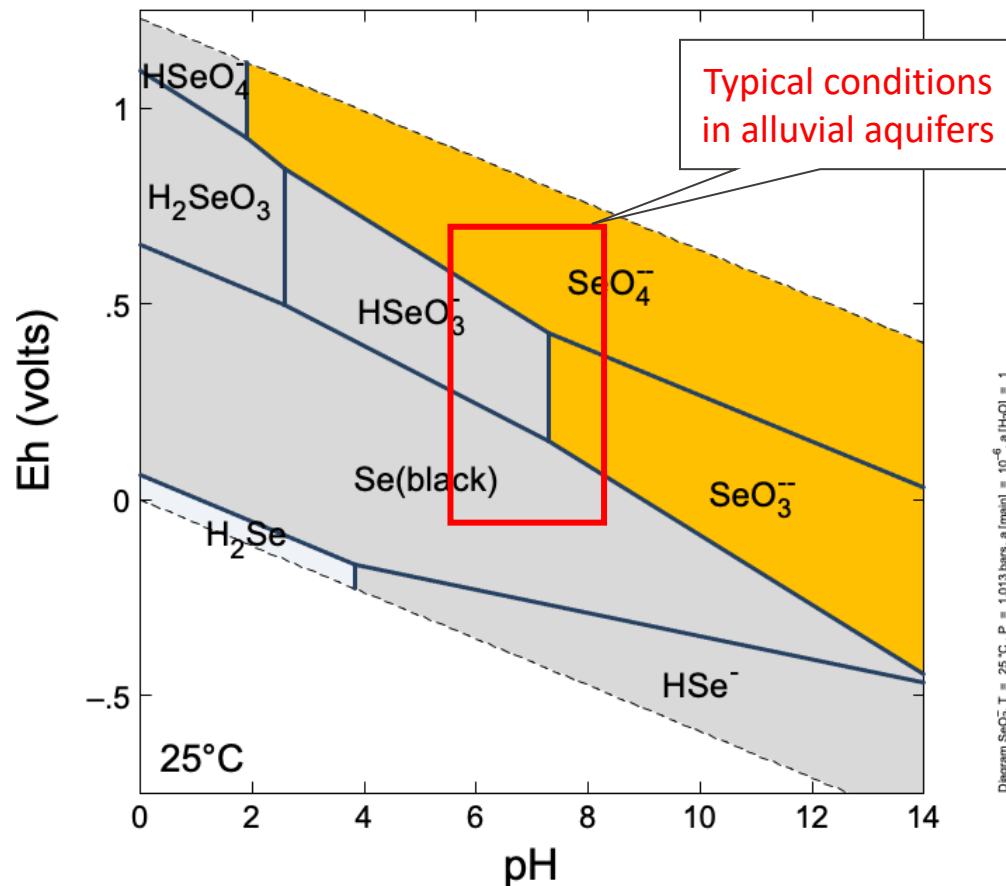


Selenium speciation in alluvial aquifers

- What are typical pe and pH conditions for alluvial aquifers? See red rectangle on the right
- Which species do you expect to be present under those conditions? The species inside the rectangle
- You find Se(0) and organic Se^{2-} under aerated conditions. Why? Due to slow kinetics



Bailey, RT, *Hydrogeol J*, **2017**, 25:1191-1217.

Exercise 1: Hypothetical freshwater



Press the Run button on the Results pane to calculate the equilibrium species distribution in the water. SpecE8 produces as output a dataset “SpecE8_output.txt”. Examine the output file. Do you expect any minerals to precipitate in this water? If so, which ones?

Exercise 1: Solution



Click on View Results on the Results pane to see calculation results in tabular form.

```

Temperature = 25.0 C      Pressure = 1.013 bar
pH = 5.000
Ionic strength      = 0.001990 molal
Charge imbalance    = 0.000062 eq/kg (2.634% error)
Activity of water   = 0.999985
Solvent mass        = 1.0000 kg
Solution mass       = 1.0001 kg
Mineral mass        = 0.0000 kg
Fluid density       = 0.996 g/cm3
  compressibility    = 4.446e-05 /bar
  expansivity       = 0.0002428 /C
  viscosity         = 0.009 poise
Chlorinity          = 0.000423 molal
Dissolved solids    = 114 mg/kg sol'n
Elect. conductivity = 149.73 uS/cm (or umho/cm)
Hardness            = 49.81 mg/kg sol'n as CaCO3
  carbonate         = 1.77 mg/kg sol'n as CaCO3
  non-carbonate     = 48.04 mg/kg sol'n as CaCO3
Carbonate alkalinity = 1.77 mg/kg sol'n as CaCO3
Water type          = Ca-SO4
Bulk volume         = 1.00e+03 cm3
Fluid volume        = 1.00e+03 cm3
Mineral volume      = 0.00 cm3
Inert volume        = 0.00 cm3
Porosity            = 100. %
Permeability        = 98.7 cm2
  
```

Exercise 1: Solution



Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
CO2(aq)	0.0007839	34.49	1.0000	-3.1058
Cl-	0.0004225	14.98	0.9513	-3.3959
Ca++	0.0003563	14.28	0.8252	-3.5317
SO4--	0.0003419	32.84	0.8208	-3.5519
Na+	0.0002172	4.993	0.9520	-3.6845
Mg++	0.0001187	2.884	0.8294	-4.0068
SiO2(aq)	4.994e-05	3.000	1.0005	-4.3014
HCO3-	3.544e-05	2.162	0.9523	-4.4718
K+	2.553e-05	0.9980	0.9513	-4.6147
CaSO4	1.723e-05	2.346	1.0000	-4.7637
H+	1.047e-05	0.01055	0.9550	-5.0000
MgSO4	4.664e-06	0.5613	1.0000	-5.3312
CaCl+	6.220e-07	0.04698	0.9520	-6.2276
NaSO4-	3.011e-07	0.03585	0.9520	-6.5426
HSO4-	2.901e-07	0.02815	0.9520	-6.5589
CaHCO3+	1.736e-07	0.01755	0.9527	-6.7814
MgCl+	5.874e-08	0.003510	0.9520	-7.2524
KSO4-	5.097e-08	0.006888	0.9520	-7.3141
MgHCO3+	3.572e-08	0.003047	0.9520	-7.4685
Al+++	1.357e-08	0.0003661	0.6599	-8.0479
AlOH++	1.265e-08	0.0005564	0.8230	-7.9825
NaHCO3	9.391e-09	0.0007888	1.0000	-8.0273
Al(OH)2+	7.412e-09	0.0004520	0.9520	-8.1515
AlSO4+	2.699e-09	0.0003320	0.9520	-8.5902
NaCl	2.090e-09	0.0001221	1.0000	-8.6798
OH-	1.083e-09	1.842e-05	0.9516	-8.9868
H3SiO4-	8.151e-10	7.751e-05	0.9520	-9.1102
Al(OH)3	6.100e-10	4.758e-05	1.0000	-9.2147
KCl	2.523e-10	1.880e-05	1.0000	-9.5981
CO3--	1.860e-10	1.116e-05	0.8219	-9.8157
CaCO3	7.389e-11	7.395e-06	1.0000	-10.1314
Al(OH)4-	6.557e-11	6.220e-06	0.9520	-10.2047

Exercise 1: Solution



Mineral saturation states	log Q/K		log Q/K
Quartz	-0.3021	Ca(OH)2(c)	-16.1091
Tridymite	-0.4679	Bloedite	-16.2163
Chalcedony	-0.5733	Margarite	-16.4969
Cristobalite	-0.8526	Diopside	-17.1108
Gibbsite	-1.0083	Artinite	-17.4205
Amorph^silica	-1.5878	KNaCO3^6H2O	-18.0936
Diaspore	-1.7997	Clinoptil-Mg	-18.2165
Kaolinite	-2.1279	MgCl2^4H2O	-18.2561
Gypsum	-2.6403	CaCl2^2H2O	-18.4197
Boehmite	-2.6441	MgOHCl	-18.4501
Anhydrite	-2.8184	Spinel	-18.4955
Bassanite	-3.4473	CaCl2^H2O	-18.5545
CaSO4^1/2H2O(beta)	-3.6159	Clinoptil-Na	-18.5887
Pyrophyllite	-4.3613	Prehnite	-19.3408
Calcite	-4.7164	Ca-Al Pyroxene	-20.3895
Beidellit-Ca	-4.8387	Forsterite	-20.4615
Aragonite	-4.8813	Talc	-20.7888
Beidellit-Mg	-4.8987	Gaylussite	-21.0728
Beidellit-H	-4.9456	Pirssonite	-21.2355
Beidellit-K	-5.5079	Saponite-Ca	-21.2662
Beidellit-Na	-5.5310	Saponite-Mg	-21.3263

Minerals will not precipitation because all saturation states are negative (remember: Q is the ion activity product, when assuming activity = 1 for mineral phases; K is the solubility product. Hence, if log Q/K is negative, IAP < K)

Exercise 2: Iron precipitation



Let's re-examine exercise 1 from Homework 4: A wastewater contains 10^{-4} M phosphate. Fe(III) is added to the system to precipitate phosphate. Is $\text{FePO}_4(\text{s})$ or $\text{Fe}(\text{OH})_3(\text{s})$ precipitated at $\text{pH}=7$?

Use SpecE8 to answer this question. The following information is useful:

- Assume an oxic system ($\text{O}_2(\text{aq})$ at saturation 9 mg/L)
- Assume an Fe(III) concentration of 10^{-4} M.
- Assume typical wastewater concentrations of
 - $\text{Ca}^{2+} = 6.6$ meq/L
 - $\text{Cl}^- = 3.5$ meq/L
 - $\text{SO}_4^{2-} = 2.6$ meq/L
- Strengite is a FePO_4 mineral.



Basis	Medium	Command	Results
constraints on initial system			
	H2O	1.0	free kg solvent
	HPO4-- 	-4.0	log mol/l
	Fe+++  Fe++	-4.0	log mol/l
	Ca++ 	6.6	meq/l
	Cl- 	3.5	meq/l
	SO4-- 	2.6	meq/l
	H+ 	7.0	pH
	O2(aq) 	9.0	mg/l
	temperature	25.0	C
 advanced			
add delete			



Mineral saturation states	log Q/K
Hematite	15.8024s/sat
Hydroxyapatite	12.1110s/sat
Goethite	7.4229s/sat
Whitlockite	6.5244s/sat
Magnetite	5.8737s/sat
Ferrite-Ca	5.5997s/sat
Strengite	3.3962s/sat
Fe(OH) ₃ (ppd)	3.0338s/sat

Strengite has a higher saturation state and is therefore expected to form preferentially compared to Fe(OH)₃

Exercise 3: Redox disequilibrium



We just discussed the example on redox disequilibrium. In what speciation would As occur if it equilibrated with the solution at the specified potential of $E_h = 0.4$ V?

Use the input file Redox.sp8 and remove the As redox couple from the list of decoupled redox couples. Then, examine the output file. What is the redox state of As and why?

Exercise 3: Solution



As occurs predominantly as H_2AsO_4^- and HAsO_4^{2-} :

Aqueous species	molality	mg/kg sol'n	act. coef.	log act.
Cl-	3.948e-05	1.400	0.9843	-4.4104
SO4--	3.100e-05	2.978	0.9390	-4.5359
Mg++	2.457e-05	0.5972	0.9401	-4.6364
Fe++	1.248e-05	0.6968	0.9395	-4.9309
Ca++	9.921e-06	0.3976	0.9395	-5.0305
CO2(aq)	6.840e-06	0.3010	1.0000	-5.1649
K+	5.114e-06	0.2000	0.9843	-5.2981
H2AsO4-	4.730e-06	0.6666	0.9844	-5.3320
Na+	4.349e-06	0.09999	0.9844	-5.3684
HCO3-	2.991e-06	0.1825	0.9844	-5.5309
H+	1.015e-06	0.001024	0.9847	-6.0000
HAsO4--	8.655e-07	0.1211	0.9390	-6.0901
MgSO4	1.135e-07	0.01367	1.0000	-6.9448

The redox state of As is therefore +V (in $\text{As}(\text{OH})_4^-$, As has redox state +III). This makes sense because the system Eh is higher than the Eh of the As redox couple in the previous example. When equilibrating the solution to higher Eh, As(III) oxidizes to As(V)

	Eh (volts)	pe
$\text{e}^- + \frac{1}{4} \text{O}_2(\text{aq}) + \text{H}^+ \rightleftharpoons \frac{1}{2} \text{H}_2\text{O}$	0.400	6.762
$2 \text{e}^- + 4 \text{H}^+ + \text{AsO}_4^{3-} \rightleftharpoons \text{As}(\text{OH})_4^-$	0.081	1.362
$\text{e}^- + \text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+}$	-0.002	-0.035

How many kgs of calcite are precipitating each year?

On your field trip, you measured a flowrate of 60 L/s and the parameters in the table below. Use SpecE8 to calculate the amount of calcite precipitating.

Table 1. Some Averaged Results (Micro-Titrations Only) of All Ten Excursions from 2008 until 2017^a

parameter	head	foot	difference
conductivity ($\mu\text{S cm}^{-1}$)	602	575	-27
temperature ($^{\circ}\text{C}$)	8.8	10.2	+1.4
pH (units)	7.61	7.96	+0.35
$\beta(\text{Ca}^{2+})$ (mg L^{-1})	108.7	101.7	-7.0
$c(\text{Ca}^{2+})$ (mmol L^{-1})	2.711	2.537	-0.17
$\beta(\text{CaCO}_3\text{aq})$ (mg L^{-1}) (= Ca-hardness)	271.4	253.9	-17.4
$c(\text{M}^{2+})$ (mmol L^{-1}) (M = Ca, Mg)	3.409	3.164	-0.24
$c(\text{HCO}_3^-)$ (mmol L^{-1})	5.57	5.18	-0.39

^aFor more data and conversion into other common units, see [Supporting Information pdf 2](#).



Dreumühlen waterfall: Solution

SpecE8 Community Edition - C:\Users\maepli\OneDrive - epfl.ch\GWB

File Edit Run Config View Help

Basis	Medium	Command	Results
constraints on initial system			
H2O		1.0	free kg
H+	↔	7.61	pH
Calcite	↔ Ca++	108.7	free mg/l as Ca
HCO3-	↔	5.57	mmol/kg
temperature		8.8	C
+ advanced			
add delete			

Ready

Minerals in system	moles	log moles	grams	volume (cm3)
Calcite	0.002715	-2.566	0.2717	0.1003
(total)			0.2717	0.1003

0.2717 g/L calcite are precipitating

Using a flow rate of 60 L/s, we obtain 16.302 g/s

$16.302 \text{ g/s} * 60 \text{ s/min} * 60 \text{ min/h} * 24 \text{ h/d} * 365 \text{ d/y} = \underline{514'100 \text{ kg/y}}$