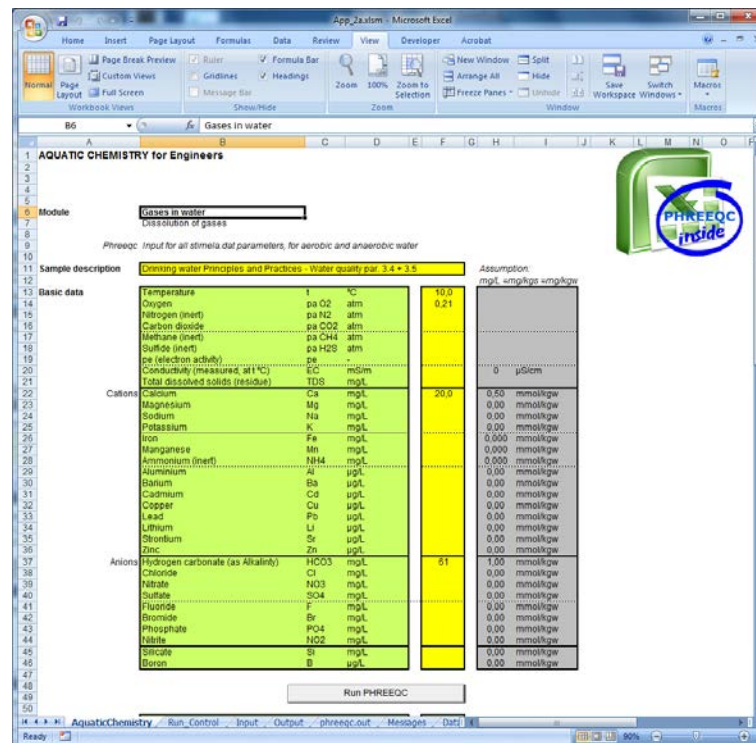
- Solubility of O₂
 - Drinking water: aeration of groundwater
 - Aerobic wastewater treatment
 - Influences of temperature and ionic strength
- Solubility of other gases
 - Carbon dioxide - CO₂
 - Methane – CH₄
 - Anaerobic wastewater treatment
- Application
 - Drinking water : aeration / stripping (gas exchange)
 - Sewerage / wastewater: aerobic and anaerobic treatment, digisters



Water quality
3.4 + 3.5

App 2a - Gases in water

- Open App_2a.xlsm:



The screenshot shows the Microsoft Excel interface with the 'PHREEQC inside' logo in the top right corner. The spreadsheet is titled 'Gases in water' and contains a table of chemical parameters and their calculated values. The table is organized into sections: Basic data, Cations, and Anions. The 'Basic data' section includes parameters like Temperature, Oxygen, Nitrogen (inert), Carbon dioxide, Methane (inert), Sulfide (inert), pe (electron activity), Conductivity (measured, at 25 °C), and Total dissolved solids (residue). The 'Cations' section lists various elements such as Calcium, Magnesium, Sodium, Potassium, Iron, Manganese, Ammonium (inert), Aluminum, Barium, Cadmium, Copper, Lead, Lithium, Strontium, and Zinc. The 'Anions' section lists Hydrogen carbonate (as Alkalinity), Chloride, Nitrate, Sulfate, Fluoride, Bromide, Phosphate, Nitrite, Silicate, and Boron. The table columns include the parameter name, its units, and numerical values. A 'Run PHREEQC' button is visible at the bottom of the spreadsheet area.

Parameter	Units	Value	Assumption
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 25 °C)	κC mS/cm		0 μS/cm
Total dissolved solids (residue)	TDS mg/L	20.0	
Cations			
Calcium	Ca mg/L		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
Aluminum	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	51	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

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.

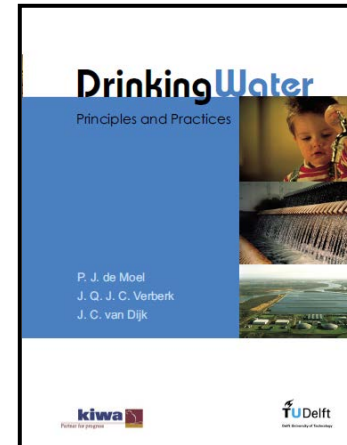
The partial pressure is 0.21 bar or $(101,325 \cdot 0.21 =) 21,300$ Pa.

The oxygen concentration in air is: $(21,300 / (8.3143 \cdot (273+10)) =) 9.05$ mol/m³.

Having a Henry coefficient of 0.041 for oxygen, the oxygen concentration in water will be:

$(0.041 \cdot 9.05 =) 0.37$ mol/m³.

At a molar mass of 32 g this amounts to $(0.37 \cdot 32 =) 12$ g/m³ (mg/l).



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

Aquatic Chemistry for engineers

Item : Solubility of gases in water - oxygen

- Atmospheric (dry) air
 - O₂ 21% p_a = 0.21 atm
- Water
 - Ca= 20 mg/L Alk=61 mg/L HCO₃
- Calculate O₂ content in water:
 - A: at 10 °C
 - B: at 25 °C
 - C: at 90 °C
 - D: at 10 °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:
Dissolution of gases

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

Sample description: Assumption: mg/L, mmol/kgw, mmol/kgw

Basic data	Parameter	Unit	Value	Assumption
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	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
Anions	Lithium	Li	µg/L	0.00 mmol/kgw
	Strontium	Sr	µg/L	0.00 mmol/kgw
	Zinc	Zn	µg/L	0.00 mmol/kgw
	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	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:
 Dissolution of gases

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

Sample description: Assumption:

Basic data	Parameter	Unit	Value	Assumption
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	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
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	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:

- O₂ content mmol/kgw mg/L
 - A: 10 °C 0.36 11.5
 - B: 25 °C 0.27 8.6
 - C: 90 °C 0.16 5.2
 - D: 10 °C seawater 0.32 10.2
- Higher temperature (phreeqc.out)
 - 10 °C: $H=K=10^{-2.77} = 0.00170$
 - 90 °C: $H=K=10^{-3.11} = 0.00079$
- Higher salt content (phreeqc.out)
 - "Salting out" $\{O_2\} = \gamma [O_2]$
 - Seawater: $\gamma = 10^{0.053} = 1.13$

Run PHREEQC					
Overall parameters	Cations	meq/kgw	0.99		
	Anions	meq/kgw	1.00		
	Conductivity (calculated, at 1 °C)	EC	8.7	1 μS/cm	
	Total dissolved solids	TDS	81		
	Ionic strength	IS	1.5		
	Total hardness	TH	0.50	2.8 °D	
	Vapor pressure water	pa	0.01		
	Density	rho	1.000		
	Redox conditions	Oxygen	O2	mmol/kgw	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%		
Carbon equilibrium	pH change by electron balancing (Phreeqc)		0.00		
	pe change by electron balancing (Phreeqc)		-		
	pH (Hydrogen activity)	pH	7.00		
	Alkalinity	m meq/kgw	1.00		
	Total Inorganic Carbon (TIC)	TIC	1.28	15 mg/L C	
	CO2	CO2	0.28	12.21 mg/L	
	HCO3-	HCO3	0.99	61 mg/L	
	CO3 2-	CO3	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	11.5 mg/L	
	Nitrogen	N2	mmol/kgw	0.0 mg/L	
	Carbon dioxide	CO2	mmol/kgw	12.21 mg/L	
	Methane	CH4	mmol/kgw	0.00 mg/L	
	Sulfide	H2S	mmol/kgw	0.00 mg/L	
	Ammonia	NH3	mmol/kgw	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 °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

```

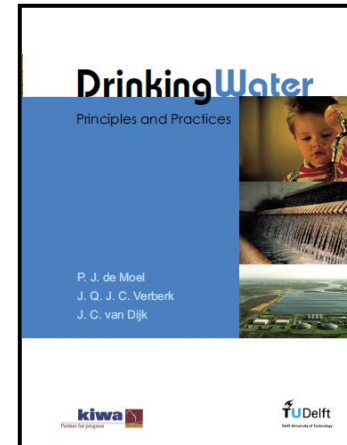

Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases

- Page 227/228

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 (O₂), 17.9 mg/l of nitrogen (N₂) and 0.75 mg/l of carbon dioxide (CO₂).

- 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
 - N₂ 78% p_a = 0.78 atm
 - O₂ 21% p_a = 0.21 atm
 - Ar 1% p_a = 0.01 atm
 - CO₂ 0.032% p_a = 0.00032 atm
 - Argon is not in stimela.dat
- Water
 - Ca= 20 mg/L Alk=61 mg/L HCO₃
- Calculate gas contents in water:
 - A: at 10 °C
- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Modelle: 

Disolution of gases

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

Sample description: Assumption: mg/L, mmol/kgw, umol/kgw

Basic data	Parameter	Value	Unit	Assumption
Cations	Temperature	10.0	°C	
	Oxygen	0.21	pa O2 atm	
	Nitrogen (inert)	0.78	pa N2 atm	
	Carbon dioxide	0.00032	pa CO2 atm	
	Methane (inert)		pa CH4 atm	
	Sulfide (inert)		pa H2S atm	
	pe (electron activity)			
	Conductivity (measured, at 1 °C)		mS/m	0 µS/cm
	Total dissolved solids (residue)		mg/L	
	Calcium	20.0	mg/L	0.50 mmol/kgw
	Magnesium		mg/L	0.00 mmol/kgw
	Sodium		mg/L	0.00 mmol/kgw
	Potassium		mg/L	0.00 mmol/kgw
	Iron		mg/L	0.00 mmol/kgw
Manganese		mg/L	0.00 mmol/kgw	
Anions	Ammonium (inert)		mg/L	0.00 mmol/kgw
	Aluminum		µg/L	0.00 mmol/kgw
	Barium		µg/L	0.00 mmol/kgw
	Cadmium		µg/L	0.00 mmol/kgw
	Copper		µg/L	0.00 mmol/kgw
	Lead		µg/L	0.00 mmol/kgw
	Lithium		µg/L	0.00 mmol/kgw
	Strontium		µg/L	0.00 mmol/kgw
	Zinc		µg/L	0.00 mmol/kgw
	Hydrogen carbonate (as Alkalinity)	61	mg/L	1.00 mmol/kgw
	Chloride		mg/L	0.00 mmol/kgw
	Nitrate		mg/L	0.00 mmol/kgw
	Sulfate		mg/L	0.00 mmol/kgw
	Fluoride		mg/L	0.00 mmol/kgw
Bromide		mg/L	0.00 mmol/kgw	
Phosphate		mg/L	0.00 mmol/kgw	
Nitrite		mg/L	0.00 mmol/kgw	
Silicate		mg/L	0.00 mmol/kgw	
Boron		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

Model: **Cases in water**
 Dissolution of gases

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

Sample description: **Drinking water Principles and Practices - Water quality par. 3.4 + 3.5** Assumption: mg/L, mmol/kgw, umol/kgw

Basic data	Parameter	Unit	Value	Assumption	
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 1 °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	
Aluminum		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

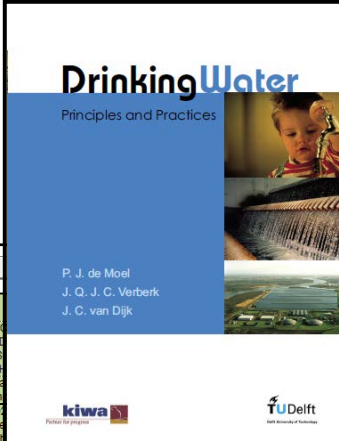
Aquatic Chemistry for engineers

Item : Solubility of gases in water – mixed gases

Answers:

Content	PHREEQC		DW P&P
	mmol/kgw	mg/L	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

- O₂ more soluble than N₂
 - $p_a N_2 = 4 * p_a O_2$
- CO₂ is very soluble
 - $p_a O_2 = 650 * p_a CO_2$ [O₂] = 18 * [CO₂]
 - CO₂ stripping > 1 mg/L



Overall parameters	Calons	meq/kgw	0,00	
Conductivity (calculated, at 25°C)	EC	0,0%		
Total dissolved solids	TDS			
Ionic strength	IS			
Total hardness	TH			
Vapor pressure water	pv			
Density	D			
Oxygen	O2			
pe (electron activity)	pe			
Redox potential	ER			
Charge difference		meq/kgw	0,00	
Percentage error (100*(Cat-An)/(Cat+An))			0,0%	
EC ratio, calculated/measured			-	
TDS ratio, measured/calculated			102,2%	
Oxygen saturation (with air at sea level)		atm/atm	0,0%	
pH change by electron balancing (Phreeqc)			-	
pe change by electron balancing (Phreeqc)			-	
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
pH by 0.1 mmol HCl / kgw	pH		-0,84	
Buffer capacity	BI	mmol/kgw/pH	0,06	
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
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
Elements / Species		mmol/kgw		
C			1,01	
CO2			1,7%	1 mg/L
HCO3			97,1%	



Aquatic Chemistry for engineers

Module : Solubility of gases in water - PHREEQC code

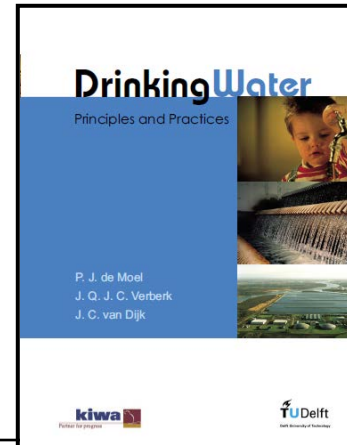
- Code for output
 - PRINT / SELECTED OUTPUT etc
- SOLUTION 1
 - O(0) 1 O2(g) -0.6778
element dummy phase SI = log(p_a)
 - Other gases
- Others
 - electron balance
 - CCPP
 - Buffer capacity
 - CCPP at 60 / 90 °C

```
SOLUTION 1
-units mg/kgs
-redox O(-2)/O(0) # if O2>0 then "O(-2)/O(0)" else if O
-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)



AQUATIC CHEMISTRY for Engineers

Module: Gases in water
 Description of gases

Phreeqc: Input for all stimuli and parameters, for aerobic and anaerobic water

Sample description: Drinking water Principles and Practices - water quality par. 3.4 + 3.5 Assumption: mg/L, mmol/kg, umol/kg

Basic data	Parameter	Unit	Value	Assumption
	Temperature	°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		
	Salinity (electron activity)	pe		
	Conductivity (measured, at 1°C)	EC mS/cm		0 µS/cm
	Total dissolved solids (residue)	TDS mg/L		
Cations	Calcium	Ca mg/L	20.0	0.50 mmol/kg
	Magnesium	Mg mg/L		0.00 mmol/kg
	Sodium	Na mg/L		0.00 mmol/kg
	Potassium	K mg/L		0.00 mmol/kg
	Iron	Fe mg/L		0.000 mmol/kg
	Manganese	Mn mg/L		0.000 mmol/kg
	Ammonium (inert)	NH4 mg/L		0.000 mmol/kg
	Aluminum	Al µg/L		0.00 mmol/kg
	Barium	Ba µg/L		0.00 mmol/kg
	Cadmium	Cd µg/L		0.00 mmol/kg
	Copper	Cu µg/L		0.00 mmol/kg
	Lead	Pb µg/L		0.00 mmol/kg
	Lithium	Li µg/L		0.00 mmol/kg
	Strontium	Sr µg/L		0.00 mmol/kg
Zinc	Zn µg/L		0.00 mmol/kg	
Anions	Hydrogen carbonate (as Alkalinity)	HCO3 mg/L	51	1.00 mmol/kg
	Chloride	Cl mg/L		0.00 mmol/kg
	Nitrate	NO3 mg/L		0.00 mmol/kg
	Sulfate	SO4 mg/L		0.00 mmol/kg
	Fluoride	F mg/L		0.00 mmol/kg
	Bromide	Br mg/L		0.00 mmol/kg
	Phosphate	PO4 mg/L		0.00 mmol/kg
	Nitrite	NO2 mg/L		0.00 mmol/kg
	Silicate	Si mg/L		0.00 mmol/kg
	Boron	B µg/L		0.00 mmol/kg

Run PHREEQC

Questions?



Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO₂ and pH

Dissociation of carbon dioxide

A spring water factory puts 4.4 g CO₂ in 1 liter of demineralized water.

What will be the pH value of this water?

What amount of true CO₂ will be in the water?

What will be the pH value when 1 mmol/l HCO₃⁻ is added?

The inserted amount of CO₂ (or H₂CO₃) is $4.4 / 44 = 0.1$ mol.

When x mol of CO₂ dissociates, x mol H⁺, x mol HCO₃⁻ and 1 - x mol CO₂ will be formed (neglecting the amount of HCO₃⁻ that is transformed into CO₃²⁻).

From $K_1 = x \cdot x / (0.1 - x) = 4.5 \cdot 10^{-7}$ it follows that $x = 0.00021$ mol/l or 0.21 mmol/l.

Thus, the pH value will be $\text{pH} = -\log(0.00021) = 3.68$.

From $K_2 = 4.7 \cdot 10^{-11} = [\text{H}^+][\text{CO}_3^{2-}] / [\text{HCO}_3^-]$ and after entering the known values for H⁺ and HCO₃⁻ it follows that $[\text{CO}_3^{2-}] = 4.7 \cdot 10^{-11}$. This can indeed be neglected, so that:

$[\text{CO}_2] = 100 - 0.21 = 99.79$ mmol/l and $[\text{HCO}_3^-] = 0.21$ mmol/l

(meaning that 0.2% has dissociated)

After adding 1 mmol/l HCO₃⁻ the pH value will be:

$\text{pH} = 6.35 - \log \{99.79 / (0.21+1.00)\} = 6.35 - 1.92 = 4.43$

CO₂ = 4.4 g/L = 4,400 mg/L : p_a CO₂ = 2.94 atm at 25 °C

DrinkingWater

Principles and Practices

P. J. de Moel
J. O. J. C. Verberk
J. C. van Dijk

kiwa

TU Delft

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO₂ and pH

- CO₂ in water
 - CO₂
 - Temperature
- Calculate pH:
 - A: Alkalinity
 - B: Alkalinity

$$p_a = 2.94 \text{ atm}$$

$$25 \text{ }^\circ\text{C}$$

$$12.8 \text{ mg/L HCO}_3$$

$$(=0.21 \text{ meq/L})$$

$$73.8 \text{ mg/L HCO}_3$$

$$(= 1.21 \text{ meq/L})$$

- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module: Gases in water
Dissolution of gases

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

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

Assumption: mg/L, mmol/kg, mmol/kgw

Basic data	Parameter	Unit	Value	Assumption
Temperature	T	°C	25.0	
Oxygen	pa O2	atm		
Nitrogen (inert)	pa N2	atm		
Carbon dioxide	pa CO2	atm	2.94009	
Methane (inert)	pa CH4	atm		
Sulfide (inert)	pa H2S	atm		
pH (electron activity)	pH			
Conductivity (measured, at 1 °C)	EC	µS/cm		0
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
	Aluminum	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
	Selenium	Se	µg/L	0.00 mmol/kgw
Zinc	Zn	µg/L	0.00 mmol/kgw	
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	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	1.00 mmol/kgw	
Boron	B	µg/L	0.00 mmol/kgw	

Run PHREEQC

Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO₂ and pH

Answers:

AQUATIC CHEMISTRY for Engineers


Module: Gases in water
Dissolution of gases

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

Sample description: **Drinking water Principles and Practices - Water quality par 3.4 + 3.5** Assumption: mg/L, mmol/kgw, mmol/kgw

Basic data	Parameter	Unit	Value	Assumption	
	Temperature	°C	25.0		
	Oxygen	pa O2 atm			
	Nitrogen (inert)	pa N2 atm			
	Carbon dioxide	pa CO2 atm	2.84009		
	Methane (inert)	pa CH4 atm			
	Sulfide (inert)	pa H2S atm			
	pH (electron activity)	pH			
	Conductivity (measured, at 1°C)	EC		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	
	Aluminum	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	
	Sr	Sr	µg/L	0.00 mmol/kgw	
	Zinc	Zn	µg/L	0.00 mmol/kgw	
	Anions	Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	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	1.00 mmol/kgw	
Boron		B	µg/L	0.00 mmol/kgw	

Run PHREEQC



Aquatic Chemistry for engineers

Item : Solubility of gases in water – CO₂ and pH

Answers:

pH

PHREEQC

DW P&P

pH

pH

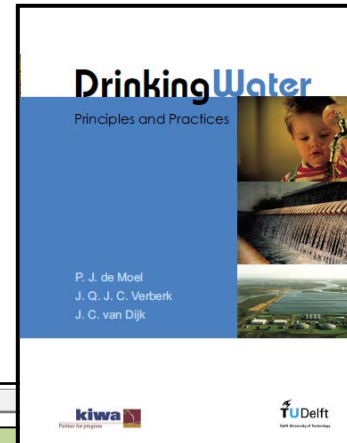
- A: Alk = 0.21 3.88 3.68
- B: Alk= 1.21 4.44 4.43

(Alk in meq/kgw)

- PHREEQC calculates pH from $\text{HCO}_3^- + \text{CO}_2$:

$$\text{pH} = \text{pK}_1 - \log\left(\frac{\{\text{CO}_2\}}{\{\text{HCO}_3^-\}}\right)$$
- DW P&P calculates pH from $\text{HCO}_3^- + \text{CO}_2$:

$$\text{pH} = \text{pK}_1 - \log\left(\frac{[\text{CO}_2]}{[\text{HCO}_3^-]}\right)$$



Overall parameters	Parameter	Unit	Value	Target
Overall parameters	Conductivity (calculated, att °C)	EC mS/m	8.7	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
pe (electron activity)		pe -	15.36	
Redox potential		Eh mV	987	
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%	
Carbon equilibrium	pH change by electron balancing (Phreeqc)	-	0.00	
	pe change by electron balancing (Phreeqc)	-	-	
	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
Calcite equilibrium	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	
	SI (calcite)	SI-c -	-	
	Equilibrium-pH (pHs or pH-Langelier)	pH-L -	-	
Gases in water	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
	Oxygen	O2 mmol/kgw	1.28	41.0 mg/L
Gases in water	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	0.0 mg/L
	Sulfide	H2S mmol/kgw	0.00	0.0 mg/L
	Ammonia	NH3 mmol/kgw	0.00	0.0 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 CO₂ + Alk
- Others
 - electron balance
 - CCPP + Buffer capacity + CCPP at 60 / 90 °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) #NUMI # SI = log(pa)
# N(0) 1 N2(g) #NUMI # SI = log(pa)
# N(g) 1 N(g) #NUMI # SI = log(pa)
# C(4) 1 CO2(g) 0.4683 # SI = log(pa)
# [C-4] 1 [C-4]H4(g) #NUMI # SI = log(pa)
# [S-2] 1 H2[S-2](g) #NUMI # 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
 - $\text{pH} < 3 - 5$
 - At 25 °C and 1 atm: $\text{CO}_2 = 1,500 \text{ mg/L}$
 - Pressure bottles if $\text{CO}_2 > 1,500 \text{ mg/L}$
- PHREEQC brings more:
 - Influence gamma (ionic strength)
 - Combined water quality $\text{CO}_2 - \text{HCO}_3$

The image shows a spreadsheet interface with a PHREEQC calculation. The spreadsheet is titled 'Lab 2a.xlsm' and contains a table of chemical species and their concentrations. The table is organized into sections: 'Basic data', 'Cations', 'Anions', and 'Overall paramete'. The 'Basic data' section includes parameters like Temperature, Oxygen, Nitrogen, Carbon dioxide, Methane, Sulfide, and pH. The 'Cations' section lists various ions such as Calcium, Magnesium, Sodium, Potassium, Iron, Manganese, Ammonium, Aluminum, Barium, Cadmium, Copper, Lead, Lithium, Strontium, and Zinc. The 'Anions' section lists Hydrogen carbonate, Nitrate, Sulfate, Fluoride, Bromide, Phosphate, Nitrite, Silicate, and Boron. The 'Overall paramete' section shows calculated parameters like Calcium, Magnesium, Conductivity, Total dissolved solids, Ionic strength, Total dissolved solids, and Water temperature. The 'Redox conditions' section shows Oxygen and Redox potential.

Next to the spreadsheet is the cover of the book 'Drinking Water: Principles and Practices' by P. J. de Moel, J. O. J. C. Verberk, and J. C. van Dijk. The cover features a photograph of a child drinking water from a fountain.

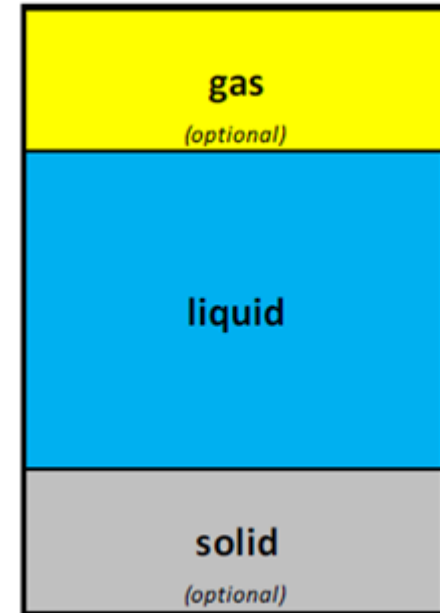
Questions?



Aquatic Chemistry for engineers

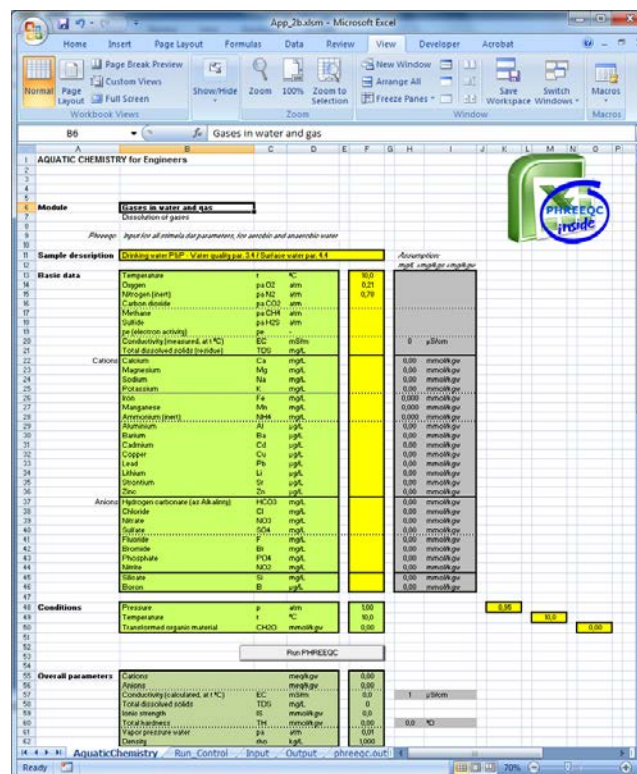
Module : Gases in water and gas (App 2b)

- Solubility of gases
 - Drinking water: aeration of groundwater
 - Wastewater: Aerobic and anaerobic treatment
- Mass balance between water and gas phase
 - Gas saturation ($p_{\text{total}} = \sum p_a > \text{water pressure}$)
 - 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:



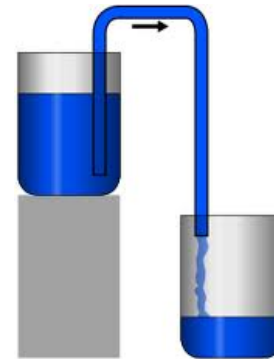
Requires:

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

Aquatic Chemistry for engineers

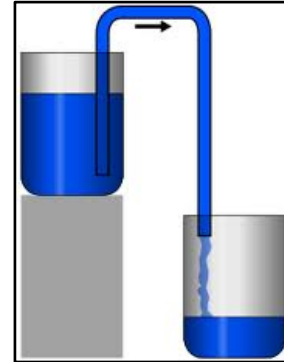
Item : Gas bubbles formed in water

- 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 digester
 - Anaerobic water treatment



Aquatic Chemistry for engineers

Item : Bubbles from pressure reduction



- Water
 - Temperature 10 °C
 - $p_a \text{ O}_2 = 0.21 \text{ atm}$
 - $p_a \text{ N}_2 = 0.78 \text{ atm}$
 - No gas bubbles (gas volume = 0 mL)
- Calculate gas volume at pressure:
 - A: $p = 0.95 \text{ atm}$ (filter -0.5 mwc)
 - B: $p = 0.50 \text{ atm}$ (siphon)
 - C: $p = 0.05 \text{ atm}$ (vacuum degasifier)

AQUATIC CHEMISTRY for Engineers

Module: Gases in water and gas
Dissolution of gases

Phreeqc: Input for all stimuli.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, mmol/kg, mmol/kg

Basic data	Parameter	Unit	Value	Unit	Value	
Basic data	Temperature	t	10.0	°C		
	Oxygen	pa O2	0.21	atm		
	Nitrogen (nert)	pa N2	0.78	atm		
	Carbon dioxide	pa CO2		atm		
	Methane	pa CH4		atm		
	Sulfide	pa H2S		atm		
	pe (electron activity)	pe				
	Conductivity (measured, at 1 °C)	EC		mS/m	0	
	Total dissolve solids (residue)	TDS		mg/L		
	Cations	Calcium	Ca	0.00	mmol/kgw	
Magnesium		Mg	0.00	mmol/kgw		
Sodium		Na	0.00	mmol/kgw		
Potassium		K	0.00	mmol/kgw		
Iron		Fe	0.000	mmol/kgw		
Manganese		Mn	0.000	mmol/kgw		
Ammonium (NH4)		NH4	0.000	mmol/kgw		
Aluminum		Al	0.00	mmol/kgw		
Barium		Ba	0.00	mmol/kgw		
Cadmium		Cd	0.00	mmol/kgw		
Copper		Cu	0.00	mmol/kgw		
Lead		Pb	0.00	mmol/kgw		
Lithium		Li	0.00	mmol/kgw		
Strontium		Sr	0.00	mmol/kgw		
Zinc		Zn	0.00	mmol/kgw		
Anions		Hydrogen carbonate (as Alkalinity)	HCO3	0.00	mmol/kgw	
		Chloride	Cl	0.00	mmol/kgw	
		Nitrate	NO3	0.00	mmol/kgw	
		Sulfate	SO4	0.00	mmol/kgw	
		Fluoride	F	0.00	mmol/kgw	
	Bromide	Br	0.00	mmol/kgw		
	Phosphate	PO4	0.00	mmol/kgw		
	Nitrite	NO2	0.00	mmol/kgw		
	Silicate	Si	0.00	mmol/kgw		
	Boron	B	0.00	mmol/kgw		
Conditions	Pressure	p	1.00	atm		
	Temperature	t	10.0	°C		
	Transformed organic material	CH2O	0.00	mmol/kgw		

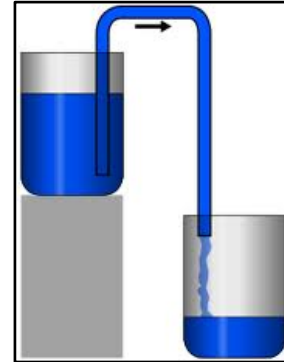
Run PHREEQC

- 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 stimuli.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, mmol/kg, mmol/kg

Basic data		10.0	
Temperature	t °C	10.0	
Oxygen	pa O2 atm	0.21	
Nitrogen (nert)	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 1 °C)	EC mS/m	0	µS/cm
Total dissolve 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 (NH4)	NH4 mg/L	0.000	mmol/kgw
Aluminum	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	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
Iodide	I 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	
Temperature	t °C	10.0	
Transformed organic material	CH2O mmol/kgw	0.00	

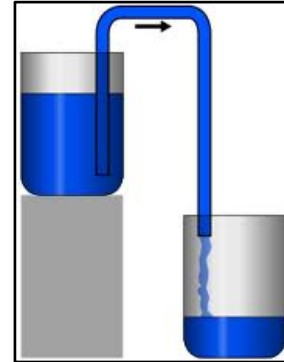
0.95 10.0 0.00

Run PHREEQC



Aquatic Chemistry for engineers

Item : Bubbles from pressure reduction



Answers:

- Volume of gas bubbles
 - A: $p = 0.95 \text{ atm}$ 0.93 mL
 - B: $p = 0.50 \text{ atm}$ 23.6 mL
 - C: $p = 0.05 \text{ atm}$ 604 mL
- Bubble diameter 1 mm:
 - Volume per bubble = $5.3 \cdot 10^{-4} \text{ mL}$
 - 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			
	Alkalis	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 * Cation - Anion / Cation)		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)		-	-3.00		
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
	CO3 ²⁻ split by 0.1 mmol HCl/kgw					
	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
	Nitrogen (inert)	Ntg	mmol/kgw	0.66		18.6 mg/L
	Carbon dioxide	CO2	mmol/kgw	0.00		0.00 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	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)
 - O2(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 °C
 - $p_a \text{ O}_2 = 0.21 \text{ atm}$
 - $p_a \text{ N}_2 = 0.78 \text{ atm}$
 - No gas bubbles (gas volume = 0 mL)
- Calculate gas volume at temperature:
 - A: 25 °C (cold water in the kitchen)
 - B: 70 °C (heating water, noise)

- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module: Gases in water and gas
Dissolution of gases

Phreeqc: Input for all stimuli.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, umol/kgw, umg/kgw

Basic data	Value	Unit	Assumption
Temperature	10.0	°C	
Oxygen	0.21	atm	
Nitrogen (inert)	0.78	atm	
Carbon dioxide		atm	
Methane		atm	
Sulfide		atm	
pe (electron activity)			
Conductivity (measured, at 1 °C)		mS/m	
Total dissolved solids (residue)	0	µS/cm	
Cations			
Calcium	0.00	mmol/kgw	
Magnesium	0.00	mmol/kgw	
Sodium	0.00	mmol/kgw	
Potassium	0.00	mmol/kgw	
Iron	0.00	mmol/kgw	
Manganese	0.00	mmol/kgw	
Ammonium (NH ₄ ⁺)	0.00	mmol/kgw	
Aluminum	0.00	mmol/kgw	
Barium	0.00	mmol/kgw	
Cadmium	0.00	mmol/kgw	
Copper	0.00	mmol/kgw	
Lead	0.00	mmol/kgw	
Lithium	0.00	mmol/kgw	
Strontium	0.00	mmol/kgw	
Zinc	0.00	mmol/kgw	
Anions			
Hydrogen carbonate (as Alkalinity)	0.00	mmol/kgw	
Chloride	0.00	mmol/kgw	
Nitrate	0.00	mmol/kgw	
Sulfate	0.00	mmol/kgw	
Fluoride	0.00	mmol/kgw	
Bromide	0.00	mmol/kgw	
Phosphate	0.00	mmol/kgw	
Nitrite	0.00	mmol/kgw	
Silicate	0.00	mmol/kgw	
Boron	0.00	mmol/kgw	
Conditions			
Pressure	1.00	atm	
Temperature	10.0	°C	
Transformed organic material	0.00	mmol/kgw	

Run PHREEQC

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 stimuli.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, umol/kgw, umol/kgw

Basic data	Value	Unit	Assumption
Temperature	10.0	°C	
Oxygen	0.21	pa O2 atm	
Nitrogen (fert)	0.78	pa N2 atm	
Carbon dioxide		pa CO2 atm	
Methane		pa CH4 atm	
Sulfide		pa H2S atm	
pe (electron activity)		pe	
Conductivity (measured, at 1 °C)		EC mS/m	0 µS/cm
Total dissolved solids (residue)		TDS mg/L	
Cations			
Calcium	0.00	mmol/kgw	
Magnesium	0.00	mmol/kgw	
Sodium	0.00	mmol/kgw	
Potassium	0.00	mmol/kgw	
Iron	0.00	mmol/kgw	
Manganese	0.00	mmol/kgw	
Ammonium (NH4)	0.00	mmol/kgw	
Aluminum	0.00	mmol/kgw	
Barium	0.00	mmol/kgw	
Cadmium	0.00	mmol/kgw	
Copper	0.00	mmol/kgw	
Lead	0.00	mmol/kgw	
Lithium	0.00	mmol/kgw	
Strontium	0.00	mmol/kgw	
Zinc	0.00	mmol/kgw	
Anions			
Hydrogen carbonate (as Alkalinity)	0.00	mmol/kgw	
Chloride	0.00	mmol/kgw	
Nitrate	0.00	mmol/kgw	
Sulfate	0.00	mmol/kgw	
Fluoride	0.00	mmol/kgw	
Bromide	0.00	mmol/kgw	
Phosphate	0.00	mmol/kgw	
Nitrite	0.00	mmol/kgw	
Silicate	0.00	mmol/kgw	
Boron	0.00	mmol/kgw	
Conditions			
Pressure	1.00	atm	
Temperature	10.0	°C	
Transformed organic material	0.00	mmol/kgw	

Run PHREEQC

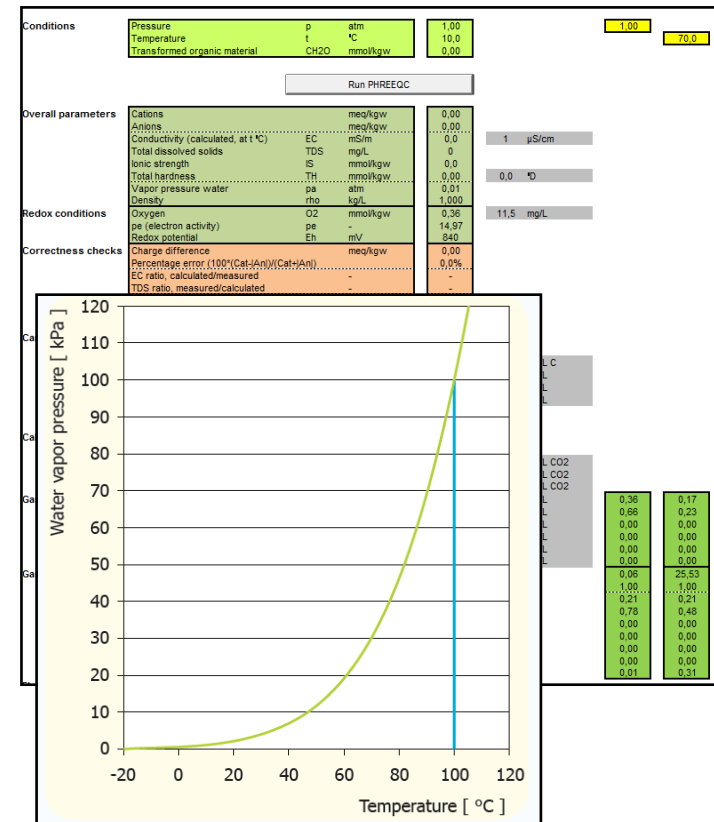
Aquatic Chemistry for engineers

Item : Bubbles from temperature increase



Answers:

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

```
END      H2S(g)      0.0
        # 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 temp
        -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 ($t = 10\text{ }^{\circ}\text{C}$, gas volume = 0 mL):
 - $p_a \text{O}_2 = 0.21\text{ atm}$
 - $p_a \text{N}_2 = 0.78\text{ atm}$
- Calculate gas volume after biodegradation of organic material $\text{CH}_2\text{O} + \text{O}_2$ into $\text{CO}_2 + \text{H}_2\text{O}$ (+ 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 (digester, 90 g/L)
- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module: Gases in water and gas
Dissolution of gases

Phreeqc: Input for all simels.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 - mmol/kgw - mmol/kgw

Basic data	Unit	Value	Unit
Temperature	t °C	10.0	
Oxygen	pa O2 atm	0.21	
Nitrogen (nert)	pa N2 atm	0.78	
Carbon dioxide	pa CO2 atm		
Methane	pa CH4 atm		
Sulfide	pa H2S atm		
pH (electron activity)	pH		
Conductivity (measured, at t °C)	EC mS/cm	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 (nert)	NH4 mg/L	0.000	mmol/kgw
Aluminum	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	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	
Temperature	t °C	10.0	
Transformed organic material	CH2O mmol/kgw	0.00	

Run PHREEQC

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 simels.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/lgs = mg/kg

Basic data	Parameter	Unit	Value	Unit	
Temperature	t	°C	10.0		
Oxygen	pa O2	atm	0.21		
Nitrogen (nert)	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/cm			
Total dissolved solids (residue)	TDS	mg/L		0 µS/cm	
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 (nert)	NH4	mg/L	0.000 mmol/kgw	
	Aluminum	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	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	
	Temperature	t	°C	10.0	
	Transformed organic material	CHOD	mmol/kgw	0.00	
					0.95

Run PHREEQC

Aquatic Chemistry for engineers

Item : Bubbles from rotting



Answers:

- Biodegradation into water and gas

OM	O ₂ w	CH ₄ w	gas
mmol/kgw	id	id	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

- Initial phase: Oxygen consumption
- Second phase: Anaerobic conversion
- Third phase: Gas formation, increasing CO₂ content in water (low pH)

Conditions	Pressure	p	atm	1.00
Temperature	t	°C	10.0	1.00
Transformed organic material	CH2O	mmol/kgw	0.00	10.00
Run PHREEQC				
Overall parameters	Calcium	meq/kgw	0.00	
	Anions	meq/kgw	0.00	
	Conductivity (calculated, at 1°C)	µS/cm	0.0	1 µS/cm
	Total dissolved solids	mg/L	0	
	ionic strength	mol/kgw	0.0	
	Total hardness	mg/L	0.00	0.0 °C
	Vapor pressure water	atm	0.01	
	Density	kg/L	1.000	
Redox conditions	Oxygen	mmol/kgw	0.30	11.5 mg/L
	pe (electron activity)	-	14.97	
	Redox potential	mV	340	
Correctness checks	Charge difference	meq/kgw	0.00	
	Percentage error (100*(Ca-IAn)/(Ca+IAn))	-	0.0%	
	EC ratio, calculated/measured	-	-	
	TDS ratio, measured/calculated	-	-	
	Oxygen saturation (with air at sea level)	atm/atm	105.2%	
	pH change by electron balancing (Phreeqc)	-	0.00	
	pe change by electron balancing (Phreeqc)	-	-	
Carbon equilibrium	pH (hydrogen activity)	-	7.00	
	alkalinity	meq/kgw	0.00	
	Total inorganic Carbon (TIC)	mmol/kgw	0.00	0 mg/L C
	CO2	mmol/kgw	0.00	0.00 mg/L
	HCO3-	mmol/kgw	0.00	0 mg/L
	CO3 2-	mmol/kgw	0.00	0 mg/L
	dipH by 0.1 mol/L HCl / kgw	-	-3.08	
	Buffer capacity	meq/kgw / pH	0.01	
Calcite equilibrium	Sr (moles)	-	-	
	Equilibrium pH (pHs or pH-Langelier)	pH-L	-	
	Calcite Precipitation Potential	CPP	-0.11	5 mg/L CO2
	Calcite Precipitation Potential at 60 C	CPP-60	-0.18	7 mg/L CO2
	Calcite Precipitation Potential at 90 C	CPP-90	-0.18	8 mg/L CO2
Gases in water	Oxygen	mmol/kgw	0.36	11.5 mg/L
	Nitrogen (inert)	mmol/kgw	0.66	18.6 mg/L
	Carbon dioxide	mmol/kgw	0.00	0.00 mg/L
	Methane	mmol/kgw	0.00	0.00 mg/L
	Sulfide	mmol/kgw	0.00	0.00 mg/L
	Ammonia	mmol/kgw	0.00	0.00 mg/L
Gases in gas	Total gas volume	atm	0.00	0.00
	Total gas pressure	atm	1.00	1.00
	Oxygen	atm	0.21	0.21
	Nitrogen (inert)	atm	0.70	0.70
	Carbon dioxide	atm	0.00	0.00
	Methane	atm	0.00	0.00
	Sulfide	atm	0.00	0.00
	Ammonia	atm	0.00	0.00
	Water (vapor)	atm	0.01	0.01

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)

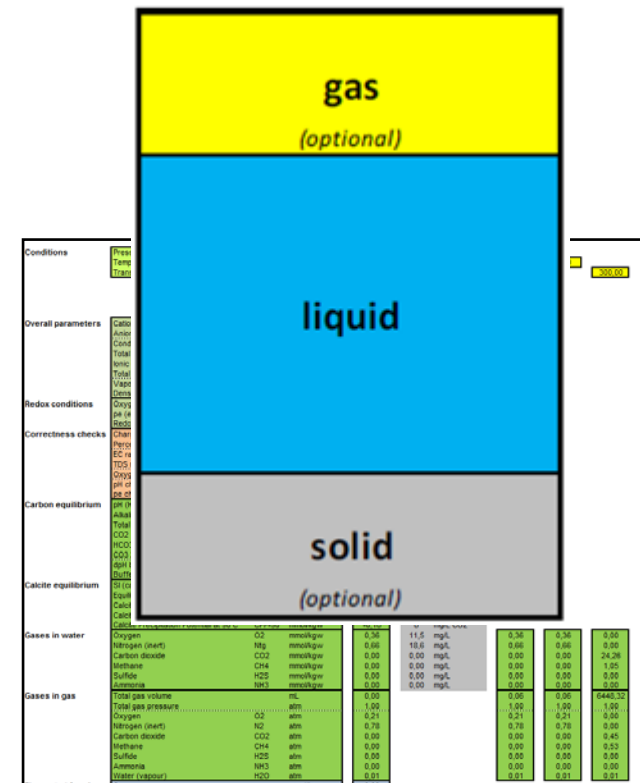
```
# NH3(g) 0.0
# H2S(g) 0.0
REACTION_TEMPERATURE
10.0
END # Simulation 7

TITLE Gas phase , for biodegradation
USE solution 1
GAS_PHASE 1 # Defines a gas phase
    -fixed_pressure # Gas phase with fixed total pressure
    -pressure 1.0 # Gas pressure in atm
    -temperature 10 # Initial gas temperature in C
    -volume 1e-8 # Initial volume in Liter (negative)
# # Gas name from PHASES
# N2(g) 0.0
# Nt(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, stoichiometric coefficient
    3000.00 mmol # Adds 1.0 * x = x mmol C
END # Simulation 8 # last END is optional (End of simulation)
```

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 temperature change



Questions?

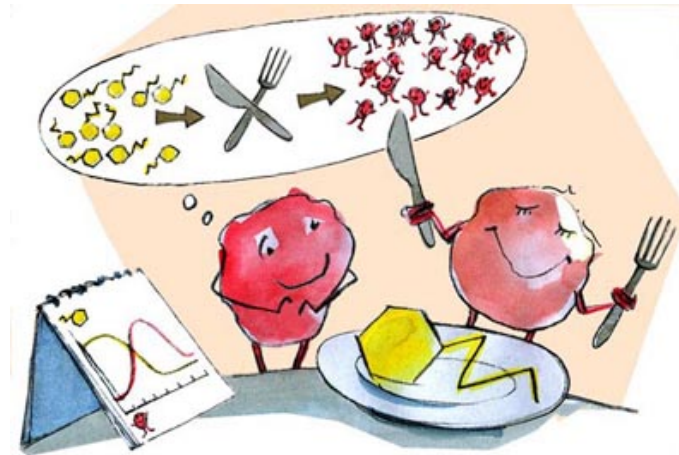


Aquatic Chemistry for engineers

Module : Biodegradation - Monod kinetics (Lab 2c)

- Organic C (oxydation)
 - Additive Monod kinetics
 - Rate = f (O₂ NO₃ SO₄)
 - dMass = Rate x Mass x Timestep

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



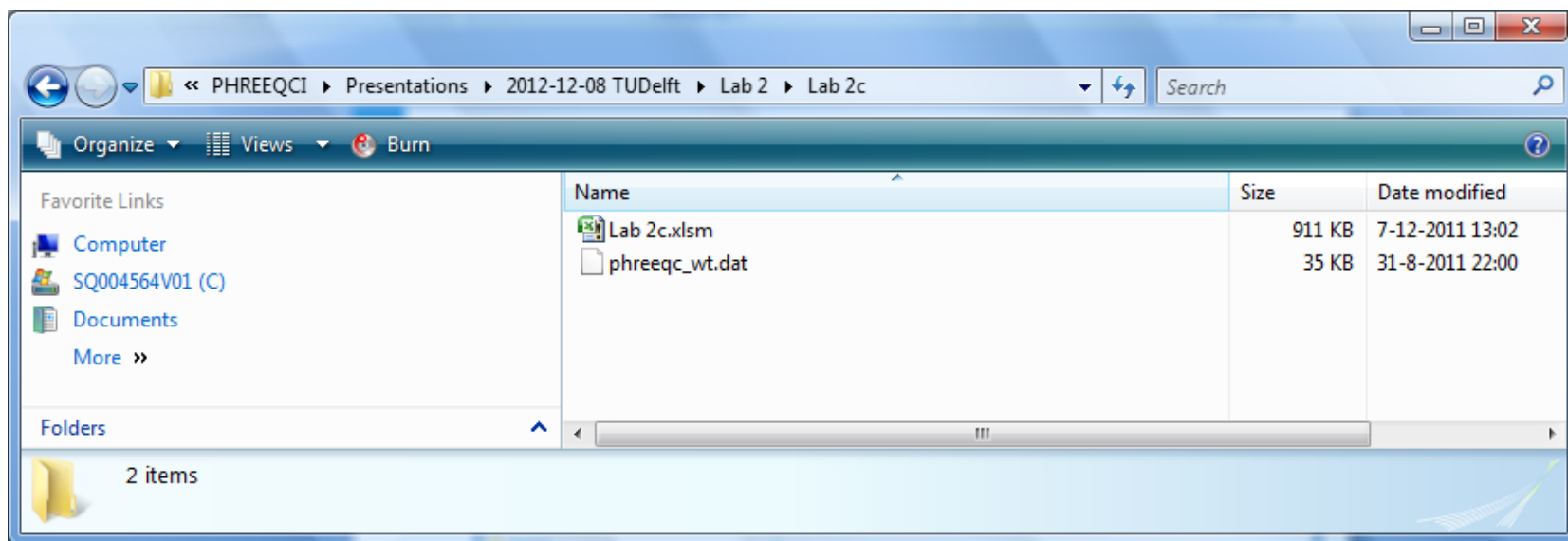
- Application

- Drinking water : O₂ in slow sand or carbon filters
- Sewerage / wastewater: O₂ / NO₃ reduction in aerobic treatment



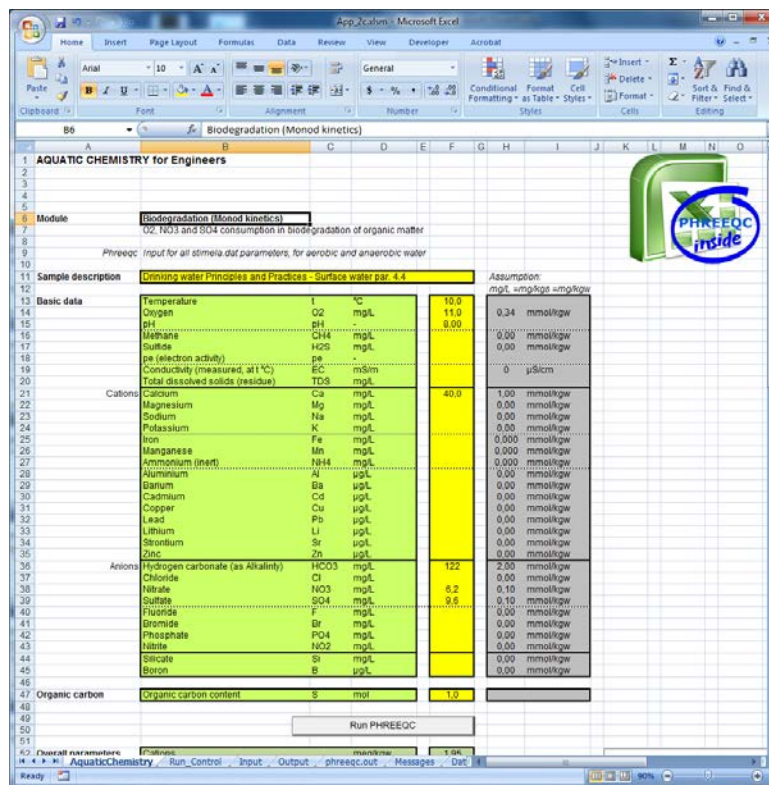
Folder App 2c

- Double click App_2c.xlsm



App 2c - Biodegradation (Monod)

- Open App_2c.xlsm:



Sample description	Concentration	Unit	Value	Assumption
Temperature	T	°C	10.0	
Oxygen	O2	mg/L	11.0	0.24 mmol/kgw
pH	pH		8.00	
Alkalinity	CH4	mg/L		0.00 mmol/kgw
Sulfide	H2S	mg/L		0.00 mmol/kgw
pe (electron activity)	pe			
Conductivity (measured, at 1°C)	EC	µS/cm		
Total dissolved solids (residue)	TDS	mg/L		0 µS/cm
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
Aluminum	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
Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	122	2.00 mmol/kgw
Chloride	Cl	mg/L		0.00 mmol/kgw
Nitrate	NO3	mg/L	8.2	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	1.0

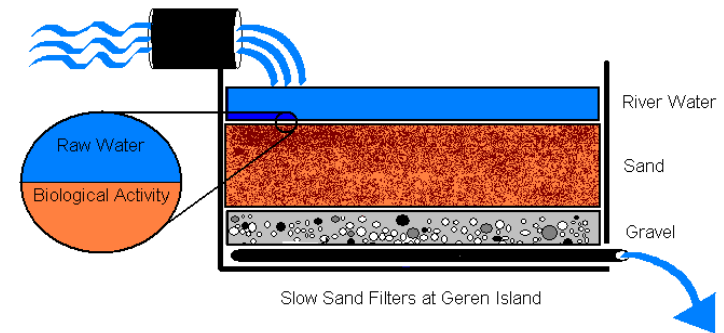
Requires:

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

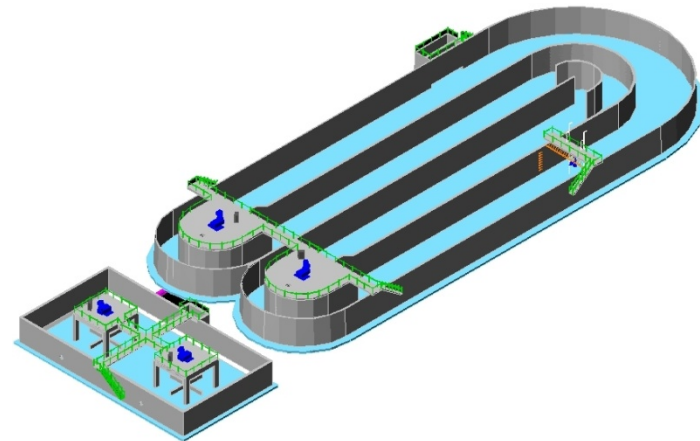
Aquatic Chemistry for engineers

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 : O₂ and NO₃ reduction

- Water

- Temperature 10 °C

- O₂ = 11 mg/L pH = 8.0

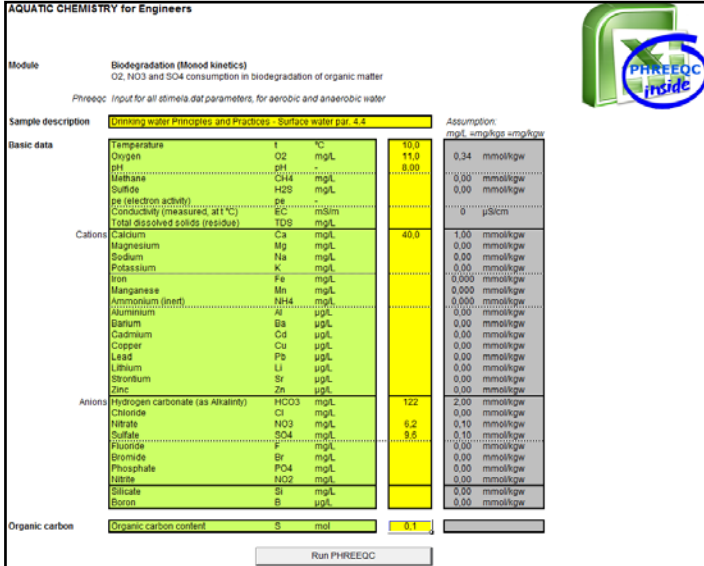
- Ca = 40 mg/L HCO₃ = 122 mg/L

- NO₃ = 6.2 mg/L SO₄ = 9.6 mg/L

- Calculate depletion time of O₂:

- A: organic C: 0.1 mol

- B: organic C: 1.0 mol



The screenshot shows the PHREEQC software interface with the following data:

Parameter	Value	Unit	Assumption
Temperature	10.0	°C	
Oxygen	11.0	mg/L	0.34 mmol/kgw
pH	8.00		
Sulfate	9.6	mg/L	0.00 mmol/kgw
Sulfide	0.00	mg/L	0.00 mmol/kgw
pe (electron activity)	-		
Conductivity (measured, at 25 °C)	0	mS/cm	
Total dissolved solids (residue)	40.0	mg/L	
Cations			
Calcium	40.0	mg/L	1.00 mmol/kgw
Magnesium	0.00	mg/L	0.00 mmol/kgw
Sodium	0.00	mg/L	0.00 mmol/kgw
Potassium	0.00	mg/L	0.00 mmol/kgw
Iron	0.000	mg/L	0.000 mmol/kgw
Manganese	0.000	mg/L	0.000 mmol/kgw
Ammonium (ined)	0.000	mg/L	0.000 mmol/kgw
Aluminum	0.00	mg/L	0.00 mmol/kgw
Barium	0.00	µg/L	0.00 mmol/kgw
Caesium	0.00	µg/L	0.00 mmol/kgw
Copper	0.00	µg/L	0.00 mmol/kgw
Lead	0.00	µg/L	0.00 mmol/kgw
Lithium	0.00	µg/L	0.00 mmol/kgw
Strontium	0.00	µg/L	0.00 mmol/kgw
Zinc	0.00	µg/L	0.00 mmol/kgw
Anions			
Hydrogen carbonate (as Alkalinity)	122	mg/L	2.00 mmol/kgw
Chloride	0.00	mg/L	0.00 mmol/kgw
Nitrate	6.2	mg/L	0.10 mmol/kgw
Sulfate	9.6	mg/L	0.10 mmol/kgw
Fluoride	0.00	mg/L	0.00 mmol/kgw
Bromide	0.00	mg/L	0.00 mmol/kgw
Phosphate	0.00	mg/L	0.00 mmol/kgw
Nitrite	0.00	mg/L	0.00 mmol/kgw
Silicate	0.00	mg/L	0.00 mmol/kgw
Boron	0.00	mg/L	0.00 mmol/kgw
Organic carbon			
Organic carbon content	0.1	mol	

- I give you 3 minutes....

Aquatic Chemistry for engineers

Item : O₂ and NO₃ reduction

Answers:

AQUATIC CHEMISTRY for Engineers


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

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

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

Basic data	Unit	Value	Assumption
Temperature	°C	10.0	
Oxygen	O ₂ mg/L	11.0	0.34 mmol/kgw
pH	pH	8.00	
Sulfate	SO ₄ mg/L		0.00 mmol/kgw
Sulfide	H ₂ S mg/L		0.00 mmol/kgw
pe (electron activity)	pe		
Conductivity (measured, at 1 °C)	µS/cm		0 µS/cm
Total dissolved solids (residue)	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 (inet)	NH ₄ mg/L		0.000 mmol/kgw
Aluminum	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)	HCO ₃ mg/L	122	2.00 mmol/kgw
Chloride	Cl mg/L		0.00 mmol/kgw
Nitrate	NO ₃ mg/L	6.2	0.10 mmol/kgw
Sulfate	SO ₄ mg/L	9.8	0.10 mmol/kgw
Fluoride	F mg/L		0.00 mmol/kgw
Bromide	Br mg/L		0.00 mmol/kgw
Phosphate	PO ₄ mg/L		0.00 mmol/kgw
Nitrite	NO ₂ mg/L		0.00 mmol/kgw
Silicate	Si mg/L		0.00 mmol/kgw
Boron	B mg/L		0.00 mmol/kgw
Organic carbon			
Organic carbon content	S mol	4.1	

Run PHREEQC

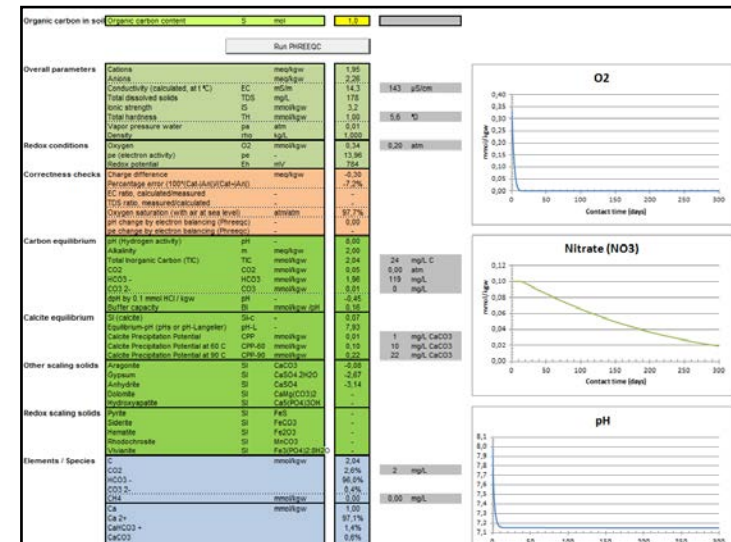
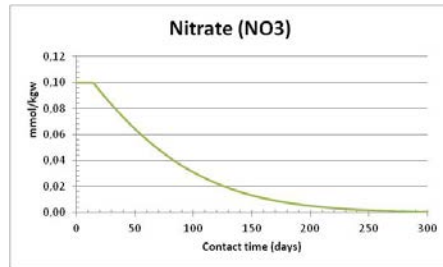
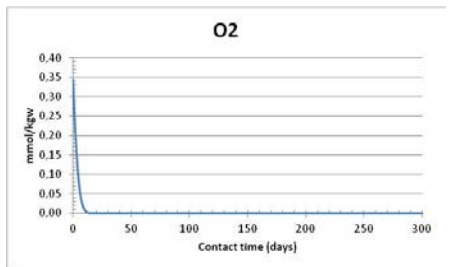
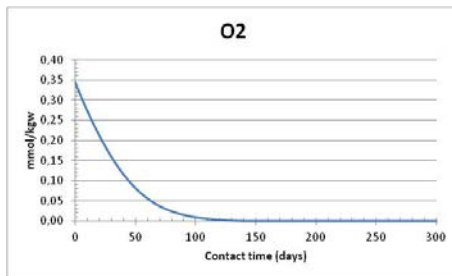
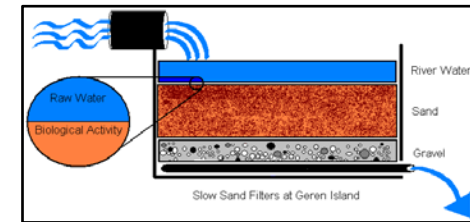


Aquatic Chemistry for engineers

Item : O₂ and NO₃ reduction

Answers:

- Depletion time O₂:
 - A: 0.1 mol 112 days
 - B: 1.0 mol 12 days
 - NO₃ 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 tolerance)
 - -step 0 300*86400 (sec)
 - INCREMENTAL_REACTIONS true

```
EQUILIBRIUM_PHASE
    Calcite
END      # Simulation 5

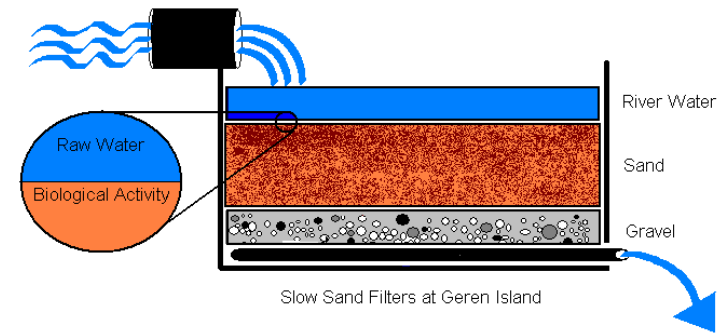
# Kinetics Organic_C

USE solution 1;
KINETICS 1
    Organic_C                                # rate name (must be defined in RATES)
    -formula CH2O 1.0                        # reactant's elements and stoichiometric
    -m0 0.1                                  # initial reactant moles (constant). Default
    -m 0.1                                    # reactant moles at the start (changes with
    -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 (EndOf
```

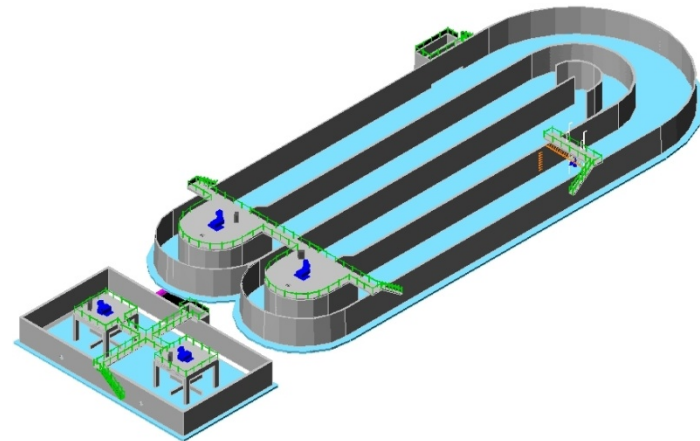
Conclusions - Lessons learned

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



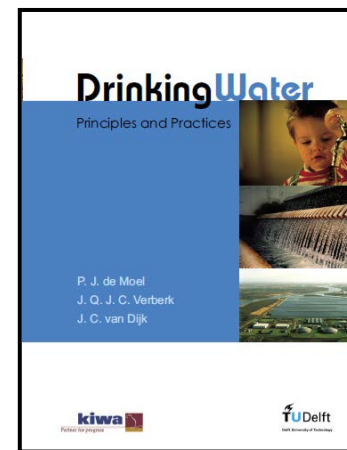
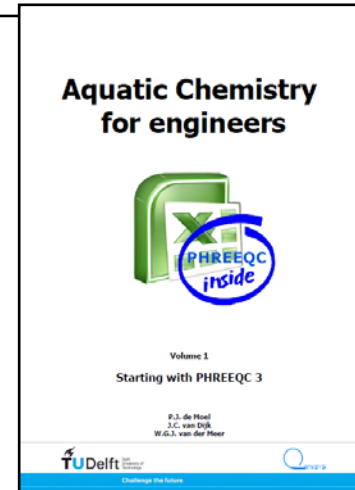
Questions?



Aquatic Chemistry for engineers

Course program

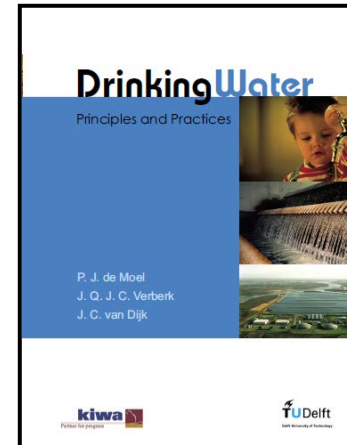
- Introduction (lecture + Starting with PHREEQC 3)
 - PHREEQC – PHREEQC Interactive – PHREEQC-COM
- Drinking water (App 1a+b)
 - Chemistry: SI / CCPP / Buffercapacity / Corrosion
 - Engineering: Ionic balance / Conductivity / Mixing
- Gases in water (App 2a+b+c)
 - Chemistry: solubility O_2 , N_2 , CO_2 , CH_4 etc
 - Engineering: $P \cdot V / T = R$ / 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)

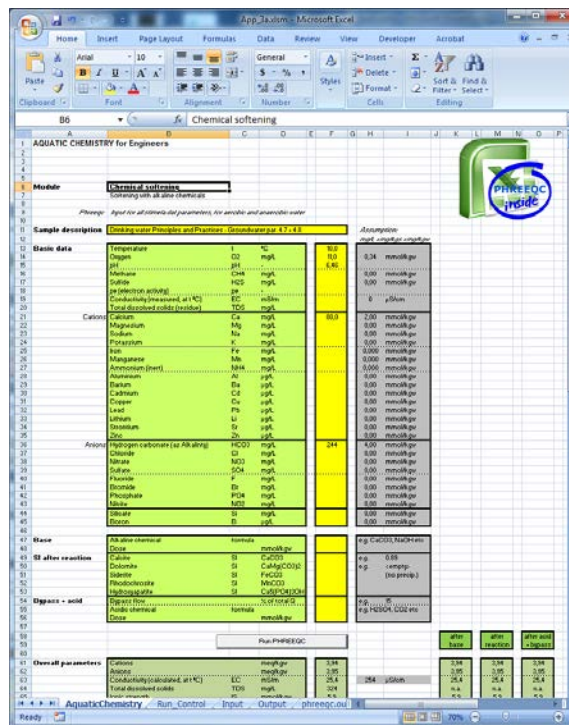
- Neutralization
 - Aeration
 - Limestone filtration
 - Caustic soda
- Softening
 - Sodium hydroxide - $\text{Ca}(\text{OH})_2$
 - Caustic soda – NaOH
 - Split-treatment
- Application
 - Drinking water : pH control + neutralization + softening
 - Sewerage / wastewater: pH control + precipitation



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:

$$\text{Ca}^{2+} = 2.0 \text{ mmol/l}, \quad \text{HCO}_3^- = 4.0 \text{ mmol/l}, \quad \text{pH} = 6.46.$$

What is the pH in equilibrium after aeration, and how much CO_2 has to be removed?

From $\text{p}K_1 = \text{pH} + \log \{ [\text{CO}_2] / [\text{HCO}_3^-] \}$ results that

$$\log \{ [\text{CO}_2] / [\text{HCO}_3^-] \} = 6.46 - 6.46 = 0, \text{ that is } [\text{CO}_2] / [\text{HCO}_3^-] = 10^0 = 1$$

$$\text{so } [\text{CO}_2] = 4.0 \text{ mmol/l} = 4.0 \cdot 44 = 176 \text{ mg/l}.$$

From $\text{pH}_s = \text{p}K_2 - \text{p}K_s - \log \{ [\text{Ca}^{2+}] \cdot [\text{HCO}_3^-] \}$ results that

$$\text{pH}_s = 10.49 - 8.36 - \log (2.0 \cdot 10^{-3} \cdot 4.0 \cdot 10^{-3}) = 2.13 + 4.80 = 7.23 \text{ and}$$

$$\text{SI} = \text{pH} - \text{pH}_s = 6.46 - 7.23 = -0.77, \text{ so the raw water is limestone aggressive.}$$

When removing CO_2 , $[\text{Ca}^{2+}]$ and $[\text{HCO}_3^-]$ remain equal and thus pH_s remains equal.

Therefore, in equilibrium $\text{pH} = \text{pH}_s = 7.23$.

$$\text{With } \text{p}K_1: \log \{ [\text{CO}_2] / [4.0 \cdot 10^{-3}] \} = \text{p}K_1 - \text{pH} = 6.46 - 7.23 = -0.77 \quad \text{so}$$

$$[\text{CO}_2] = 10^{-0.77} \cdot 4.0 \cdot 10^{-3} = 0.34 \cdot 4.0 \cdot 10^{-3} = 0.68 \cdot 10^{-3} \text{ mol/l} = 0.68 \text{ mmol/l}$$

During aeration $4.0 - 0.68 = 3.32 \text{ mmol/l}$ CO_2 is removed, that is $3.32 \cdot 44 = 146 \text{ mg/l}$.

Therefore, the required efficiency is $(146 - 1 / 176 - 1) = 83\%$.

DrinkingWater

Principles and Practices

P. J. de Moel
J. O. J. C. Verberk
J. C. van Dijk

kiwa

TU Delft

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 HCO₃
 - pH = 6.46
- Calculate raw water:
 - A: CO₂ content
 - B: SI
- Calculate at equilibrium (SI=0):
 - C: pH
 - D: CO₂ removed
- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

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

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

Sample description: **Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8** Assumption: *mg/L, mmol/kg, mmol/gw*

Basic data	Parameter	Unit	Value	Assumption
Temperature	t	°C	10.0	
Oxygen	O2	mg/L	10.0	0.34 mmol/kgw
pH	pH		6.46	
Methane	CH4	mg/L	0.00	0.00 mmol/kgw
Sulfide	H2S	mg/L	0.00	0.00 mmol/kgw
pe (electron activity)	pe		0	#Stm
Conductivity (measured, at 1 °C)	EC	mS/cm	0	
Total dissolved solids (residue)	TDS	mg/L	80.0	
Cations	Calcium	Ca	80.0	2.00 mmol/kgw
	Magnesium	Mg	0.00	0.00 mmol/kgw
	Sodium	Na	0.00	0.00 mmol/kgw
	Potassium	K	0.00	0.00 mmol/kgw
	Iron	Fe	0.00	0.00 mmol/kgw
	Manganese	Mn	0.00	0.00 mmol/kgw
	Ammonium (NH4)	NH4	0.00	0.00 mmol/kgw
	Aluminum	Al	0.00	0.00 mmol/kgw
	Barium	Ba	0.00	0.00 mmol/kgw
	Cadmium	Cd	0.00	0.00 mmol/kgw
	Copper	Cu	0.00	0.00 mmol/kgw
	Lead	Pb	0.00	0.00 mmol/kgw
	Lithium	Li	0.00	0.00 mmol/kgw
Anions	Hydrogen carbonate (as Alk. alint)	HCO3	244	4.00 mmol/kgw
	Chloride	Cl	0.00	0.00 mmol/kgw
	Nitrate	NO3	0.00	0.00 mmol/kgw
	Sulfate	SO4	0.00	0.00 mmol/kgw
	Fluoride	F	0.00	0.00 mmol/kgw
	Bromide	Br	0.00	0.00 mmol/kgw
	Phosphate	PO4	0.00	0.00 mmol/kgw
	Nitrite	NO2	0.00	0.00 mmol/kgw
	Silicate	Si	0.00	0.00 mmol/kgw
	Boron	B	0.00	0.00 mmol/kgw
Base	Alk. alk. chemical	formula		e.g. CaCO3, NaOH etc
	Dose	mmol/kgw		
SI after reaction	Calcite	SI	0.89	e.g. > 0.89
	Dolomite	SI	< 0.00	e.g. < 0.00 (no precip.)
	Siderite	SI	< 0.00	
	Rhodochrosite	SI	< 0.00	
Bypass - acid	Hydrogaspate	SI	< 0.00	e.g. < 0.00
	Bypass flow	% of total G	15	e.g. 15
Dose	Acidic chemical	formula		e.g. H2SO4, CO2 etc
	Dose	mmol/kgw		

Buttons: Run PHREEQC, after base, after reaction, after acid + bypass

Aquatic Chemistry for engineers

Item : Neutralization by aeration

Answers:

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alk-aline chemicals
Phreeqc: Input for all stimuli.dat parameters; for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8
Assumption: mg/L, mmol/kg, mmol/kg

Basic data	Parameter	Unit	Value	Assumption
Temperature	t	°C	10.0	
Oxygen	O2	mg/L	10.0	0.34 mmol/kg
pH	pH		8.48	
Methane	CH4	mg/L	0.00	0.00 mmol/kg
Sulfide	H2S	mg/L	0.00	0.00 mmol/kg
pE (electron activity)	pE			
Conductivity (measured, at 1 °C)	EC	mS/cm	0	0 #S/cm
Total dissolved solids (residue)	TDS	mg/L		
Cations			80.0	
Calcium	Ca	mg/L		2.00 mmol/kg
Magnesium	Mg	mg/L		0.00 mmol/kg
Sodium	Na	mg/L		0.00 mmol/kg
Potassium	K	mg/L		0.00 mmol/kg
Iron	Fe	mg/L		0.000 mmol/kg
Manganese	Mn	mg/L		0.000 mmol/kg
Ammonium (NH4)	NH4	mg/L		0.000 mmol/kg
Aluminum	Al	µg/L		0.00 mmol/kg
Barium	Ba	µg/L		0.00 mmol/kg
Cadmium	Cd	µg/L		0.00 mmol/kg
Copper	Cu	µg/L		0.00 mmol/kg
Lead	Pb	µg/L		0.00 mmol/kg
Lithium	Li	µg/L		0.00 mmol/kg
Strontium	Sr	µg/L		0.00 mmol/kg
Zinc	Zn	µg/L		0.00 mmol/kg
Anions			244	
Hydrogen carbonate (as Alk-aling)	HCO3	mg/L		4.00 mmol/kg
Chloride	Cl	mg/L		0.00 mmol/kg
Nitrate	NO3	mg/L		0.00 mmol/kg
Sulfate	SO4	mg/L		0.00 mmol/kg
Fluoride	F	mg/L		0.00 mmol/kg
Bromide	Br	mg/L		0.00 mmol/kg
Phosphate	PO4	mg/L		0.00 mmol/kg
Nitrite	NO2	mg/L		0.00 mmol/kg
Silicate	Si	mg/L		0.00 mmol/kg
Boron	B	mg/L		0.00 mmol/kg
Base	Alk-aline chemical	formula		e.g. CaCO3, NaOH etc
Dose		mmol/kg		
Calcite	SI	CaCO3		e.g. 0.89
Dolomite	SI	CaMg(CO3)2		e.g. <emp/2
Siderite	SI	FeCO3		(no precip.)
Rhodochrosite	SI	MnCO3		
Hydroxapatite	SI	Ca5(PO4)3OH		
Bypass - acid	Bypass flow	% of total G		e.g. 15
Dose	acid chemical	formula		e.g. H2SO4, CO2 etc

Run PHREEQC

after base after reaction after acid + bypass

Aquatic Chemistry for engineers

Item : Neutralization by aeration

Answers:

- A : $\text{CO}_2 = 3.68 \text{ mmol/kgw}$
- B : $\text{SI} = -0.90$
- C : $\text{pH} = 7.36$ (= $\text{pH}_s = \text{pH}_L$ raw water)
 - Aeration will only change pH
 - $\text{SI} = 0$
- D : $\text{CO}_2 = 0.46 \text{ mmol/kgw}$ (at $\text{pH}=7.36$)
 - Removed $3.68 - 0.46 = 3.22 \text{ mmol/kgw}$

Base	Alkaline chemical	formula			e.g. CaCO ₃ , NaOH etc	
SI after reaction	Dose	mmol/kgw				
	Calcite	SI	CaCO ₃		e.g. 0.89	
	Delomite	SI	Ca1/2(CO ₃) ₂		e.g. <empty>	
	Siderite	SI	FeCO ₃		(no precip.)	
	Rhodochrosite	SI	MnCO ₃			
Bypass + acid	Hydroxyapatite	SI	Ca ₅ (PO ₄) ₃ OH			
	Bypass flow	% of total Q			e.g. 15	
	Dose	mmol/kgw			e.g. H ₂ SO ₄ , CO ₂ etc	
Run PHREEQC						
Overall parameters	Cations	meq/kgw	3.94			
	Anions	meq/kgw	3.95			
	Conductivity (calculated, at 1 °C)	EC	mS/m	25.4	254	µS/cm
	Total dissolved solids	TDS	mg/L	324		
	Ionic strength	IS	mmol/kgw	5.9		
	Total hardness	TH	mmol/kgw	2.00		11.2 °D
	Vapor pressure water	ps	atm	0.01		
	Density	rho	kg/L	1.000		
Redox conditions	Oxygen	O ₂	mmol/kgw	0.34	0.20	atm
	pe (electron activity)	pe	-	15.50		
	Redox potential	Eh	mV	870		
Correctness checks	Charge difference	meq/kgw	-0.01			
	Percentage error (100*(Cat-Ani)/(Cat+Ani))	-	-0.1%			
	EC ratio, calculated/measured	-	-			
	TDS ratio, measured/calculated	-	-			
	Oxygen saturation (with air at sea level)	satm		87.7%		
	pH change by electron balancing (Phreeqc)	-	-	0.00		
Carbon equilibrium	pe change by electron balancing (Phreeqc)	-	-			
	pH (Hydrogen activity)	pH	-	6.46		
	Alkalinity	m	meq/kgw	4.00		
	Total Inorganic Carbon (TIC)	TIC	mmol/kgw	7.67	92	mg/L C
	CO ₂	CO ₂	mmol/kgw	3.88	0.07	atm
	HCO ₃ ⁻	HCO ₃ ⁻	mmol/kgw	3.95	241	mg/L
	CO ₃ ²⁻	CO ₃ ²⁻	mmol/kgw	0.00	0	mg/L
	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		
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	-	7.36		
	Calcite Precipitation Potential	CPP	mmol/kgw	-1.53	67	mg/L CO ₂
	Calcite Precipitation Potential at 80 C	CPP-80	mmol/kgw	-0.66	29	mg/L CO ₂
	Calcite Precipitation Potential at 90 C	CPP-90	mmol/kgw	0.02	2	mg/L CaCO ₃
	Other scaling solids	Aragonite	SI	CaCO ₃	-1.06	

- Aeration = Gas exchange with air
- Aeration = Stripping CO₂



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 °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_PHASES      # dummy to start final calculation, with ident
SAVE SOLUTION 1
END          # Simulation 2

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

Conclusions - Lessons learned

Neutralization by aeration - Compare results

- A : $\text{CO}_2 = 3.68$ vs 4.0 mmol/kgw
 - Gamma book = 0 : $[\text{HCO}_3^-] = [\text{CO}_2]$
 - Now: $0.925 [\text{HCO}_3^-] = 1.002 [\text{CO}_2]$
- B : $\text{SI} = -0.90$ vs -0.77
 - pK_s book = 8.36
 - pK_s PHREEQC = $8.41 + \text{gamma}$
- C : $\text{pH} = 7.36$ vs 7.23
- D : $\text{CO}_2 = 0.46$ 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

The screenshot displays the PHREEQC software interface, showing a detailed chemical model for water neutralization. The interface includes a menu bar, a toolbar, and a main window displaying a spreadsheet-like table of chemical parameters and their calculated values. The table is organized into sections: Overall parameters, Redox conditions, Charge balance, Carbon equilibria, Calcite equilibria, and Other scaling parameters. The 'Overall parameters' section shows values for pH (7.23), pCO2 (0.002), and various ion concentrations. The 'Carbon equilibria' section shows CO2 concentration (0.46 mmol/kgw) and total inorganic carbon (TIC). The 'Calcite equilibria' section shows saturation index (SI) for calcite (-0.90). The 'Other scaling parameters' section lists various minerals and their SI values. The bottom of the window shows the 'Run Control' dialog box with 'Run' and 'Input' buttons.

DrinkingWater

Principles and Practices

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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:

$\text{Ca}^{2+} = 2.0 \text{ mmol/l}$, $\text{HCO}_3^- = 4.0 \text{ mmol/l}$, $\text{pH} = 6.46$, $\text{CO}_2 = 4.0 \text{ mmol/l}$

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

When $x \text{ mol CaCO}_3$ reacts, then $x \text{ mol CO}_2$ is removed and $x \text{ mol Ca}^{2+}$ and $2x \text{ mol HCO}_3^-$ are formed.

From $K = \frac{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]^2}{[\text{CO}_2]} = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:
 $(2.0 + x) \cdot (4.0 + 2x)^2 / (4.0 - x) 10^{-6} = 10^{-4.33}$ so that $x = 1.20 \text{ mmol/l}$

Thus in equilibrium is:

$\text{Ca}^{2+} = 3.20 \text{ mmol/l}$, $\text{HCO}_3^- = 6.40 \text{ mmol/l}$, $\text{CO}_2 = 2.80 \text{ mmol/l}$.

From $\text{pH}_s = \text{pK}_2 - \text{pK}_s - \log\{[\text{Ca}^{2+}][\text{HCO}_3^-]\}$ results:

$$\text{pH}_s = 10.49 - 8.36 - \log\{[3.20 \cdot 10^{-3}][6.40 \cdot 10^{-3}]\} = 2.13 + 4.69 = 6.82$$

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 $1.20 \text{ mmol/l CaCO}_3$ is consumed, that is $(1.20 \cdot 100) = 120 \text{ g/m}^3$.

A production of 1 million m^3 per year corresponds to 120 tons per year.

DrinkingWater

Principles and Practices

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Aquatic Chemistry for engineers

Item : Neutralization by limestone filtration – CaCO_3

- Raw groundwater
 - $\text{Ca} = 2.0 \text{ mmol/kgw} = 80 \text{ mg/L}$
 - $\text{Alk} = 4.0 \text{ meq/kgw} = 244 \text{ mg/L HCO}_3$
 - $\text{pH} = 6.46$
 - $\text{CO}_2 = 3.68 \text{ mmol/kgw}$ (was 4.0)
- Calculate:
 - A: pH at equilibrium with CaCO_3
 - B: CaCO_3 consumption

AQUATIC CHEMISTRY for Engineers

Module: **Chemical softening**
Softening with alk-ine chemicals

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

Sample description: **Drinking water Principles and Practices - Groundwater par. 4.7-4.8** Assumption: **mg/L, mmol/kg, mmol/gw**

Basic data	Parameter	Unit	Value	Assumption
Temperature	t	°C	10.0	
Oxygen	O2	mg/L	10.0	0.34 mmol/kgw
pH	pH		6.46	
Methane	CH4	mg/L	0.00	0.00 mmol/kgw
Sulfide	H2S	mg/L	0.00	0.00 mmol/kgw
pE (electron activity)	pE		0	
Conductivity (measured, at 1 °C)	EC	mS/cm	0	0 #S/cm
Total dissolved solids (residue)	TDS	mg/L	0.00	
Cations	Calcium	Ca	80.0	2.00 mmol/kgw
	Magnesium	Mg	0.00	0.00 mmol/kgw
	Sodium	Na	0.00	0.00 mmol/kgw
	Potassium	K	0.00	0.00 mmol/kgw
	Iron	Fe	0.00	0.00 mmol/kgw
	Manganese	Mn	0.00	0.00 mmol/kgw
	Ammonium (NH4)	NH4	0.00	0.00 mmol/kgw
	Aluminum	Al	0.00	0.00 mmol/kgw
	Barium	Ba	0.00	0.00 mmol/kgw
	Cadmium	Cd	0.00	0.00 mmol/kgw
	Copper	Cu	0.00	0.00 mmol/kgw
	Lead	Pb	0.00	0.00 mmol/kgw
	Lithium	Li	0.00	0.00 mmol/kgw
	Strontium	Sr	0.00	0.00 mmol/kgw
	Zinc	Zn	0.00	0.00 mmol/kgw
Anions	Hydrogen carbonate (as Alk-ality)	HCO3	244	4.00 mmol/kgw
	Chloride	Cl	0.00	0.00 mmol/kgw
	Nitrate	NO3	0.00	0.00 mmol/kgw
	Sulfate	SO4	0.00	0.00 mmol/kgw
	Fluoride	F	0.00	0.00 mmol/kgw
	Bromide	Br	0.00	0.00 mmol/kgw
	Phosphate	PO4	0.00	0.00 mmol/kgw
	Nitrite	NO2	0.00	0.00 mmol/kgw
	Silicate	Si	0.00	0.00 mmol/kgw
	Boron	B	0.00	0.00 mmol/kgw
Base	Alk-ine chemical	formula		e.g. CaCO3, NaOH etc
	Dose	mmol/kgw		
SI after reaction	Calcite	SI	0.89	e.g. 0.89
	Dolomite	SI	<emp>	e.g. <emp>
	Siderite	SI	(no prec.)	(no prec.)
	Rhodochrosite	SI		
	Hydroxapatite	SI		
Bypass - acid	Bypass flow	% of total G	15	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 alk-ine chemicals
Phreeqc: Input for all stimuli.dat parameters; for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8 *Assumption: mg/L, cmol/kg, mmol/kg*

Basic data	Parameter	Unit	Value	Assumption
Temperature	t	°C	10.0	
Oxygen	O2	mg/L	10.0	0.34 mmol/kg
pH	pH		8.48	
Methane	CH4	mg/L	0.00	0.00 mmol/kg
Sulfide	H2S	mg/L	0.00	0.00 mmol/kg
pE (electron activity)	pE			
Conductivity (measured, at 1 °C)	EC	mS/cm	0	0 #S/cm
Total dissolved solids (residue)	TDS	mg/L		
Cations			80.0	
Calcium	Ca	mg/L		2.00 mmol/kg
Magnesium	Mg	mg/L		0.00 mmol/kg
Sodium	Na	mg/L		0.00 mmol/kg
Potassium	K	mg/L		0.00 mmol/kg
Iron	Fe	mg/L		0.000 mmol/kg
Manganese	Mn	mg/L		0.000 mmol/kg
Ammonium (NH4)	NH4	mg/L		0.000 mmol/kg
Aluminium	Al	µg/L		0.00 mmol/kg
Barium	Ba	µg/L		0.00 mmol/kg
Cadmium	Cd	µg/L		0.00 mmol/kg
Copper	Cu	µg/L		0.00 mmol/kg
Lead	Pb	µg/L		0.00 mmol/kg
Lithium	Li	µg/L		0.00 mmol/kg
Strontium	Sr	µg/L		0.00 mmol/kg
Zinc	Zn	µg/L		0.00 mmol/kg
Anions			244	
Hydrogen carbonate (as Alk-ality)	HCO3	mg/L		4.00 mmol/kg
Chloride	Cl	mg/L		0.00 mmol/kg
Nitrate	NO3	mg/L		0.00 mmol/kg
Sulfate	SO4	mg/L		0.00 mmol/kg
Fluoride	F	mg/L		0.00 mmol/kg
Bromide	Br	mg/L		0.00 mmol/kg
Phosphate	PO4	mg/L		0.00 mmol/kg
Nitrite	NO2	mg/L		0.00 mmol/kg
Silicate	Si	mg/L		0.00 mmol/kg
Boron	B	mg/L		0.00 mmol/kg
Base	Alk-ine chemical formula			e.g. CaCO3, NaOH etc
SI after reaction	Dose	mmol/kg		
	Calcite	SI	CaCO3	e.g. 0.89
	Dolomite	SI	CaMg(CO3)2	e.g. <emp>
	Siderite	SI	FeCO3	(no precip.)
	Rhodochrosite	SI	MnCO3	
	Hydroxapatite	SI	C5H9PO4(OH)	
Bypass - acid	Bypass flow	% of total G		e.g. 15
	Acidic chemical formula			e.g. H2SO4, CO2 etc

Run PHREEQC

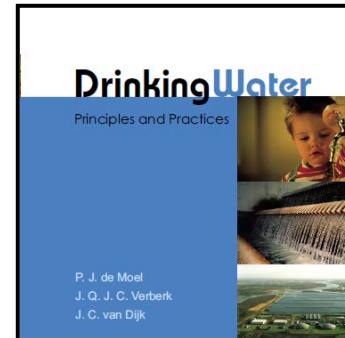
after base after reaction after acid + bypass

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	CaCO_3		e.g. CaCO_3 , NaOH etc.
Dose		mmol/kgw	1.53		
SI after reaction	Calcite	SI	CaCO_3		e.g. 0.89
	Dolomite	SI	$\text{CaMg}(\text{CO}_3)_2$		e.g. <empty>
	Siderite	SI	FeCO_3		(no precip.)
	Rhodochrosite	SI	MnCO_3		
	Hydroxapatite	SI	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$		
Bypass + acid	Bypass flow		% of total Q		e.g. 15
	Acidic chemical	formula			e.g. H_2SO_4 , CO_2 etc.
	Dose	mmol/kgw			
Run PHREEQC					
Overall parameters	Cations	meq/kgw	3.94		6.90
	Anions	meq/kgw	3.95		6.90
	Conductivity (calculated, at 1°C)	EC	25.4	25.4 $\mu\text{S/cm}$	43.3
	Total dissolved solids	TDS	324		n.a.
	Ionic strength	IS	5.9		10.3
	Total hardness	TH	2.00		3.53
	Vapor pressure water	ps	0.01	11.2 °D	0.01
	Density	rho	1.000		1.000
Redox conditions	Oxygen	O_2	0.34	0.20 atm	0.34
	pe (electron activity)	pe	15.50		15.04
	Redox potential	En	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		97.7%		97.0%
	Oxygen saturation (with air at sea level)	atm/atm	97.7%		97.0%
	pH change by electron balancing (Phreeqc)		0.00		-
	pe change by electron balancing (Phreeqc)		-		-
Carbon equilibrium	pH (Hydrogen activity)	pH	6.48		6.93
	Alkalinity	m	4.00		7.06
	Total Inorganic Carbon (TIC)	TIC	7.67	92 mg/L C	9.21
	CO_2	CO_2	3.68	0.07 atm	2.15
	HCO_3^-	HCO_3^-	3.95	241 mg/L	6.80
	CO_3^{2-}	CO_3^{2-}	0.00	0 mg/L	0.00
	d(pH) by 0.1 mmol HCl / kgw	pH	-0.02		-
	Buffer capacity	BI	4.41		-
Calcite equilibrium	SI (calcite)	SI-C	-0.90		0.00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	7.36		6.82
	Calcite Precipitation Potential	CPP	1.53	67 mg/L CO_2	0.00
	Calcite Precipitation Potential at 80 C	CPP-80	-0.66	29 mg/L CO_2	-
	Calcite Precipitation Potential at 90 C	CPP-90	0.02	2 mg/L CaCO_3	-



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
```

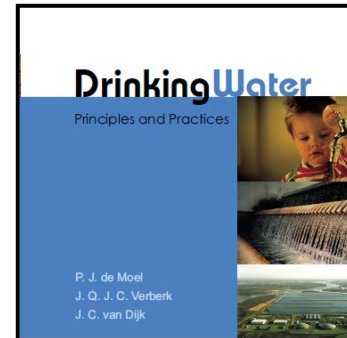
Conclusions - Lessons learned

Neutralization by limestone filtration – CaCO₃

- In water quality CaCO₃ = Calcite
- Other crystal forms of CaCO₃ :
 - Aragonite (more soluble)
 - Vaterite (more soluble)

- CPP = - Aggressive CO₂

- PHREEQC is more exact:
 - Other CO₂ content
 - Influence gamma (ionic strength)
 - Other pK_S (pK_w, pK₁, pK₂ equal)
 - Ion pairs



Base	Alkaline chemical	formula	CaCO ₃	e.g. CaCO ₃ , NaOH etc.
Dose		mmol/kgw	1.53	
Sl after reaction	Calcite	SI CaCO ₃		e.g. 0.89
	Dolomite	SI CaMg(CO ₃) ₂		e.g. <empty> (no precip.)
	Siderite	SI FeCO ₃		
	Rhodochrosite	SI MnCO ₃		
	Hydroxapatite	SI Ca ₅ (PO ₄) ₃ OH		
Bypass + acid	Bypass flow	% of total Q		e.g. 15
	Acidic chemical	formula		e.g. H ₂ SO ₄ , CO ₂ etc.
	Dose	mmol/kgw		
Run PHREEQC				
Overall parameters	Cations	meq/kgw	3.94	6.90
	Anions	meq/kgw	3.95	6.90
	Conductivity (calculated, at 1 °C)	ms/cm	25.4	43.3
	Total dissolved solids	mg/L	324	254 µs/cm
	Ionic strength	IS	5.9	n.a.
	Total hardness	TH	2.00	10.3
	Vapor pressure water	ps	0.01	11.2 °D
	Density	mg/L	1.000	3.53
Redox conditions	Oxygen	O ₂ mmol/kgw	0.34	0.20 atm
	pe (electron activity)	pe	15.50	15.04
	Redox potential	En	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%	97.0%
	pH change by electron balancing (Phreeqc)		0.00	-
	pH change by electron balancing (Phreeqc)		-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	6.48	6.53
	Alkalinity	m	4.00	7.06
	Total Inorganic Carbon (TIC)	TIC	7.57	92 mg/L C
	CO ₂	CO ₂ mmol/kgw	3.68	0.07 atm
	HCO ₃ ⁻	HCO ₃ mmol/kgw	3.95	241 mg/L
	CO ₃ ²⁻	CO ₃ mmol/kgw	0.00	0 mg/L
	dipH by 0.1 mmol HCl / kgw	pH	-0.02	-
	Buffer capacity	BI	4.41	-
Calcite equilibrium	SI (calcite)	SFC	-0.90	0.00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	7.36	6.82
	Calcite Precipitation Potential	CPP	1.53	67 mg/L CO ₂
	Calcite Precipitation Potential at 80 C	CPP-80	-0.68	29 mg/L CO ₂
	Calcite Precipitation Potential at 90 C	CPP-90	0.02	2 mg/L CaCO ₃

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:

$\text{Ca}^{2+} = 2.0 \text{ mmol/l}$, $\text{HCO}_3^- = 4.0 \text{ mmol/l}$, $\text{pH} = 6.46$, $\text{CO}_2 = 4.0 \text{ mmol/l}$.

What is the pH in equilibrium after dosing caustic soda and how much NaOH is required?

When $x \text{ mol NaOH}$ is dosed, then $x \text{ mol CO}_2$ is removed and $x \text{ mol HCO}_3^-$ is formed.

From $K = [\text{Ca}^{2+}] [\text{HCO}_3^-]^2 / [\text{CO}_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

$(2.0) \cdot (4.0 + x)^2 / (4.0 - x) \cdot 10^{-6} = 10^{-4.33}$ so that $x = 2.30 \text{ mmol/l}$

Thus, in equilibrium is:

$\text{Ca}^{2+} = 2.00 \text{ mmol/l}$, $\text{HCO}_3^- = 6.30 \text{ mmol/l}$, $\text{CO}_2 = 1.70 \text{ mmol/l}$

From $\text{pH}_s = \text{pK}_2 - \text{pK}_s - \log\{ [\text{Ca}^{2+}] [\text{HCO}_3^-] \}$ results:

$\text{pH}_s = 10.49 - 8.36 - \log\{ [2.00 \cdot 10^{-3}] [6.30 \cdot 10^{-3}] \} = 2.13 + 4.90 = 7.03$

After dosing caustic soda, the pH is lower than after aeration/gas transfer, but higher than after limestone filtration.

Because of dosing caustic soda, 2.30 mmol/l CO_2 is transformed and 2.30 mmol/l NaOH is consumed, that is $(2,30 \cdot 40 =) 92 \text{ g/m}^3$.

A production of 1 million m^3 per year corresponds to about $92 \text{ tons NaOH (100\%)}$ per year.

DrinkingWater

Principles and Practices

P. J. de Moel
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kiwa

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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 HCO₃
 - pH = 6.46
 - CO₂ = 3.68 mmol/kgw (was 4.0)
- Calculate:
 - A: pH at equilibrium with CaCO₃
 - B: NaOH consumption

AQUATIC CHEMISTRY for Engineers

Module: **Chemical softening**
Softening with alk-ine chemicals

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

Sample description: **Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8** Assumption: mg/L, mmol/kgw, mmol/gw

Basic data	Parameter	Unit	Value	Assumption
	Temperature	t °C	10.0	
	Oxygen	O2 mg/L	1.0	0.34 mmol/kgw
	pH	pH	6.46	
	Methane	CH4 mg/L	0.00	0.00 mmol/kgw
	Sulfide	H2S mg/L	0.00	0.00 mmol/kgw
	pE (electron activity)	pE		
	Conductivity (measured, at 1 °C)	EC mS/cm	0	0 #S/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	0.00 mmol/kgw
	Sodium	Na mg/L	0.00	0.00 mmol/kgw
	Potassium	K mg/L	0.00	0.00 mmol/kgw
	Iron	Fe mg/L	0.000	0.000 mmol/kgw
	Manganese	Mn mg/L	0.000	0.000 mmol/kgw
	Ammonium (NH4)	NH4 mg/L	0.000	0.000 mmol/kgw
	Aluminum	Al mg/L	0.000	0.000 mmol/kgw
	Barium	Ba mg/L	0.00	0.00 mmol/kgw
	Cadmium	Cd mg/L	0.00	0.00 mmol/kgw
	Copper	Cu mg/L	0.00	0.00 mmol/kgw
	Lead	Pb mg/L	0.00	0.00 mmol/kgw
	Lithium	Li mg/L	0.00	0.00 mmol/kgw
	Strontium	Sr mg/L	0.00	0.00 mmol/kgw
	Zinc	Zn mg/L	0.00	0.00 mmol/kgw
Anions	Hydrogen carbonate (as Alk-ality)	HCO3 mg/L	244	4.00 mmol/kgw
	Chloride	Cl mg/L	0.00	0.00 mmol/kgw
	Nitrate	NO3 mg/L	0.00	0.00 mmol/kgw
	Sulfate	SO4 mg/L	0.00	0.00 mmol/kgw
	Fluoride	F mg/L	0.00	0.00 mmol/kgw
	Bromide	Br mg/L	0.00	0.00 mmol/kgw
	Phosphate	PO4 mg/L	0.00	0.00 mmol/kgw
	Nitrite	NO2 mg/L	0.00	0.00 mmol/kgw
	Silicate	Si mg/L	0.00	0.00 mmol/kgw
	Boron	B mg/L	0.00	0.00 mmol/kgw
Base	Alk-ine chemical	formula		e.g. CaCO3, NaOH etc
	Dose	mmol/kgw		
SI after reaction	Calcite	CaCO3		e.g. 0.89
	Dolomite	CaMgCO32		e.g. <emp>
	Siderite	FeCO3		(no precip.)
	Rhodochrosite	MnCO3		
	Hydroxapatite	Ca5(PO4)3OH		
Bypass - acid	Bypass flow	% of total G		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 caustic soda - NaOH

Answers:

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alk-ine-chemicals
Phreeqc: Input for all stimuli.dat parameters; for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8
Assumption: mg/L, cmol/kg, mmol/kg

Basic data	Parameter	Unit	Value	Assumption
Temperature	t	°C	10.0	
Oxygen	O2	mg/L	11.0	0.34 mmol/kg
pH	pH		8.48	
Methane	CH4	mg/L	0.00	0.00 mmol/kg
Sulfide	H2S	mg/L	0.00	0.00 mmol/kg
pE (electron activity)	pE			
Conductivity (measured, at 1 °C)	EC	mS/cm	0	0 #S/cm
Total dissolved solids (residue)	TDS	mg/L		
Cations			80.0	
Calcium	Ca	mg/L		2.00 mmol/kg
Magnesium	Mg	mg/L		0.00 mmol/kg
Sodium	Na	mg/L		0.00 mmol/kg
Potassium	K	mg/L		0.00 mmol/kg
Iron	Fe	mg/L		0.000 mmol/kg
Manganese	Mn	mg/L		0.000 mmol/kg
Ammonium (NH4)	NH4	mg/L		0.000 mmol/kg
Aluminum	Al	µg/L		0.00 mmol/kg
Barium	Ba	µg/L		0.00 mmol/kg
Cadmium	Cd	µg/L		0.00 mmol/kg
Copper	Cu	µg/L		0.00 mmol/kg
Lead	Pb	µg/L		0.00 mmol/kg
Lithium	Li	µg/L		0.00 mmol/kg
Strontium	Sr	µg/L		0.00 mmol/kg
Zinc	Zn	µg/L		0.00 mmol/kg
Anions			244	
Hydrogen carbonate (as Alk-ality)	HCO3	mg/L		4.00 mmol/kg
Chloride	Cl	mg/L		0.00 mmol/kg
Nitrate	NO3	mg/L		0.00 mmol/kg
Sulfate	SO4	mg/L		0.00 mmol/kg
Fluoride	F	mg/L		0.00 mmol/kg
Bromide	Br	mg/L		0.00 mmol/kg
Phosphate	PO4	mg/L		0.00 mmol/kg
Nitrite	NO2	mg/L		0.00 mmol/kg
Silicate	Si	mg/L		0.00 mmol/kg
Boron	B	mg/L		0.00 mmol/kg
Base	Alk-ine-chemical	formula		e.g. CaCO3, NaOH etc
Dose		mmol/kg		
Calcite	CaCO3	Si		e.g. 0.89
Dolomite	CaMg(CO3)2	Si		e.g. <emp/2
Siderite	FeCO3	Si		(no precip.)
Rhodochrosite	MnCO3	Si		
Hydroxapatite	Ca5(PO4)3OH	Si		
Bypass - acid	Bypass flow	% of total G		e.g. 15
Dose	Acidic chemical	formula		e.g. H2SO4, CO2 etc

Run PHREEQC

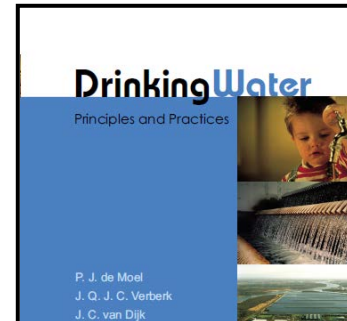
after base after reaction after acid + bypass

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	mmol/kgw	NaOH	e.g. CaCO3, NaOH etc
SI after reaction	Calcite	SI	CaCO3	2.56	e.g. 0.89
	Dolomite	SI	CaMg(CO3)2		e.g. <empty> (no precip.)
	Siderite	SI	FeCO3		
	Rhodochrosite	SI	MnCO3		
	Hydroxapatite	SI	Ca5(PO4)3OH		
Bypass + acid	Bypass flow	% of total O			e.g. 16
	Acidic chemical	formula	mmol/kgw		e.g. H2SO4, CO2 etc
	Dose				

Overall parameters	after base			
Cations	meq/kgw	3.84	6.45	
Anions	meq/kgw	3.95	8.46	
Conductivity (calculated, at 25 °C)	Ec	mS/cm	254	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	2.00
Vapor pressure water	ps	atm	0.01	0.01
Density	rho	kg/L	1.000	1.000
Redox conditions	O2	mmol/kgw	0.34	0.20
	pe (electron activity)	pe	15.50	14.78
	Redox potential	Eh	mV	870
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	87.7%	87.8%
	pH change by electron balancing (Phreeqc)		0.00	-
	pe change by electron balancing (Phreeqc)		-	-
Carbon equilibrium	pH (Hydrogen activity)	pH	6.45	7.18
	Alkalinity	m	4.00	8.56
	Total inorganic Carbon (TIC)	mmol/kgw	7.67	7.57
	CO2	mmol/kgw	3.68	0.07
	HCO3-	mmol/kgw	3.95	241
	CO3 2-	mmol/kgw	0.00	0
	pH by 0.1 mmol HCl / kgw	pH	-0.02	-
	Buffer capacity	SI	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	-1.53	67
	Calcite Precipitation Potential at 60 C	CPP-60	-0.66	29
	Calcite Precipitation Potential at 90 C	CPP-90	0.02	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 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

- 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	mmol/kgw	NaOH	e.g. CaCO ₃ , NaOH etc
Dose				2.56	
SI after reaction	Calcite	SI	CaCO ₃		e.g. 0.89
	Dolomite	SI	CaMg(CO ₃) ₂		e.g. <empty> (no precip.)
	Siderite	SI	FeCO ₃		
	Rhodochrosite	SI	MnCO ₃		
	Hydroxapatite	SI	Ca ₅ (PO ₄) ₃ OH		
Bypass + acid	Bypass flow		% of total Q		e.g. 15
	Acidic chemical	formula			e.g. H ₂ SO ₄ , CO ₂ etc
	Dose		mmol/kgw		

Run PHREEQC				after
Overall parameters	Cations	meq/kgw	3.94	6.45
	Anions	meq/kgw	3.95	6.46
	Conductivity (calculated, at 1 °C)	ns/cm	25.4	25.4 μS/cm
	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	2.00
	Vapor pressure water	pa atm	0.01	0.01
	Density	rho kg/L	1.000	1.000
Redox conditions	Oxygen	O ₂ mmol/kgw	0.34	0.20 atm
	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	7.67
	CO ₂	CO ₂ mmol/kgw	3.68	0.07 atm
	HCO ₃ ⁻	HCO ₃ ⁻ mmol/kgw	3.95	241 mg/L
	CO ₃ ²⁻	CO ₃ ²⁻ mmol/kgw	0.00	0 mg/L
	dH 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 CO ₂
	Calcite Precipitation Potential at 60 °C	CPP-60 mmol/kgw	-0.66	29 mg/L CO ₂
	Calcite Precipitation Potential at 90 °C	CPP-90 mmol/kgw	0.02	2 mg/L CaCO ₃

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:

$\text{Ca}^{2+} = 2.0 \text{ mmol/l}$, $\text{HCO}_3^- = 4.0 \text{ mmol/l}$, $\text{CO}_2 = 1.0 \text{ mmol/l}$

What is the required dosing with sodium hydroxide for softening down to $\text{Ca}^{2+} = 1.0 \text{ mmol/l}$ and what is the final water composition?

The content of Ca^{2+} has to be lowered with $2.0 - 1.0 = 1.0 \text{ mmol/l}$, for which 1.0 mmol/l NaOH is needed, then $1.0 \text{ mmol/l HCO}_3^-$ is removed and $1.0 \text{ mmol/l CaCO}_3$ is formed.

The amount of CO_2 that has to be removed can be calculated assuming that $x \text{ mol NaOH}$ is dosed, then $x \text{ mol CO}_2$ is removed and $x \text{ mol HCO}_3^-$ is formed.

From $K = [\text{Ca}^{2+}] [\text{HCO}_3^-]^2 / [\text{CO}_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

$(1.0) (4.0 - 1.0 + x)^2 / (1.0 - x) \cdot 10^{-6} = 10^{-4.33}$, so $x = 0.71 \text{ mmol/l}$

Therefore $1.0 + 0.71 = 1.71 \text{ mmol/l NaOH}$ is needed, that is $(1.71 \cdot 40 =) 68 \text{ g/m}^3$.

The production of 1 million m^3 per year corresponds to 68 tons NaOH (100%) per year.

$1.0 \text{ mmol/l CaCO}_3$ is formed, that is $(1.0 \cdot 100 =) 100 \text{ g/m}^3$.

A production of 1 million m^3 per year corresponds to 100 tons CaCO_3 per year.

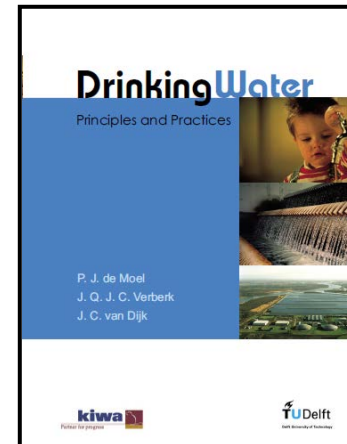
After softening:

$\text{Ca}^{2+} = 1.00 \text{ mmol/l}$, $\text{HCO}_3^- = 3.71 \text{ mmol/l}$, $\text{CO}_2 = 0.29 \text{ mmol/l}$, $\text{Na}^+ = \text{Na}^+_0 + 1.71 \text{ mmol/l}$, $\text{pH} = \text{pH}_s$ (equilibrium)

From $\text{pH}_s = \text{pK}_2 - \text{pKs} - \log\{ [\text{Ca}^{2+}] [\text{HCO}_3^-] \}$ results :

$\text{pH}_s = 10.49 - 8.36 - \log\{ [1.00 \cdot 10^{-3}] [3.71 \cdot 10^{-3}] \} = 2.13 + 5.43 = 7.56$

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 HCO₃
 - CO₂ = 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

Module Chemical softening
Softening with alkaine chemicals

Phreeqc: input for all stimuli dat parameters, for aerobic and anaerobic water

Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8 *Assumption: mg/L, mmol/kgw, mmol/gw*

Sample description		10.0	7.02
Basic data			
Temperature	t °C	10.0	
Oxygen	O2 mg/L		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 1°C)	EC mS/cm		
Total dissolved solids (residue)	TDS mg/L		0 µS/cm
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 (part)	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	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			
Alkaine 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. cemptp
Silvite	SI FeCO3		(no precip.)
Phosphorite	SI MnCO3		
Hydroxapatite	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:

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alkali chemicals

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

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8 *Assumption: mg/L, mmol/kg, cmol/kg*

Parameter	Unit	Value	Unit
Temperature	t °C	10.0	
Oxygen	O2 mg/L	11.0	0.34 mmol/kg
pH	pH	7.0	
Methane	CH4 mg/L	0.00	mmol/kg
Sulfide	H2S mg/L	0.00	mmol/kg
pe (electron activity)	pe		
Conductivity (measured, at 1 °C)	EC mS/cm	0	µS/cm
Total dissolved solids (residue)	TDS mg/L		
Cations			
Calcium	Ca mg/L	80.0	2.00 mmol/kg
Magnesium	Mg mg/L	0.00	mmol/kg
Sodium	Na mg/L	0.00	mmol/kg
Potassium	K mg/L	0.00	mmol/kg
Iron	Fe mg/L	0.000	mmol/kg
Manganese	Mn mg/L	0.000	mmol/kg
Ammonium (part)	NH4 mg/L	0.000	mmol/kg
Aluminium	Al µg/L	0.00	mmol/kg
Barium	Ba µg/L	0.00	mmol/kg
Cadmium	Cd µg/L	0.00	mmol/kg
Copper	Cu µg/L	0.00	mmol/kg
Lead	Pb µg/L	0.00	mmol/kg
Lithium	Li µg/L	0.00	mmol/kg
Strontium	Sr µg/L	0.00	mmol/kg
Zinc	Zn µg/L	0.00	mmol/kg
Anions			
Hydrogen carbonate (as Alkali)	HCO3 mg/L	244	4.00 mmol/kg
Chloride	Cl mg/L	0.00	mmol/kg
Nitrate	NO3 mg/L	0.00	mmol/kg
Sulfate	SO4 mg/L	0.00	mmol/kg
Fluoride	F mg/L	0.00	mmol/kg
Bromide	Br mg/L	0.00	mmol/kg
Phosphate	PO4 mg/L	0.00	mmol/kg
Nitrite	NO2 mg/L	0.00	mmol/kg
Silicate	Si mg/L	0.00	mmol/kg
Boron	B µg/L	0.00	mmol/kg
Base			
Alkali chemical	formula		e.g. CaCO3, NaOH etc
Dose	mmol/kg		
SI after reaction			
Calcite	SI CaCO3		e.g. 0.89
Dolomite	SI CaMg(CO3)2		e.g. ∞ (no precip.)
Silvite	SI FeCO3		
Rhodochrosite	SI MnCO3		
Hydroxapatite	SI Ca5(PO4)3OH		
Bypass - acid			
Bypass flow	% of total Q		e.g. 15
Acidic chemical	formula		e.g. H2SO4, CO2 etc
Dose	mmol/kg		

Run PHREEQC

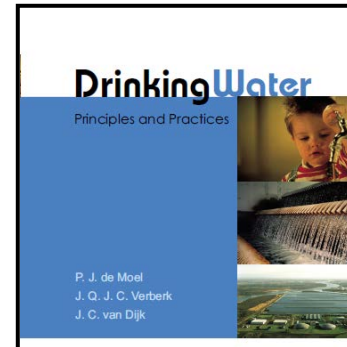
after base after reaction after soft + bypass

Aquatic Chemistry for engineers

Item : Softening by caustic soda - NaOH

Answers:

- Estimate required NaOH dose
 - $\text{NaOH} = \Delta \text{CO}_2 + \Delta \text{Ca}$
 - $\text{NaOH} = 1.0 + 1.0 = 2.0$
 - Clever trial-and-error and $\text{SI} = 0$
 - $\text{NaOH dose} = 1.80 \text{ mmol/kgw}$
- A : pH after softening = 7.67
 - CO_2 after softening = 0.22 mmol/kgw
- B : $\text{NaOH} = 1.80 \text{ mmol/kgw}$
- Book Drinking water P&P:
 - $\text{pH} = 7.56 / \text{NaOH} = 1.71 \text{ mmol/kgw}$
 - Other pK_s , ionic strength, ion pairs



		NaOH		
Base	Alkaline chemical	formula	1.80	E.g. CaCO ₃ , NaOH etc
St after reaction	Dose	mmol/kgw	0.00	e.g. 0.89
	Calcite	SI CaCO ₃		e.g. <empty>
	Dolomite	SI CaMg(CO ₃) ₂		(no precip.)
	Siderite	SI FeCO ₃		
	Rhodochnosite	SI MnCO ₃		
	Hydroxyapatite	SI Ca ₅ (PO ₄) ₃ OH		
Bypass + acid	Bypass flow	% of total Q		E.g. 15
	Acidic chemical	formula		e.g. H ₂ SO ₄ , CO ₂ 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 1°C)	ms/cm	25.4	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	2.00 1.00
	Vapor pressure water	pa	0.01	0.01 0.01
	Density	rho kg/L	1.000	1.000 1.000
Redox conditions	Oxygen	O ₂ 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
	Percentwise error (100*(Cat-Ani)/(Cat+Ani))		-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
	CO ₂	CO ₂ mmol/kgw	1.01	0.02 atm 0.01 0.22
	HCO ₃ ⁻	HCO ₃ mmol/kgw	3.94	240 mg/L 3.75 3.75
	CO ₃ ²⁻	CO ₃ mmol/kgw	0.00	0 mg/L 0.38 0.01
	pH by 0.1 mol 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	7.38	7.45 7.67
	Calcite Precipitation Potential	CPP	-0.32	14 mg/L CO ₂ 1.00 0.00
	Calcite Precipitation Potential at 60 C	CPP-60	0.13	14 mg/L CaCO ₃
	Calcite Precipitation Potential at 90 C	CPP-90	0.56	56 mg/L CaCO ₃



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 - $\text{Ca}(\text{OH})_2$

Softening by dosing lime

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

$\text{Ca}^{2+} = 2.0 \text{ mmol/l}$, $\text{HCO}_3^- = 4.0 \text{ mmol/l}$, $\text{CO}_2 = 1.0 \text{ mmol/l}$

What is the required dosage of lime to soften up to $\text{Ca}^{2+} = 1,0 \text{ mmol/l}$ and what is the water composition?

The content of Ca^{2+} has to be lowered with $2.0 - 1.0 = 1.0 \text{ mmol/l}$, for which $1.0 \text{ mmol/l Ca}(\text{OH})_2$ is needed, then $2.0 \text{ mmol/l HCO}_3^-$ is removed and $2.0 \text{ mmol/l CaCO}_3$ is formed.

The amount of CO_2 that has to be removed can be calculated assuming that $x \text{ mol Ca}(\text{OH})_2$ is dosed, then $x \text{ mol CO}_2$ is removed and $x \text{ mol CaCO}_3$ is formed.

From $K = [\text{Ca}^{2+}] [\text{HCO}_3^-]^2 / [\text{CO}_2] = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

$(1.0) (4.0 - 2.0)^2 / (1.0 - x) \cdot 10^{-8} = 10^{-4.33}$ so that $x = 0.91 \text{ mmol/l}$

And thus $1.0 + 0.91 = 1.91 \text{ mmol/l Ca}(\text{OH})_2$ is needed, that is $(1.91 \cdot 77 =) 147 \text{ g/m}^3$.

The production of 1 million m^3 per year corresponds to 147 tons $\text{Ca}(\text{OH})_2$ per year.

$2.0 + 0.91 \text{ mmol/l CaCO}_3$ is formed, that is $(2.91 \cdot 100 =) 291 \text{ g/m}^3$.

The production of 1 million m^3 per year corresponds to 291 tons CaCO_3 per year.

After softening:

$\text{Ca}^{2+} = 1.00 \text{ mmol/l}$, $\text{HCO}_3^- = 2.00 \text{ mmol/l}$, $\text{CO}_2 = 0.09 \text{ mmol/l}$, $\text{pH} = \text{pH}_s$ (equilibrium)

From $\text{pH}_s = \text{pK}_2 - \text{pK}_s - \log\{ [\text{Ca}^{2+}] [\text{HCO}_3^-] \}$ results:

$\text{pH}_s = 10.49 - 8.36 - \log\{ [1.00 \cdot 10^{-3}] [2.00 \cdot 10^{-3}] \} = 2.13 + 5.70 = 7.83$

With this pH it is permissible to neglect the formation of OH^- .

DrinkingWater

Principles and Practices

P. J. de Moel
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kiwa

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Aquatic Chemistry for engineers

Item : Softening by (hydrated) lime - $\text{Ca}(\text{OH})_2$

- Raw groundwater
 - $\text{Ca} = 2.0 \text{ mmol/kgw} = 80 \text{ mg/L}$
 - $\text{Alk} = 4.0 \text{ meq/kgw} = 244 \text{ mg/L HCO}_3^-$
 - $\text{CO}_2 = 1.0 \text{ mmol/kgw}$
 - $\text{pH} = 7.02$
- Calculate:
 - A: $\text{Ca}(\text{OH})_2$ for $\text{Ca} = 1.0 \text{ mmol/kgw}$
 - B: pH after softening
 - Hint: assume SI calcite = 0

- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alk-ine chemicals

Phreeqc Input for all streams, dat parameters, for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 - 4.8 Assumption: mg/L, mmol/kg, mmol/gw

Basic data	Parameter	Value	Unit
Temperature	t	10.0	°C
Oxygen	O2	11.0	mg/L
pH	pH	7.02	
Methane	CH4	0.00	mmol/kgw
Sulfite	H2S	0.00	mmol/kgw
pe (electron activity)	pe		
Conductivity (measured, at 1°C)	EC	0	µS/cm
Total dissolved solids (residue)	TDS		mg/L
Cations		80.0	
Calcium	Ca	2.00	mmol/kgw
Magnesium	Mg	0.00	mmol/kgw
Sodium	Na	0.00	mmol/kgw
Potassium	K	0.00	mmol/kgw
Iron	Fe	0.00	mmol/kgw
Manganese	Mn	0.00	mmol/kgw
Ammonium (free)	NH4	0.00	mmol/kgw
Aluminum	Al	0.00	mmol/kgw
Barium	Ba	0.00	mmol/kgw
Cadmium	Cd	0.00	mmol/kgw
Copper	Cu	0.00	mmol/kgw
Lead	Pb	0.00	mmol/kgw
Lithium	Li	0.00	mmol/kgw
Strontium	Sr	0.00	mmol/kgw
Zinc	Zn	0.00	mmol/kgw
Anions		244	
Hydrogen carbonate (as Alkalinity)	HCO3	4.00	mmol/kgw
Chloride	Cl	0.00	mmol/kgw
Nitrate	NO3	0.00	mmol/kgw
Sulfate	SO4	0.00	mmol/kgw
Fluoride	F	0.00	mmol/kgw
Bromide	Br	0.00	mmol/kgw
Phosphate	PO4	0.00	mmol/kgw
Nitrite	NO2	0.00	mmol/kgw
Silicate	Si	0.00	mmol/kgw
Boron	B	0.00	mmol/kgw
Base	Alk-ine chemical formula	0.00	e.g. CaCO3, NaOH etc
SI after reaction	Dose	0.00	e.g. 0.89
	Calcite		e.g. calcite (no precip.)
	Dolomite		
	Siderite		
	Rhodochrosite		
	Hydroxapatite		
Bypass - acid	Bypass flow		e.g. 0.0
	Acidic chemical formula		e.g. H2SO4, CO2 etc

Run PHREEQC after base after reaction after acid + bypass

Aquatic Chemistry for engineers

Item : Softening by (hydrated) lime - $\text{Ca}(\text{OH})_2$

Answers:

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alkali-chemicals

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

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8 Assumption:
mg/L, mmol/kg, mmol/gw

Basic data	Parameter	Unit	Value	Unit	Value
	Temperature	t	10.0	°C	
	Oxygen	O2	11.0	mg/L	0.34 mmol/kg
	pH	pH	7.02		
	Methane	CH4		mg/L	0.00 mmol/kg
	Sulfide	H2S		mg/L	0.00 mmol/kg
	pe (electron activity)	pe			
	Conductivity (measured, at 1°C)	EC		mS/m	0 µS/cm
	Total dissolved solids (residue)	TDS		mg/L	
Cations	Calcium	Ca	80.0	mg/L	2.00 mmol/kg
	Magnesium	Mg		mg/L	0.00 mmol/kg
	Sodium	Na		mg/L	0.00 mmol/kg
	Potassium	K		mg/L	0.00 mmol/kg
	Iron	Fe		mg/L	0.000 mmol/kg
	Manganese	Mn		mg/L	0.000 mmol/kg
	Ammonium (free)	NH4		mg/L	0.000 mmol/kg
	Aluminum	Al		µg/L	0.00 mmol/kg
	Barium	Ba		µg/L	0.00 mmol/kg
	Cadmium	Cd		µg/L	0.00 mmol/kg
	Copper	Cu		µg/L	0.00 mmol/kg
	Lead	Pb		µg/L	0.00 mmol/kg
	Lithium	Li		µg/L	0.00 mmol/kg
	Strontium	Sr		µg/L	0.00 mmol/kg
Zinc	Zn		µg/L	0.00 mmol/kg	
Anions	Hydrogen carbonate (as Alkalinity)	HCO3	244	mg/L	4.00 mmol/kg
	Chloride	Cl		mg/L	0.00 mmol/kg
	Nitrate	NO3		mg/L	0.00 mmol/kg
	Sulfate	SO4		mg/L	0.00 mmol/kg
	Fluoride	F		mg/L	0.00 mmol/kg
	Bromide	Br		mg/L	0.00 mmol/kg
	Phosphate	PO4		mg/L	0.00 mmol/kg
	Nitrite	NO2		mg/L	0.00 mmol/kg
	Silicate	Si		mg/L	0.00 mmol/kg
	Boron	B		µg/L	0.00 mmol/kg
	Base	Alkali-chemical	formula	$\text{Ca}(\text{OH})_2$	
Dose				mmol/kg	
SI after reaction	Calcite	SI	0.00	mmol/kg	e.g. 0.89
	Dolomite	SI		mmol/kg	e.g. <empty>
	Siderite	SI		mmol/kg	(no precip.)
	Rhodochrosite	SI		mmol/kg	
	Hydroxapatite	SI		mmol/kg	
Bypass - acid	Bypass flow			% of total Q	e.g. 15
	Acidic chemical	formula		mmol/kg	e.g. H2SO4, CO2 etc

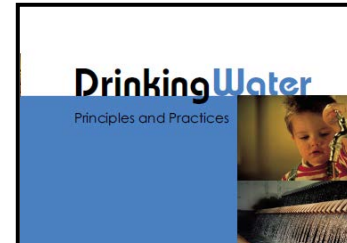
Run PHREEQC after base after reaction after acid + bypass

Aquatic Chemistry for engineers

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

Answers:

- Estimate required Ca(OH)_2 dose
 - $\text{Ca(OH)}_2 = \Delta \text{CO}_2 + \Delta \text{Ca}$
 - $\text{Ca(OH)}_2 = 1.0 + 1.0 = 2.0$
 - Clever trial-and-error and $\text{SI} = 0$
 - Ca(OH)_2 dose = 1.95 mmol/kgw
- A : pH after softening = 7.92
 - CO_2 after softening = 0.07 mmol/kgw
- B : $\text{Ca(OH)}_2 = 1.95$ mmol/kgw
- Book Drinking water P&P:
 - pH = 7.83 / $\text{Ca(OH)}_2 = 1.91$ mmol/kgw
 - Other pK_s , ionic strength, ion pairs



Base	Alkaline chemical	formula	Ca(OH) ₂	e.g. CaCO ₃ , NaOH etc
SI after reaction	Calcite	SI CaCO ₃	0.00	e.g. 0.89
	Dolomite	SI CaMg(CO ₃) ₂		e.g. empty (no precip.)
	Siderite	SI FeCO ₃		
	Rhodochrosite	SI MnCO ₃		
	Hydroxapatite	SI Ca ₅ (PO ₄) ₃ OH		
Bypass - acid	Excess flow	% of total G		e.g. 10
	Acidic chemical	formula		e.g. H ₂ SO ₄ , CO ₂ etc
	Dose	mmol/kgw		
Run PHREEQC				
Overall parameters	Cations	meq/kgw	3.94	4.45 197
	Anions	meq/kgw	3.94	4.45 198
	Conductivity (calculated, at t °C)	EC mS/m	25.4	254 131
	Total dissolved solids	TDS mg/L	224	n.a. n.a.
	Ionic strength	IS mmol/kgw	5.9	7.8 3.0
	Total hardness	TH mmol/kgw	2.00	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	O ₂ mmol/kgw	0.34	0.34 0.34
	pe (electron activity)	pe	14.94	11.88 14.05
	Redox potential	Eh mV	839	665 788
Correctness checks	Charge difference	meq/kgw	-0.01	-0.01 -0.01
	Percentage error (100 C _{an} -A _{an} /C _{an} +A _{an})		-0.1%	-0.1% -0.2%
	EC ratio, calculated/measured			
	TDS ratio, measured/calculated			
	Oxygen saturation (with air at sea level)	atm/atm	37.7%	37.8% 37.7%
	pH change by electron balancing (PHreeqc)		0.00	
	pe change by electron balancing (PHreeqc)			
Carbon equilibrium	pH (Hydrogen activity)	pH	7.92	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 2.08
	CO ₂	CO ₂ mmol/kgw	1.01	0.02 atm 0.00 0.07
	HCO ₃ ⁻	HCO ₃ ⁻ mmol/kgw	3.94	240 mg/L 2.10 1.97
	CO ₃ ²⁻	CO ₃ ²⁻ mmol/kgw	0.00	0 mg/L 0.14 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	-0.34	2.51 0.00
	Equilibrium-pH (pHs or pH-Langelier)	pH-L	7.26	7.80 7.92
	Calcite Precipitation Potential	CPP	-0.32	2.95 0.00
	Calcite Precipitation Potential at 60 °C	CPP-60	0.13	
	Calcite Precipitation Potential at 80 °C	CPP-80	0.56	
Other scaling solids	Aragonite	SI CaCO ₃	-0.50	2.35 -0.16
	Gypsum	SI CaSO ₄ ·2H ₂ O		
	Anhydrite	SI CaSO ₄		
	Dolomite	SI CaMg(CO ₃) ₂		
	Hydroxapatite	SI Ca ₅ (PO ₄) ₃ OH		
Redox scaling solids	Pyrite	SI FeS		
	Siderite	SI FeCO ₃		
	Hematite	SI Fe ₂ O ₃		
	Rhodochrosite	SI MnCO ₃		
	Uvanite	SI Fe ₃ (PO ₄) ₂ ·8H ₂ O		
Elements / Species	C	mmol/kgw	5.01	5.01 2.08



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)2·8H2O
    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

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

Base	Alkaline chemical	formula	mmol/kgw	Ca(OH) ₂	1.95	e.g. CaCO ₃ , NaOH etc
SI after reaction	Calcite	SI	CaCO ₃	0.00	e.g. 0.89	(no precip.)
	Dolomite	SI	CaMg(CO ₃) ₂			
	Siderite	SI	FeCO ₃			
	Rhodochrosite	SI	MnCO ₃			
	Hydroxapatite	SI	Ca ₅ (PO ₄) ₃ OH			
Bypass - acid	Bypass flow		% of total Q		15	e.g. H ₂ SO ₄ , CO ₂ etc
	Acidic chemical	formula	mmol/kgw			
	Dose					
Run PHREEQC						
						after base
						after reaction
Overall parameters	Cations	meq/kgw	3.94			4.45
	Anions	meq/kgw	3.94			4.45
	Conductivity (calculated, at 25°C)	DS/m	25.4	254 µS/cm		31.8
	Total dissolved solids	mg/L	324			n.a.
	Ionic strength	IS	6.9			7.8
	Total hardness	TH	2.00	112 °D		3.95
	Vapor pressure water	pa	0.01			0.01
	Density	rho	1.000			1.000
Redox conditions	Oxygen	O ₂	0.34			0.34
	pe (electron activity)	pe	14.94			11.85
	Redox potential	Eh	833			665
Correctness checks	Charge difference	meq/kgw	-0.01			-0.01
	Percentage error (100*(Ca+An)/(Cat+An))		-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%
	pH change by electron balancing (PHeaq)		0.00			-
	pe change by electron balancing (PHeq)		-			-
Carbon equilibrium	pH (hydrogen activity)	pH	7.02			10.30
	Alkalinity	m	4.00			7.90
	Total Inorganic Carbon (TIC)	TIC	5.01	60 mg/L C		5.01
	CO ₂	CO ₂	1.01	0.02 atm		0.00
	HCO ₃ ⁻	HCO ₃ ⁻	3.94	240 mg/L		2.13
	CO ₃ ²⁻	CO ₃ ²⁻	0.00	0 mg/L		1.14
	d(pH) by 0.1 mmol HCl/kgw	pH	-0.05			-
	Buffer capacity	BI	1.88			-
Calcite equilibrium	SI (calcite)	SI-c	-0.34			2.51
	Equilibrium pH (pH ₀ or pH _L -Langlier)	pH-L	7.25			7.50
	Calcite Precipitation Potential	CPP	-0.32	14 mg/L CO ₂		2.95
	Calcite Precipitation Potential at 60 C	CPP-60	0.13	14 mg/L CaCO ₃		0.00
	Calcite Precipitation Potential at 80 C	CPP-80	0.55	56 mg/L CaCO ₃		-
Other scaling solids	Aragonite	SI	CaCO ₃	-0.60		2.35
	Gypsum	SI	CaSO ₄ ·2H ₂ O	-		-
	Anhydrite	SI	CaSO ₄	-		-
	Dolomite	SI	CaMg(CO ₃) ₂	-		-
	Hydroxapatite	SI	Ca ₅ (PO ₄) ₃ OH	-		-
Redox scaling solids	Pyrite	SI	FeS	-		-
	Siderite	SI	FeCO ₃	-		-
	Hematite	SI	Fe ₂ O ₃	-		-
	Rhodochrosite	SI	MnCO ₃	-		-
	Vivianite	SI	Fe ₃ (PO ₄) ₂ ·8H ₂ O	-		-
Elemental / Species	C		6.01			6.01
						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:

$\text{Ca}^{2+} = 2.0 \text{ mmol/l}$, $\text{Mg}^{2+} = 0.2 \text{ mmol/l}$, $\text{HCO}_3^- = 4.0 \text{ mmol/l}$, $\text{CO}_2 = 1.0 \text{ mmol/l}$

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 $(1.0 - 0.2 =) 0.8 \text{ mmol/l}$ (content of Mg remains equal).

In the pellet reactor softening down to $\text{Ca}^{2+} = 0.5 \text{ mmol/l}$ (on condition that $[\text{HCO}_3^-]$ softened $> 1.0 \text{ mmol/l}$)

Assume that a fraction x is softened, then a fraction $(1-x)$ will not be softened.

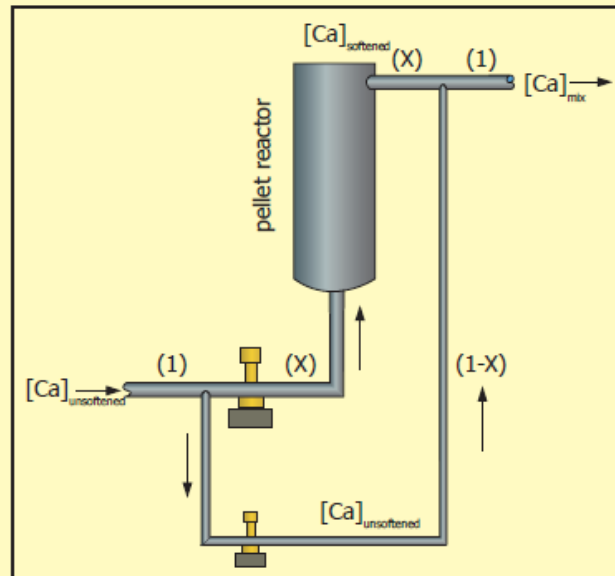
When mixing both flows, the following Ca-balance applies:

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

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

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

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



DrinkingWater

Principles and Practices

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kiwa

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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 HCO₃
 - CO₂ = 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

Threeq: *input for all stimuli, det parameters, for aerobic and anaerobic water*

Sample description: **Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8** Assumption: mg/L, mmol/kgw, mmol/kgw

Basic data	Parameter	Unit	Value	Unit	Value
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 1°C)	EC	µS/cm			0 µS/cm
Total dissolved solids (residue)	TDS	mg/L			
Cations	Ca	mg/L	80.0		2.00 mmol/kgw
	Mg	mg/L	4.90		0.20 mmol/kgw
	Na	mg/L			0.00 mmol/kgw
	K	mg/L			0.00 mmol/kgw
	Fe	mg/L			0.000 mmol/kgw
	Mn	mg/L			0.000 mmol/kgw
	NH4	mg/L			0.000 mmol/kgw
	Al	µg/L			0.00 mmol/kgw
	Ba	µg/L			0.00 mmol/kgw
	Cd	µg/L			0.00 mmol/kgw
	Cu	µg/L			0.00 mmol/kgw
	Pb	µg/L			0.00 mmol/kgw
	Li	µg/L			0.00 mmol/kgw
	Sr	µg/L			0.00 mmol/kgw
	Zn	µg/L			0.00 mmol/kgw
Anions	HCO3	mg/L	244		4.00 mmol/kgw
	Cl	mg/L			0.00 mmol/kgw
	NO3	mg/L			0.00 mmol/kgw
	SO4	mg/L			0.00 mmol/kgw
	F	mg/L			0.00 mmol/kgw
	Br	mg/L			0.00 mmol/kgw
	PO4	mg/L			0.00 mmol/kgw
	NO2	mg/L			0.00 mmol/kgw
	Si	mg/L			0.00 mmol/kgw
	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. <empt>
	Siderite	SI	FeCO3		(no precip.)
	Rhodochrosite	SI	MnCO3		
	Hydroxapatite	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:

AQUATIC CHEMISTRY for Engineers

Module Chemical softening
Softening with alkaline chemicals

Phreeqc: input for all stimuli, det parameters, for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater par. 4.7 + 4.8 *Assumption: mg/L = mg/kg = mmol/kg*

Basic data	Parameter	Unit	Value	Unit	Value
Temperature	t	°C	10.0		
Oxygen	O2	mg/L	11.0	0.34	mmol/kg
pH	pH		7.82		
Methane	CH4	mg/L			0.00 mmol/kg
Sulfide	H2S	mg/L			0.00 mmol/kg
pE (electron activity)	pE				
Conductivity (measured at 1°C)	EC	µS/cm			0 µS/cm
Total dissolved solids (residue)	TDS	mg/L			
Cations					
Calcium	Ca	mg/L	80.0	2.00	mmol/kg
Magnesium	Mg	mg/L	4.90	0.20	mmol/kg
Sodium	Na	mg/L			0.00 mmol/kg
Potassium	K	mg/L			0.00 mmol/kg
Iron	Fe	mg/L			0.000 mmol/kg
Manganese	Mn	mg/L			0.000 mmol/kg
Ammonium (inert)	NH4	mg/L			0.000 mmol/kg
Aluminium	Al	µg/L			0.00 mmol/kg
Barium	Ba	µg/L			0.00 mmol/kg
Cadmium	Cd	µg/L			0.00 mmol/kg
Copper	Cu	µg/L			0.00 mmol/kg
Lead	Pb	µg/L			0.00 mmol/kg
Lithium	Li	µg/L			0.00 mmol/kg
Strontium	Sr	µg/L			0.00 mmol/kg
Zinc	Zn	µg/L			0.00 mmol/kg
Anions					
Hydrogen carbonate (as Alkalinity)	HCO3	mg/L	244	4.00	mmol/kg
Chloride	Cl	mg/L			0.00 mmol/kg
Nitrate	NO3	mg/L			0.00 mmol/kg
Sulfate	SO4	mg/L			0.00 mmol/kg
Fluoride	F	mg/L			0.00 mmol/kg
Bromide	Br	mg/L			0.00 mmol/kg
Phosphate	PO4	mg/L			0.00 mmol/kg
Nitrite	NO2	mg/L			0.00 mmol/kg
Silicate	Si	mg/L			0.00 mmol/kg
Boron	B	µg/L			0.00 mmol/kg
Base	Alkaline chemical	formula	Ca(OH)2		e.g. CaCO3, NaOH etc
SI after reaction	Dose	mmol/kg	0.00		
	Calcite	SI	CaCO3	e.g.	0.89
	Dolomite	SI	CaMg(CO3)2	e.g.	< empty (no precip.)
	Siderite	SI	FeCO3		
	Rhodochrosite	SI	MnCO3		
	Hydroxapatite	SI	Ca5(PO4)3OH		
Bypass + acid	Bypass flow	% of total Q		e.g.	15
	Acidic chemical	formula		e.g.	H2SO4, CO2 etc
	Dose	mmol/kg			

Run PHREEQC

after base
 after reaction
 after acid + bypass

Aquatic Chemistry for engineers

Item : Split treatment for softening

Answers:

- Estimate required $\text{Ca}(\text{OH})_2$ dose
 - $\text{Ca}(\text{OH})_2 = \Delta \text{CO}_2 + \Delta \text{Ca}$
 - $\text{Ca}(\text{OH})_2 = 1.0 + 1.5 = 2.5$
 - Clever trial-and-error and $\text{SI} = 0$
 - $\text{Ca}(\text{OH})_2$ dose = 2.51 mmol/kgw
- A : pH after softening = 8.50
 - CO_2 after softening = 0.01 mmol/kgw
 - $\text{Ca}(\text{OH})_2 = 2.51$ mmol/kgw
- B : Bypass = 20%
- Book Drinking water P&P:
 - Same bypass flow / No equilibrium reactions

				DrinkingWater		
				after base	after reaction	after acid + bypass
Base	Alkaline chemical	formula	mmol/kgw			
SI after reaction	Dose	CaCO_3	2.51			
	Calcite	SI	0.00			
	Dolomite	SI	$\text{CaMg}(\text{CO}_3)_2$			
	Siderite	SI	FeCO_3			
	Rhodochrosite	SI	MnCO_3			
Bypass + acid	Hydrogarnite	SI	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$			
	Dose	mmol/kgw	20			
	Acidic chemical	formula	mmol/kgw			
	Dose	mmol/kgw				
Run PHREEQC						
Overall parameters	Cations	meq/kgw	4.33	4.70	1.38	1.99
	Anions	meq/kgw	3.94	4.30	0.89	1.59
	Conductivity (calculated, at 1°C)	ms/cm	25.5	33.7	6.0	11.9
	Total dissolved solids	TDS mg/L	329	n.a.	n.a.	n.a.
	Ionic strength	IS mmol/kgw	6.3	8.4	1.9	2.9
	Total hardness	TH mmol/kgw	2.21	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
	Diphen	D2	0.34	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* C-A /(C+A))		4.8%	4.4%	16.7%	11%
	EC ratio, calculated/measured					
	TDS ratio, measured/calculated					
	Diphen saturation (with all ions level)	SI	97.8%	97.8%	97.7%	97.7%
Carbon equilibrium	pH (Hydrogen activity)	pH	7.02	10.62	8.50	7.35
	Alkalinity	m	4.00	3.02	1.01	1.81
	Total Inorganic Carbon (TIC)	TIC mmol/kgw	5.00	5.00	1.00	1.80
	CO_2	CO_2 mmol/kgw	1.01	0.02	0.01	0.19
	HCO_3^-	HCO_3^- mmol/kgw	3.93	240	1.09	0.96
	CO_3^{2-}	CO_3^{2-} mmol/kgw	0.00	0	1.95	0.01
	pH by 0.1 mmol HCl / kgw	pH	6.05			6.21
	Buffer capacity	BI	0.05			0.42
	Si(saline)	SIe	-0.25		2.63	0.00
	Equilibrium-pH (pHs or pH-Langelier)	pHL	1.87		7.99	8.50
Calcite Precipitation Potential	CPP	-0.33		4.01	0.00	
Calcite Precipitation Potential at 50 C	CPP-60	0.13		13	-0.07	
Calcite Precipitation Potential at 90 C	CPP-90	0.55		55	0.04	
Other scaling solids	Zirconite	SI	CaCO_3	-0.50	2.48	-0.16
	Gypsum	SI	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	-	-	-
	Aringite	SI	CaSO_4	-	-	-
	Dolomite	SI	$\text{CaMg}(\text{CO}_3)_2$	-1.79	3.92	-0.49
	Hydrogarnite	SI	$\text{Ca}_5(\text{PO}_4)_3\text{OH}$	-	-	-
Redox scaling solids	Pyrite	SI	FeS	-	-	-
	Siderite	SI	FeCO_3	-	-	-
	Hematite	SI	Fe_2O_3	-	-	-
	Rhodochrosite	SI	MnCO_3	-	-	-
	Vivianite	SI	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	-	-	-
Elements / Species	C	mmol/kgw	5.00	5.00	1.00	1.80
	CO_2		20.1%	0.0%	0.8%	10.8%
	HCO_3^-		78.8%	21.8%	96.8%	88.4%
	CO_3^{2-}		0.0%	0.0%	0.0%	0.0%
	CH ₄		0.0%	0.0%	0.0%	0.0%
	Ca	mmol/kgw	2.00	4.51	0.50	0.80
	Ca ₂		97.3%	49.1%	99.2%	98.7%
	CaHCO_3^+		2.8%	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 - $\text{CaMg}(\text{CO}_3)_2 = \text{CaCO}_3.\text{MgCO}_3$
 - after $\text{Ca}(\text{OH})_2 = +3.92$ (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. CaCO ₃ , NaOH etc
Dose	mmol/kgw		2.81	
SI after reaction	SI	CaCO ₃	0.00	e.g. 0.89 emptyp (no precip.)
Dolomite	SI	CaMgCO ₃ 2		
Siderite	SI	FeCO ₃		
Rhodochrosite	SI	MnCO ₃		
Hydrogaganite	SI	Ca ₈ (PO ₄) ₃ OH		
Bypass + acid		% of total D	20	e.g. 15 e.g. H ₂ SO ₄ , CO ₂ etc
Bypass flow	mmol/kgw			
Acidic chemical	formula			
Dose	mmol/kgw			

	Pur PHREEQC	after base	after reaction	after acid + bypass
Overall parameters				
Cations	meq/kgw	4.33	4.70	1.38
Anions	meq/kgw	3.94	4.30	0.99
Conductivity (calculated, at 25°C)	EC	28.5	33.8	8.0
Total dissolved solids	TDS	329	n.a.	n.a.
Ionic strength	IS	6.3	8.4	2.8
Total hardness	TH	2.20	4.71	0.70
Vapor pressure water	pa	0.01	0.01	0.01
Density	rho	1.000	1.000	1.000
Redox conditions				
Oxygen	O ₂	0.34	0.34	0.34
pe (electron activity)	pe	14.94	11.44	13.46
Redox potential	Eh	339	262	300
Correctness checks				
Charge difference	meq/kgw	0.40	0.40	0.40
Percentage error (100* C _{an} -A _{an} /(C _{an} +A _{an}))		4.8%	4.4%	16.7%
EC ratio, calculated/measured		-	-	-
TDS ratio, measured/calculated		37.8%	37.8%	37.7%
Oxygen saturation level, as at sea level	atm*atm	0.00	0.00	0.00
pH change by electron balancing (Pfreeeq)		-	-	-
pH change by electron balancing (Pfreeeq)		-	-	-
Carbon equilibrium				
pH (hydrogen activity)	pH	7.02	10.52	8.50
Alkalinity	m	4.00	9.02	1.01
Total Inorganic Carbon (TIC)	TIC	5.00	5.00	1.00
CO ₂	CO ₂	1.01	0.02	0.01
HCO ₃ ⁻	HCO ₃ ⁻	3.93	240	0.96
CO ₃ ²⁻	CO ₃ ²⁻	0.00	0	0.00
gH by 10 mmol HCl / kgw	pH	-0.05	1.55	0.01
Buffer capacity	SI	187	-	-0.21
Calcite equilibrium				
SI (calcite)	SIc	-0.35	2.63	0.00
Equilibrium-pH (pHs or pH-Langelier)	pHLL	7.37	7.89	8.50
Calcite Precipitation Potential	CPP	-0.33	4.01	0.00
Calcite Precipitation Potential at 50 C	CPP-50	0.13	14	0.01
Calcite Precipitation Potential at 30 C	CPP-30	0.55	55	0.04
Other scaling solids				
Aragonite	SI	CaCO ₃	-0.50	2.48
Gypsum	SI	CaSO ₄ ·2H ₂ O	-	-
Anhydrite	SI	CaSO ₄	-	-
Dolomite	SI	CaMgCO ₃ 2	-1.79	3.92
Hydrogaganite	SI	Ca ₈ (PO ₄) ₃ OH	-	-0.49
Redox scaling solids				
Pyrite	SI	FeS	-	-
Siderite	SI	FeCO ₃	-	-
Hematite	SI	Fe ₂ O ₃	-	-
Rhodochrosite	SI	MnCO ₃	-	-
Vivianite	SI	Fe ₃ (PO ₄) ₂ ·8H ₂ O	-	-
Elements / Species				
C	mmol/kgw	5.00	5.00	1.00
CO ₂	mmol/kgw	20.1%	0.0%	0.8%
HCO ₃ ⁻	mmol/kgw	78.6%	21.9%	98.8%
CO ₃ ²⁻	mmol/kgw	0.0%	31.1%	1.2%
CH ₄	mmol/kgw	0.00	0.00	0.00
Ca	mmol/kgw	37.3%	49.1%	99.2%
Ca ₂	mmol/kgw	0.00	0.00	0.00
CaHCO ₃ ⁺	mmol/kgw	2.8%	0.3%	0.7%

Questions?



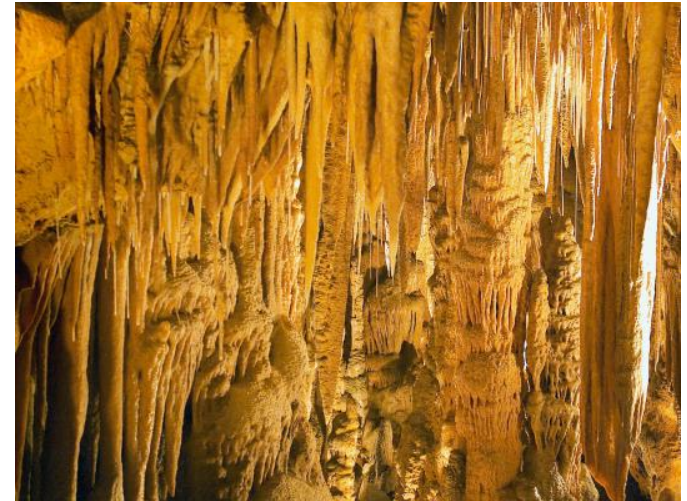
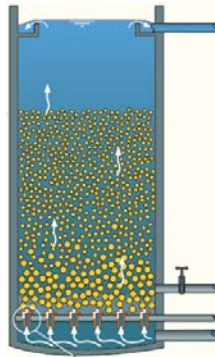
Aquatic Chemistry for engineers

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

- Dissolution of calcite
 - Limestone filtration



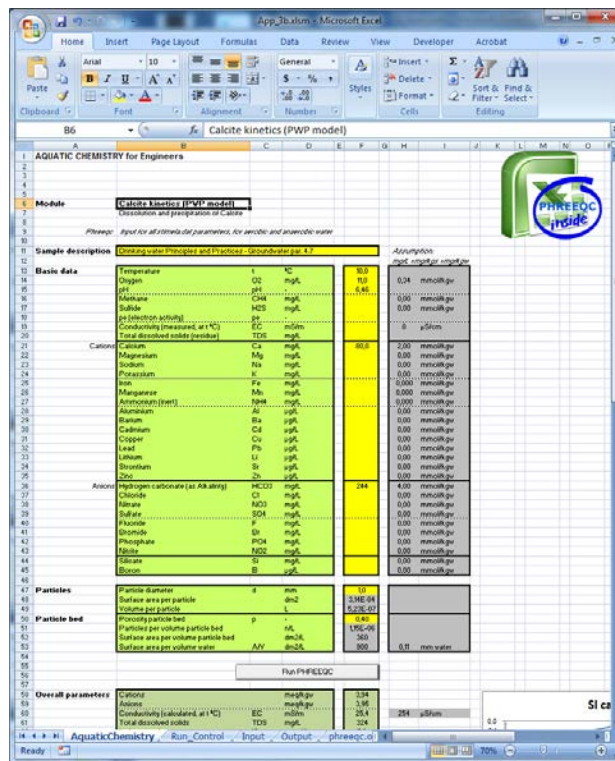
- Precipitation of calcite
 - Softening



- 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 – CaCO₃

Neutralization by limestone filtration

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

Ca²⁺ = 2.0 mmol/l, HCO₃⁻ = 4.0 mmol/l, pH = 6.46, CO₂ = 4.0 mmol/l

What is the pH in equilibrium after limestone filtration and how much CaCO₃ is required?

When x mol CaCO₃ reacts, then x mol CO₂ is removed and x mol Ca²⁺ and 2x mol HCO₃⁻ are formed.

From $K = \frac{[\text{Ca}^{2+}] \cdot [\text{HCO}_3^-]^2}{[\text{CO}_2]} = 10^{-(8.36+6.46-10.49)} = 10^{-4.33}$ results:

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

Thus in equilibrium is:

Ca²⁺ = 3.20 mmol/l, HCO₃⁻ = 6.40 mmol/l, CO₂ = 2.80 mmol/l.

From $\text{pH}_s = \text{pK}_2 - \text{pK}_s - \log\{[\text{Ca}^{2+}][\text{HCO}_3^-]\}$ results:

$$\text{pH}_s = 10.49 - 8.36 - \log\{[3.20 \cdot 10^{-3}][6.40 \cdot 10^{-3}]\} = 2.13 + 4.69 = 6.82$$

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

During filtration 1.20 mmol/l CO₂ is transformed and 1.20 mmol/l CaCO₃ is consumed, that is (1.20 · 100 =) 120 g/m³.

A production of 1 million m³ per year corresponds to 120 tons per year.

DrinkingWater

Principles and Practices

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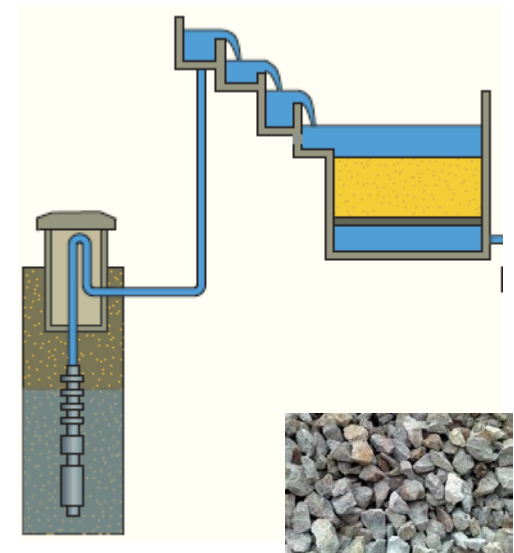
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TU Delft

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)
 - $d\text{Mass} = \text{Rate} \times \text{Area} \times \text{Timestep}$
- Area : $A/V = \text{Area calcite} / \text{volume water}$
 - $A = f$ (diameter particles, sphere)
 - $V = f$ (porosity)
- Limestone filter/contactator
 - Diameter limestone = 1 or 2 mm
 - Porosity = 0.4
 - Empty Bed Contact Time (EBCT) = $1 \text{ m} / 5 \text{ m/h} = 12 \text{ minutes}$
 - Real contact time = $12 * 0.4 = 4.8 \text{ minutes} = 288 \text{ sec}$



Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – CaCO_3

- Raw groundwater
 - $\text{Ca} = 2.0 \text{ mmol/kgw} = 80 \text{ mg/L}$
 - $\text{Alk} = 4.0 \text{ meq/kgw} = 244 \text{ mg/L HCO}_3$
 - $\text{pH} = 6.46$
 - $\text{CO}_2 = 3.68 \text{ mmol/kgw}$ (was 4.0)
 - $\text{Temp} = 10 \text{ }^\circ\text{C}$
- Calculate SI after 300 sec ($p=0.4$):
 - A: for $d = 1 \text{ mm}$
 - B: for $d = 2 \text{ mm}$
- I give you 3 minutes....

AQUATIC CHEMISTRY for Engineers

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

Phreeqc: input for all stimuli.dat parameters, for aerobic and anaerobic water

Sample description Drinking water Principles and Practices - Groundwater, p. 4.7 *Assumption: mg/L = mmol/kgw = meq/kgw*

Basic data	Parameter	Unit	Value	Assumption	
Temperature	T	°C	10.0		
Dissgen	O2	mg/L	11.0	0.24 mmol/kgw	
pH	pH		6.46		
Methane	CH4	mg/L	0.00	0.00 mmol/kgw	
Sulfide	H2S	mg/L	0.00	0.00 mmol/kgw	
pe (electron activity)	pe				
Conductivity (measured, at t °C)	EC	µS/cm			
Total dissolved solids (residue)	TDS	mg/L			
Cations	Calcium	Ca	80.0	2.00 mmol/kgw	
	Magnesium	Mg		0.00 mmol/kgw	
	Sodium	Na		0.00 mmol/kgw	
	Potassium	K		0.00 mmol/kgw	
	Iron	Fe		0.000 mmol/kgw	
	Manganese	Mn		0.000 mmol/kgw	
	Ammonium (inert)	NH4		0.000 mmol/kgw	
	Aluminium	Al		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	244	4.00 mmol/kgw
		Chloride	Cl		0.00 mmol/kgw
Nitrate		NO3		0.00 mmol/kgw	
Sulfate		SO4		0.00 mmol/kgw	
Fluoride		F		0.00 mmol/kgw	
Bromide		Br		0.00 mmol/kgw	
Phosphate		PO4		0.00 mmol/kgw	
Nitrite		NO2		0.00 mmol/kgw	
Silicate		Si		0.00 mmol/kgw	
Boron		B	µg/L	0.00 mmol/kgw	
Particles	Particle diameter	d	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	nL	1.92E-06		
	Surface area per volume particle bed	dm2/L	360		
	Surface area per volume water	AV	900	0.11 mm water	

Run PHREEQC

Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – CaCO₃

Answers:

AQUATIC CHEMISTRY for Engineers

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

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

Sample description Drinking water Principles and Practices - Groundwater, par. 4.7 *Assumption: mg/L = mg/L/g; mmol/kg = mmol/kg*

Basic data	Parameter	Unit	Value	Unit
Cations	Temperature	°C	10.0	
	Dissig	mg/L	11.0	0.24 mmol/kg.g
	pH		6.46	
	Methane	CH4 mg/L	0.00	0.00 mmol/kg.g
	Sulfide	H2S mg/L	0.00	0.00 mmol/kg.g
	pe (electron activity)	pe		
	Conductivity (measured, at 25°C)	EC µmS/cm		0 µS/cm
	Total dissolved solids (residue)	TDS mg/L	80.0	
	Calcium	Ca mg/L		2.00 mmol/kg.g
	Magnesium	Mg mg/L		0.00 mmol/kg.g
Sodium	Na mg/L		0.00 mmol/kg.g	
Potassium	K mg/L		0.00 mmol/kg.g	
Iron	Fe mg/L		0.000 mmol/kg.g	
Manganese	Mn mg/L		0.000 mmol/kg.g	
Ammonium (inert)	NH4 mg/L		0.000 mmol/kg.g	
Aluminium	Al µg/L		0.00 mmol/kg.g	
Barium	Ba µg/L		0.00 mmol/kg.g	
Cadmium	Cd µg/L		0.00 mmol/kg.g	
Copper	Cu µg/L		0.00 mmol/kg.g	
Lead	Pb µg/L		0.00 mmol/kg.g	
Lithium	Li µg/L		0.00 mmol/kg.g	
Strontium	Sr µg/L		0.00 mmol/kg.g	
Zinc	Zn µg/L		0.00 mmol/kg.g	
Anions	Hydrogen carbonate (as Alkalinity)	HCO3 mg/L	244	4.00 mmol/kg.g
	Chloride	Cl mg/L		0.00 mmol/kg.g
	Nitrate	NO3 mg/L		0.00 mmol/kg.g
	Sulfate	SO4 mg/L		0.00 mmol/kg.g
	Fluoride	F mg/L		0.00 mmol/kg.g
	Bromide	Br mg/L		0.00 mmol/kg.g
	Phosphate	PO4 mg/L		0.00 mmol/kg.g
	Nitrite	NO2 mg/L		0.00 mmol/kg.g
	Silicate	Si µg/L		0.00 mmol/kg.g
	Boron	B µg/L		0.00 mmol/kg.g
Particles	Particle diameter	d mm	10	
	Surface area per particle	dm ²	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	1.92E-06	
	Surface area per volume particle bed	dm ² /L	360	
	Surface area per volume water	A/V dm ² /L	900	0.11 mm water

Run PHREEQC

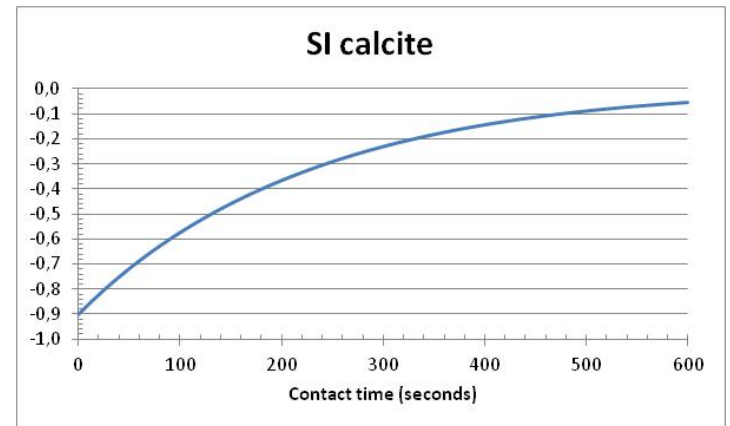
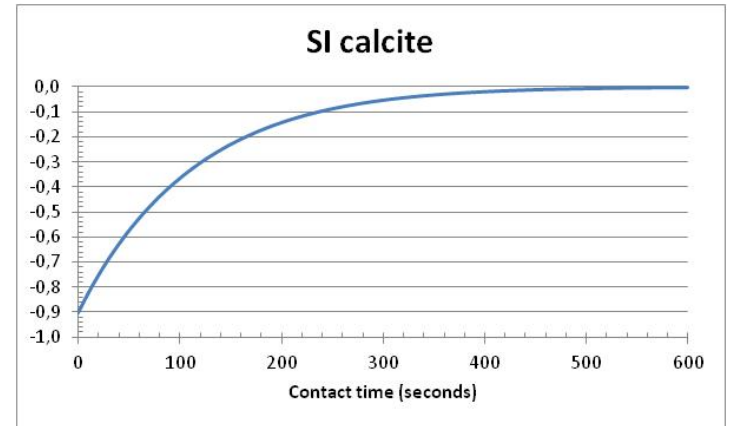


Aquatic Chemistry for engineers

Item : Kinetics of limestone filtration – CaCO_3

Answers:

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





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)

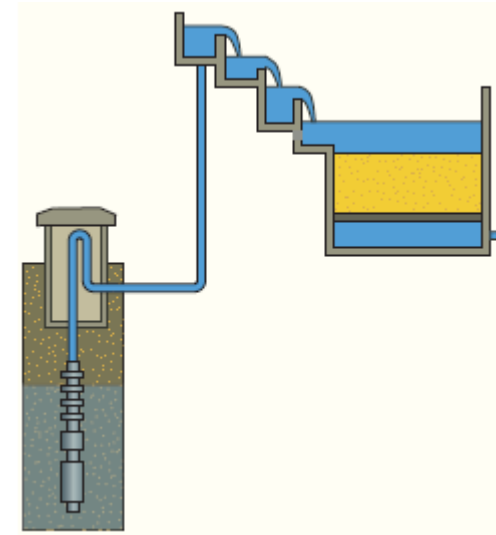
```
# Kinetics Calcite

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