



Mine water discharge in the Leitzach valley, Bavaria, Germany

From Ground Water to Mine Water
Environmental Hydrogeology in Mining
Mine Water Geochemistry

Kassel, 6. September 2022

Prof. Dr. habil. Christian Wolkersdorfer
Elke Mugova M. Sc.



From Mine Water to Ground Water

Environmental Hydrogeology in Mining

Mine Water Geochemistry

Prof. Dr. Christian Wolkersdorfer (云村)

South African Research Chair for Acid Mine Drainage Treatment

1

Contents – Whole Course

- Introduction, Historical Background
- Mining Methods, Technical Terms
- Water and Water Inrushes
- Dewatering methods; Recharge
- Mine Flooding
- Mine Water Geochemistry
- Prediction of Mine Flooding
- Mine Water Treatment

Mine Water Chemistry
2

2

Contents

- Introduction
- Master Variables (pH, redox)
- Pyrite Weathering
- Weathering Kinetics and Calculation Example
- Secondary Minerals
- Acidity & Alkalinity
- Chemical Thermodynamics

Periodic Table of the Elements

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008	2 He Helium 4.002602																
3 Li Lithium 6.94	4 Be Beryllium 9.012182																
11 Na Sodium 22.9897	12 Mg Magnesium 24.305																
19 K Potassium 39.0963	20 Ca Calcium 40.078	21 Sc Scandium 44.9559	22 Ti Titanium 45.967	23 V Vanadium 50.956	24 Cr Chromium 51.996	25 Mn Manganese 54.9380	26 Fe Iron 55.845	27 Co Cobalt 58.9331	28 Ni Nickel 58.6934	29 Cu Copper 63.545	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.925	33 As Arsenic 74.924	34 Se Selenium 78.63	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.4678	38 Sr Strontium 87.62	39 Y Yttrium 88.9085	40 Zr Zirconium 91.224	41 Nb Niobium 92.90538	42 Ta Tantalum 96.956	43 W Tungsten 102.905	44 Re Rhodium 101.07	45 Os Osmium 102.905	46 Ir Iridium 106.42	47 Rh Ruthenium 107.882	48 Pd Palladium 108.411	49 Ag Silver 108.918	50 Cd Cadmium 112.411	51 In Indium 113.411	52 Sn Tin 118.716	53 Sb Sb 121.769	54 Te Tellurium 127.69
55 Cs Cesium 132.905	56 Ba Barium 137.327	57 La Lanthanum 138.955	58 Ce Cerium 140.116	59 Pr Praseodymium 140.907	60 Nd Neodymium 144.242	61 Pm Promethium 144.954	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 160.500	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668	
87 Fr Francium 223	88 Ra Radium 226	89 Ac Actinium 227	90 Th Thorium 228	91 Pa Protactinium 231.035	92 U Uranium 238.028	93 Np Neptunium 237.035	94 Pu Plutonium 239.035	95 Am Americium 243.035	96 Cm Curium 247.035	97 Bk Neptunium 247.035	98 Cf Curium 247.035	99 Es Americium 251.035	100 Fm Curium 252.035	101 Md Neptunium 252.035	102 No Americium 253.035	103 Lr Neptunium 252.035	

Where are the "Heavy Metals"?

For elements with no stable isotopes, the mass number of the isotope with the longest half-life is in parentheses.

57 La Lanthanum 138.955	58 Ce Cerium 140.116	59 Pr Praseodymium 140.907	60 Nd Neodymium 144.242	61 Pm Promethium 144.954	62 Sm Samarium 150.36	63 Eu Europium 151.964	64 Gd Gadolinium 157.25	65 Tb Terbium 160.500	66 Dy Dysprosium 162.500	67 Ho Holmium 164.930	68 Er Erbium 167.259	69 Tm Thulium 168.934	70 Yb Ytterbium 173.054	71 Lu Lutetium 174.9668	
89 Ac Actinium 227	90 Th Thorium 228	91 Pa Protactinium 231.035	92 U Uranium 238.028	93 Np Neptunium 237.035	94 Pu Plutonium 239.035	95 Am Americium 243.035	96 Cm Curium 247.035	97 Bk Neptunium 247.035	98 Cf Curium 247.035	99 Es Americium 251.035	100 Fm Curium 252.035	101 Md Neptunium 252.035	102 No Americium 253.035	103 Lr Neptunium 252.035	

6

Periodic Table of the Elements



Mine Water Chemistry

5



6

Why to deal with mine water chemistry?



Mine Water Chemistry

Cape Breton Island/Canada

Mine Water Outfall

6



6

Why to deal with mine water chemistry?



eMalahleni, South Africa unremediated open pit mine



7

Why to deal with mine water chemistry?



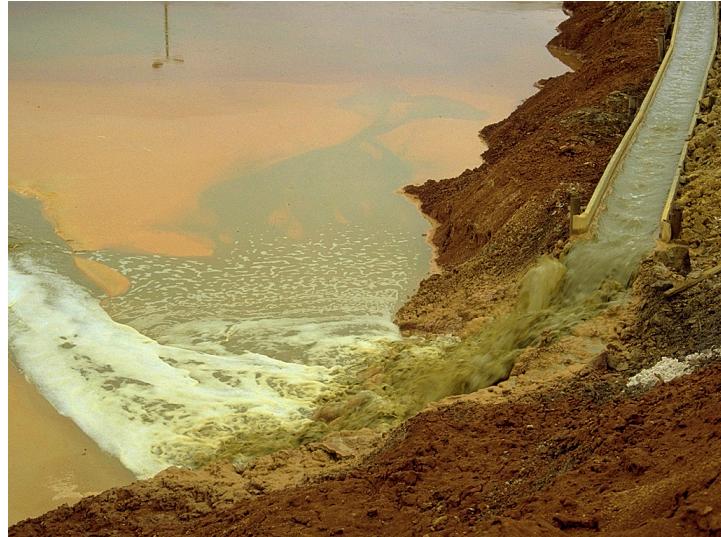
Eagle Picher Superfund Site/USA Mark R. Boardman



8

6

Why to deal with mine water chemistry?



Former Königstein Uranium Mine, Saxony, Germany



9

Why to deal with mine water chemistry?



Pfunderer Berg/Southern Tyrol



Armin Hanneberg



10

6

Why to deal with mine water chemistry?



Georgi Unterbau, Tyrol, Austria



11

Why to deal with mine water chemistry?



Natural Acid Rock Drainage at Halifax Airport; Nova Scotia/Canada



12

6

Why to deal with mine water chemistry?



Phillipsthal, Thuringia, Germany

13



13

6

History Pryce William (1778)

"By means of these acids, the Miners are often put to an extraordinary expence for Brafs pumps instead of Iron; for many of the Mines have water so fully imbued with acid, that the Iron working-pieces, in which the piston of the pump works, will be entirely corroded therewith in six months; and a great expence and losf of time will be incurred, if the pumps are not previously furnished with Brafs working pieces, as on them the acids, which are already saturated with kindred particles, have little effe&t."

Pryce William (1778) *Mineralogia Cornubiensis; a treatise on minerals, mines and mining containing the theory and natural history of strata, fissures and lodes, with the methods of discovering and working of tin, copper and lead mines and of cleansing and metalizing their products; shewing each particular process for dressing, assaying and smelting of ores. To which is added an explanation of the terms and idioms of miners.* Phillips, London, p. 6

Mine Water Chemistry
14

14

6

Mine Water Chemistry

Factors to be taken into account (1/2)

- Source – Pathway – Target-Concept
- Type of mine water
 - AMD acid mine drainage (< pH 5.6)
 - circumneutral mine drainage (> ≈ pH 5.6 – 8)
 - SD saline mine drainage (> ≈ 1000 mgL⁻¹)
 - salt mine water NaCl, KCl dominated
- Pyrite (di-sulfide) weathering
 - pH-dependence of metal dissolution

15

15



6

Mine Water Chemistry

Factors to be taken into account (2/2)

- Natural attenuation of contaminants
- Buffer reactions
- Microbiological processes
- Control of the source ("in-situ-methods")
- Evaluation on a case-to-case basis **every site is unique**

16

16



6

What affects Mobility and Bioavailability

- Speciation
 - Hydrolyses, complexation
 - Solubility effects
- Redox transformations
 - $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{e}^-$
 - $\text{U}^{4+} \rightarrow \text{U}^{6+} + 2 \text{e}^-$
- Sorption (Adsorption/Absorption)
 - Especially onto iron hydroxide mineral
 - Silt, clay
 - Wood
 - Pore space

Mine Water Chemistry

17



17

6

Source – Pathway – Target-Concept

- Sources of contamination
 - Acidity pyrite ("di-sulfide") weathering
 - Metal ions sulfide weathering
 - Chemical reactants (ore processing)
 - Organic substances (e.g. timber impregnation)
- Pathways
 - Alkalinity (calcite, aluminosilicate weathering feldspars, zeolites)
 - Precipitation, sorption of metal ions
 - ochre precipitation
- "Targets"
 - Surface water
 - Ground water

Mine Water Chemistry

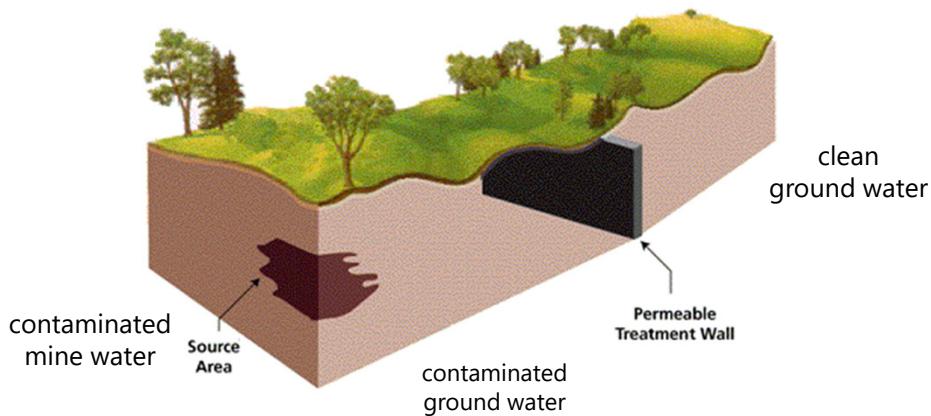
18



18

6

Source – Pathway – Target-Concept



Source → **Pathway** → **Target**



19

6

Source – Pathway – Target-Concept

Sources

- Tailings
- Waste rock stockpiles
- Ore stockpiles
- Heap leach material
- Pit walls
- Underground workings
- Processing wastes



modified from GARD guide

Pathways

- Infiltration through mine waste
- Infiltration through soil/vadose zone
- Movement of mine waters
- Uptake by biota
- Groundwater
- Surface Water
- Runoff
- Air



Targets

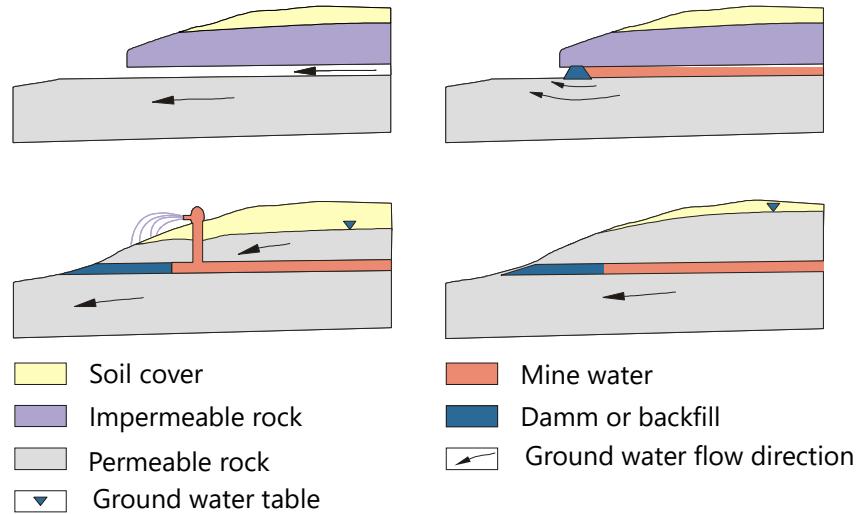
- Groundwater
- Surface water
- Sediment
- Air
- Soil



20

6

Mine Closure Systems



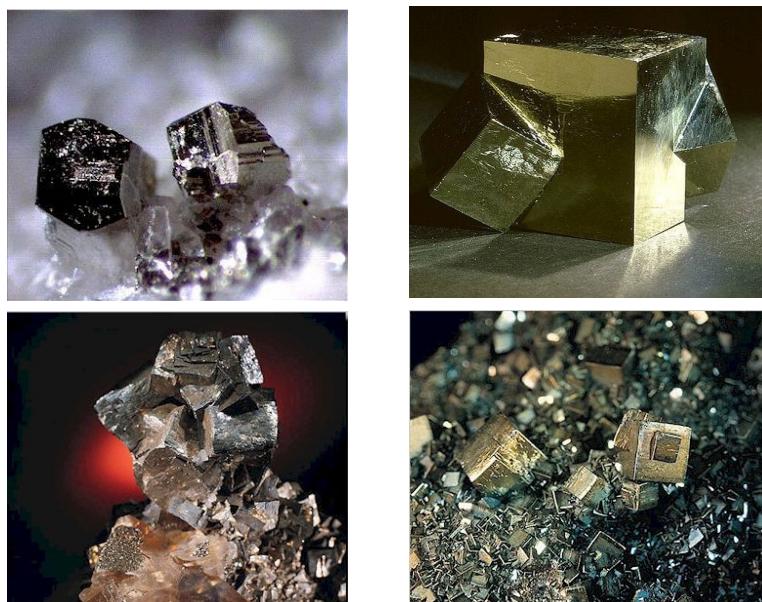
Parizek & Karr 1972

21



6

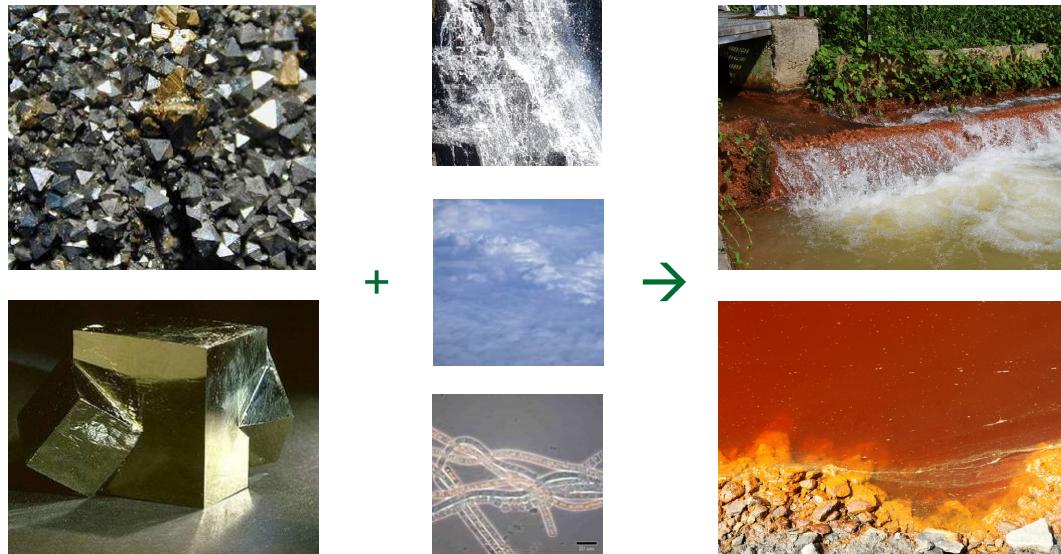
Pyrite Weathering Processes

Mine Water Chemistry
22

22

6

Pyrite Weathering Processes



Mine Water Chemistry

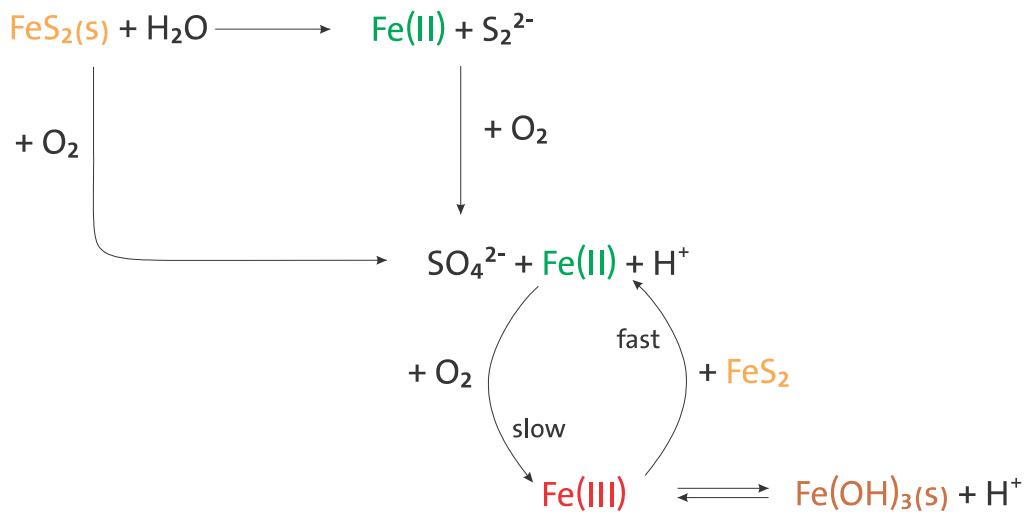
23

23



6

Pyrite Weathering Processes



Mine Water Chemistry

24

Wolkersdorfer 2022



6

Salt Dissolution



Asse Salt Mine, Germany

25

25

6

Salt Dissolution

Datum	Laborwerte									Werte vor Ort	
	CaSO ₄ [g/l]	CaCl ₂ [g/l]	MgSO ₄ [g/l]	MgCl ₂ [g/l]	KCl [g/l]	NaCl [g/l]	MgBr ₂ [g/l]	H ₂ O [g/l]	Mg ₃ B ₈ O ₁₅ [g/cm ³]	T [°C]	p [g/cm ³]
10.04.1997	0,12	0	43,39	432,20	4,94	7,90					
06.05.1997	0,10	0	39,36	424,40	4,57	7,40					
12.08.1997	0,11		42,24	412,95	7,19	8,03	6,60	856,00	1,333		
06.11.1997	0,08		43,09	411,54	4,73	6,71	6,15	866,00	1,338		
09.02.1998	0,07		45,42	435,16	3,74	6,31	6,69	848,00	1,345		
11.05.1998	0,07		45,21	435,33	3,30	5,82	6,66	853,61	1,350		
18.08.1998	0,07	< 0,1	42,86	417,51	5,57	9,56	6,06	853,00	1,335		
12.11.1998	0,08		44,11	401,98	6,22	11,78	6,61	866,00	1,337		
26.02.1999	0,10		43,43	420,10	5,26	6,99	5,88	853,00	1,335		
02.06.1999	0,07		42,92	417,35	5,82	9,80	6,21	851,00	1,333		
27.08.1999	0,08	< 0,05	40,91	398,22	9,70	9,99	5,80	862,00	1,327		
29.11.1999	0,07	< 0,01	42,62	409,98	7,09	8,51	6,56	853,17	1,328	34,7	1,322
29.02.2000	0,08	< 0,01	43,47	429,89	3,91	8,23	6,37	845,90	6,13	34,4	1,344



Stockmann et al. 2006, sampling location AS010 | Salzwelten Salzburg, Austria

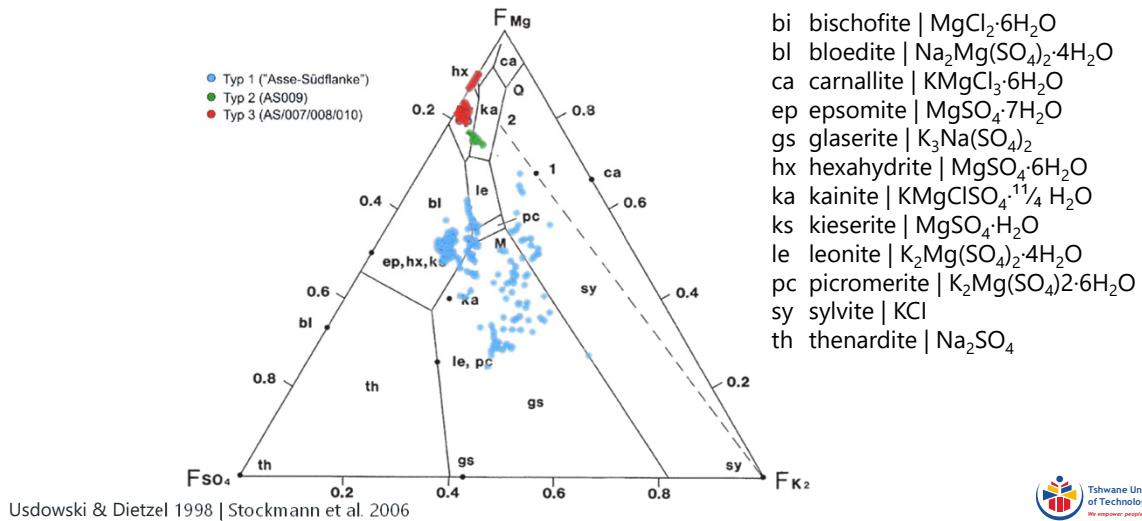
26

26

6

Salt Dissolution – Jänecke Diagramm

- $\text{Na}_2\text{Cl}_2\text{-K}_2\text{Cl}_2\text{-MgCl}_2\text{-Na}_2\text{SO}_4\text{-K}_2\text{SO}_4\text{-MgSO}_4\text{-H}_2\text{O}$



Mine Water Chemistry

27



27

6

What to measure? On-site parameters ...

- ... are meta-stable, redox or pressure-dependent
- Temperature
- Electrical conductivity
- pH
- Oxygen concentration
- Redox-potential
- k_A (Acid Capacity, Alkalinity)
- k_B (Base Capacity, Acidity)
- Fe^{2+} , Fe_{total}
- Filtered/unfiltered samples



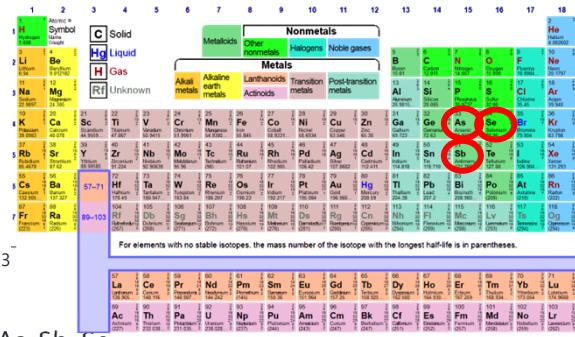
Mine Water Chemistry

28



Naming of parameters

- Physico-chemical Parameters (selection, there are many more)
 - Temperature
 - Electrical conductivity
 - pH
 - Redox-potential
- Chemical Parameters
 - k_A, k_B , Oxygen concentration
 - Main ions
 - Cations $\text{Na}^+, \text{K}^+, \text{Ca}^{2+}, \text{Mg}^{2+}$
 - Anions $\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}, \text{HCO}_3^-$
 - Trace elements
 - Semi-metals (metalloids) e.g. As, Sb, Se
 - Metals e.g. Al, Fe, Co, Ni, Cu, Cr, Mn, U, Zn, Cd, Hg, Pb, Bi, Sr, Ba



"master variables" in mine water

- \bullet pH
- \bullet E_h
 - Proton-activity
 - \bullet $\boxed{\text{pH} = -\log \{\text{H}^+\}}$
 - \bullet $\text{FeS}_2 + 3 \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} \rightarrow \text{Fe}^{2+} + \text{SO}_4^{2-} + 2 \text{H}^+$
 - measurement
 - pH-meter
 - no units
 - no conversion
 - \bullet Redox potential or
 - \bullet Oxidation-reduction potential (ORP)
 - \bullet Electron-activity
 - \bullet $\boxed{\text{pE} = -\log \{\text{e}^-\}}$
 - \bullet $\text{U}^{4+} \rightarrow \text{U}^{6+} + 2 \text{e}^-$
 - \bullet $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + 1 \text{e}^-$
 - measurement
 - Redox-probe
 - mV (or V)
 - conversion to SHE

6

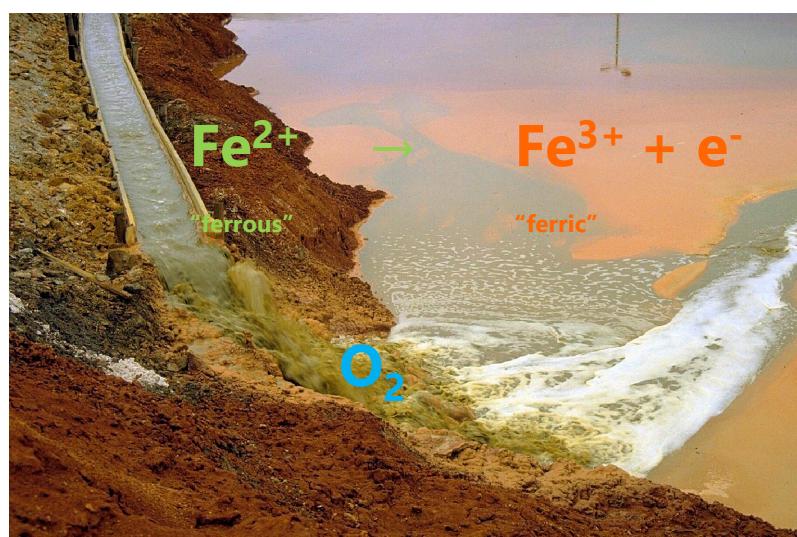
Redox Process

"The extent to which redox reactions occur in groundwater systems is therefore significant with respect to many practical problems, for example issues of groundwater quality for drinking water, the attenuation of landfill leachate plumes and the remediation of sites contaminated by organic pollutants."

HISCOCK KM and BENSE VF (2014) *Hydrogeology – Principles and Practice*, Blackwell, Oxford, 2nd ed, 519 p.

6

Redox Process



6

Redox potential – Nernst equation

$$E_h = E_h^0 + \frac{RT}{nF} \ln \left(\frac{[\text{oxidants}]}{[\text{reductants}]} \right) = E_h^0 + \frac{2.303 \cdot RT}{nF} \log \left(\frac{[\text{oxidants}]}{[\text{reductants}]} \right)$$

with

E_h^0 reference condition, mV

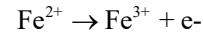
R gas constant, $8.3144621 \text{ J mol}^{-1}\text{K}^{-1}$

T temperature, K

n number of electrons involved, –

F Faraday constant, $96\,485.3365 \text{ C mol}^{-1}$

$$E_h = \frac{2.303RT}{nF} pE \quad pE = 13.05 + \log \left(\frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \right)$$



$$K = \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}] [\text{e}^-]} = 10^{13.05}$$



6

Redox potential – Correction to SHE

$$E_{0(25^\circ\text{C})} = E_t - 0.198 \times (T - 25) + \sqrt{a - b \times T}$$

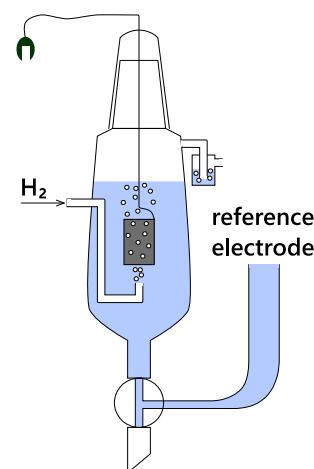
with

$E_{0(25^\circ\text{C})}$ redox potential corrected to SHE, mV

E_t measured potential of secondary electrode, mV

T temperature, °C

a, b coefficients



Sensor Type	Coefficient a	Coefficient b
Mercury calomel KCl	67798	324
Ag/AgCl KCl 1 mol L ⁻¹	62775	284
Ag/AgCl KCl 3 mol L ⁻¹	50301	297



6

Redox potential – Correction to SHE

Sensor Type	Coefficient <i>a</i>	Coefficient <i>b</i>
Hanna Ag/AgCl, KCl, 1 mol/L	69791	196
Hanna Ag/AgCl, KCl, 3 mol/L	49296	298
Hanna Ag/AgCl, KCl, 3.5 mol/L	50301	297
Hach Ag/AgCl, KCl, 3 mol/L	50301	297
Ag/AgCl, KCl, 4 mol/L	56544	287
Calomel Hg/Hg ₂ C ₂ , KCl , 0.1 mol/L	112238	58
Calomel Hg/Hg ₂ C ₂ , KCl , 1 mol/L	82571	183
Calomel Hg/Hg ₂ C ₂ , KCl , saturated	67798	324
Mercury sulfate Hg/Hg ₂ SO ₄ , K ₂ SO ₄ , saturated	451702	1.090
Silver chloride, Argenthal, Silamid Ag/AgCl KCl, 1 mol/L	62755	284
KCl, 3 mol/L	50301	297
KCl, 3.5 mol/L	49083	310
KCl, saturated	47591	356
Thalamid Ti, Hg/TlCl, KCl , 3.5 mol/L	no solution found	

www.wolkersdorfer.info/ORP

35



6

Redox potential – Correction to SHE Example

- Measured values (Ag/AgCl KCl 3 mol L⁻¹-electrode)

- ORP -44 mV
- Temp. 23.4 °C

$$E_{0(25\text{ }^{\circ}\text{C})} = E_t - 0.198 \times (T - 25) + \sqrt{a - b \times T}$$

Sensor Type	Coefficient <i>a</i>	Coefficient <i>b</i>
Ag/AgCl KCl 3 mol L ⁻¹	50301	297

$$0.198 \times (T - 25) + \sqrt{a - b \times T} =$$

$$0.198 \times (23.4 - 25) + \sqrt{50301 - 297 \times 23.4} =$$

$$0.198 \times (-1.6) + \sqrt{43351} =$$

$$-0.3168 + 208.2095 =$$

$$E_{0(25\text{ }^{\circ}\text{C})} = -44 \text{ mV} + 208 \text{ mV} = 164 \text{ mV} \quad (160 \text{ mV according to ISO DIN 38404-C6})$$

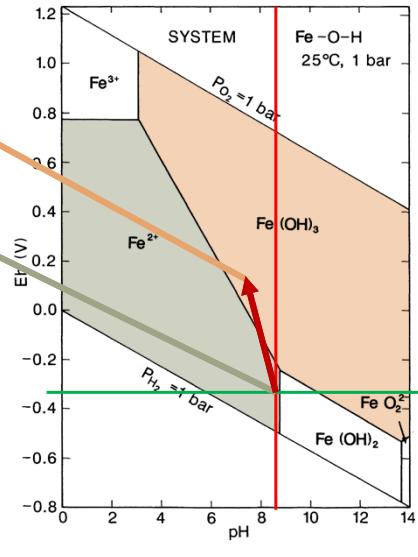
Mine Water Chemistry
36



36

6

Redox Process



6

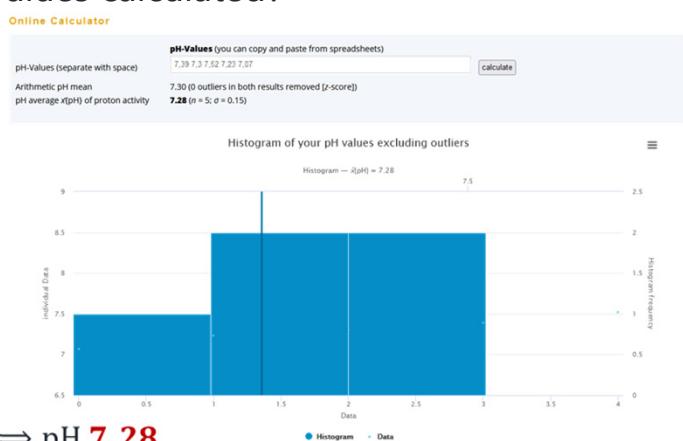
pH-calculations

- How is the average of pH-values calculated?

pH Value
7.39
7.30
7.52
7.23
7.07

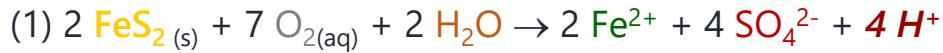
~~$$\overline{\text{pH}} = \frac{\sum \text{pH}}{5} = 7.30 \quad \text{wrong!}$$~~

$$\{\overline{\text{H}^+}\} = \frac{\sum \{\text{H}^+\}}{5} = 5.30 \times 10^{-8} \Rightarrow \text{pH } 7.28$$



6

Pyrite Weathering Processes (1/4)



(5) Fe^{2+} further reacts in reactions 2-4

(1) and (2) are catalysed by bacteria e.g. *Acidithiobacillus thiooxidans*,
Gallionella

6

Pyrite Weathering Processes (2/4)



Reiche Zeche shaft, Germany

6

Pyrite Weathering Processes ($\frac{3}{4}$)



Straßberg silver mine, Germany



41

41

6

Pyrite Weathering Processes ($\frac{3}{4}$)



Characteristics of Richmond Portal Effluent
(1983-91)

	Mean	Range
Discharge (L/s)	4.4	0.5 – 50
pH	0.8	0.02 – 1.5
iron (mg/L)	12,000	10,000 – 15,000
zinc (mg/L)	1,600	700 – 2,600
copper (mg/L)	250	120 – 650
zinc/copper (weight ratio)	7.5	2 – 13

Mass balance calculations (PHREEQC)

- 2,300 tons of pyrite weathered per year
- Assuming constant weathering rate applied to 7 M tons of pyrite remaining in Richmond Mine, acid discharge will continue for ~ 3,000 yrs



Iron Mountain, California (Michael Kersten 2014)

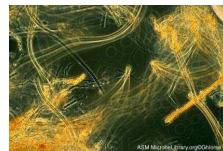


42

6

Bacterial Processes

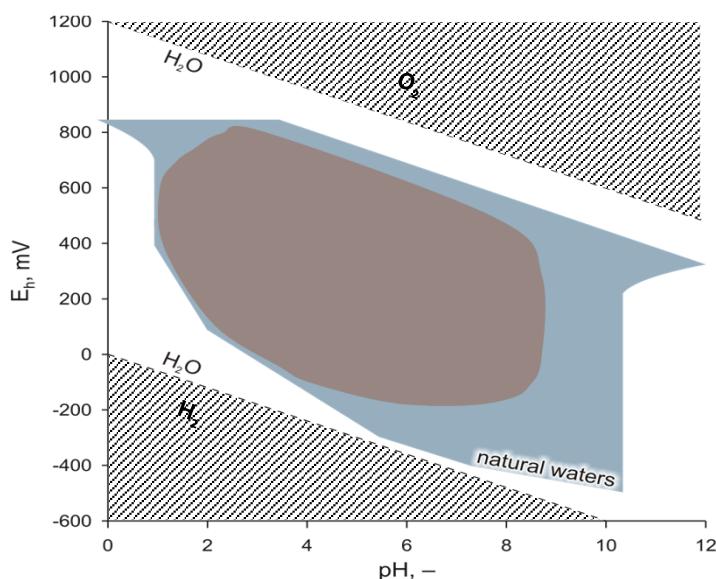
Acidithiobacillus thiooxidans, Gallaionella, Beggiatoa and Thiomicrospira increase the reaction speed 10^6 -fold



	pH-range	Eh-range, mV
Sulfate reducing	4.2 ... 9.9	- 450 ... + 115
Thiobacteria	1.0 ... 9.2	- 190 ... + 855
Niederschlema	6.4 ... 8.9	+ 3 ... + 530

6

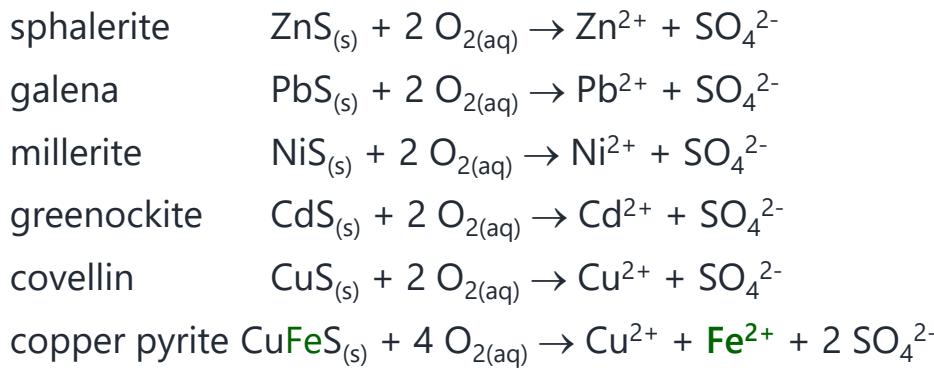
Bacterial Processes



Baas Becking *et al.* 1960

6

Sulfide Weathering



Release of potentially toxic metals and sulfate, but no acidity (except copper pyrite)

Mine Water Chemistry

45



45

6

Mineral weathering

- Depending on the pH-value, different metals coexist ("species")
- pH-value controls the release of contaminants ("master variable")
- At low pH-values the metal solubility, usually, is high
- Mobility and bioavailability at low pH-values is usually high

Mine Water Chemistry

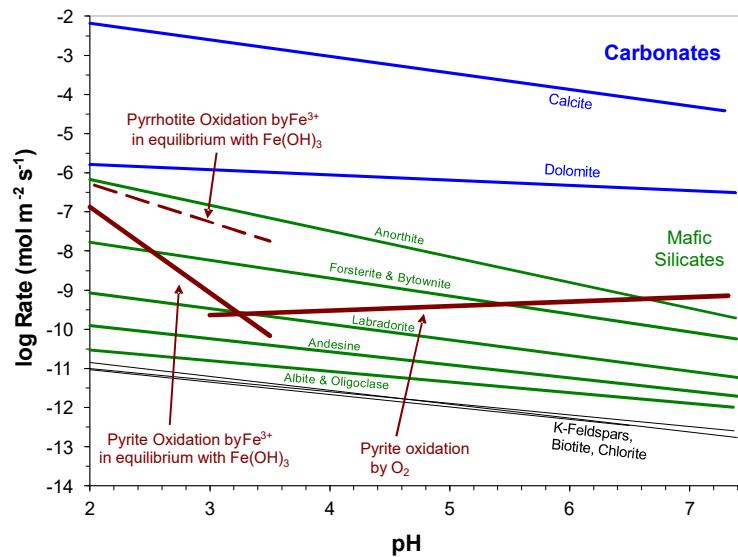
46



46

6

Weathering Kinetics



from Geller *et al.* 2013; data from Williamson & Rimstidt (1994
pyrite); Palandri & Karaka (2004 pyrrhotite, carbonates,
silicates)



47

6

pH-Values and Metal Concentrations

locality	pH	[SO ₄ ²⁻]	[Fe]	[Al]	[Mn]	[Zn]	[Cu]
Iron Mountain, Cal (Cu) ¹	-2.5	760,000	111,000	1,420	23	23,500	4,760
Iron Mountain, Cal (Cu)	1.1	41,000	7,820	1,410	11	1,860	360
Pyrite mine	2.5	5,110	1,460	84	3	1	0.2
abandoned coal mine	3.6	1,044	101	17	4	0.2	0.007
abandoned coal mine	4.2	1,554	180	< 0.5	6	0.06	
waste rock dump (coal)	5.5	146	287	1	5	0.05	< 0.007
St. Johannes Stollen ²	6.7	272	6	< 0.1	1.2	< 0.01	< 0.01
Straßberg Germany	6.3	359	31		6	0.9	0.08
abandoned coal mine	6.3	83	5	0.08	0.4	0.05	0.005
metal mine	6.5	124	15	0.1	2	0.003	
Niederschlema Germany	7.1	1,138	3	0.4	3	0.1	0.03
mine water (coal)	8.2	7	< 0.01	< 0.02	0.004	0.055	< 0.005

concentrations in mg L⁻¹

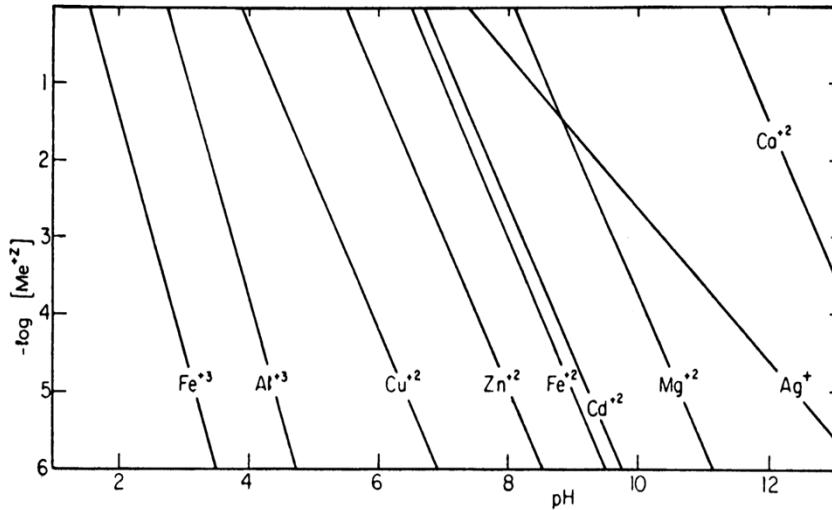
from Wolkersdorfer 2008, ¹Nordstrom 2011, ²Wedewardt 1995



48

6

pH-Dependency of Metal Solubility



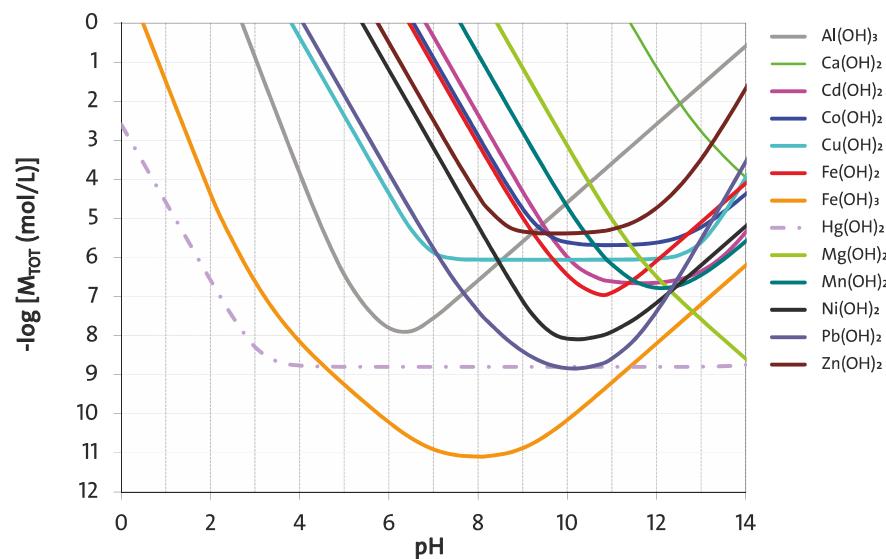
Stumm & Morgan 1996

49



6

pH-Dependency of Me-oxide solubility



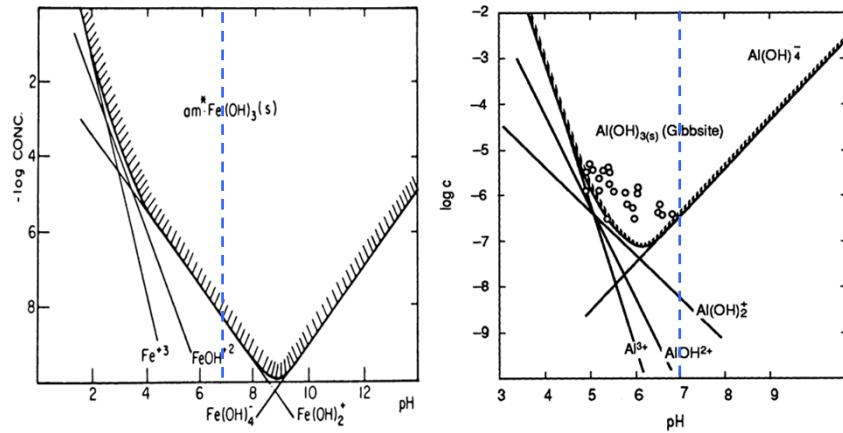
from Wolkersdorfer 2014, after Cravotta pers. comm.

50



6

pH-Dependency of Metal Solubility



Stumm & Morgan 1996; Sigg & Stumm 1994

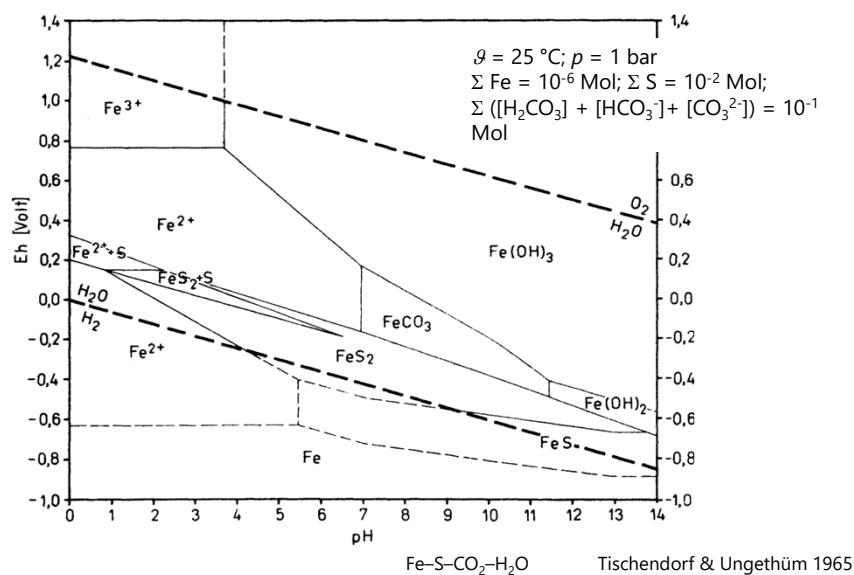


51

51

6

Pourbaix-diagram (Confusogram sensu P. Wade)

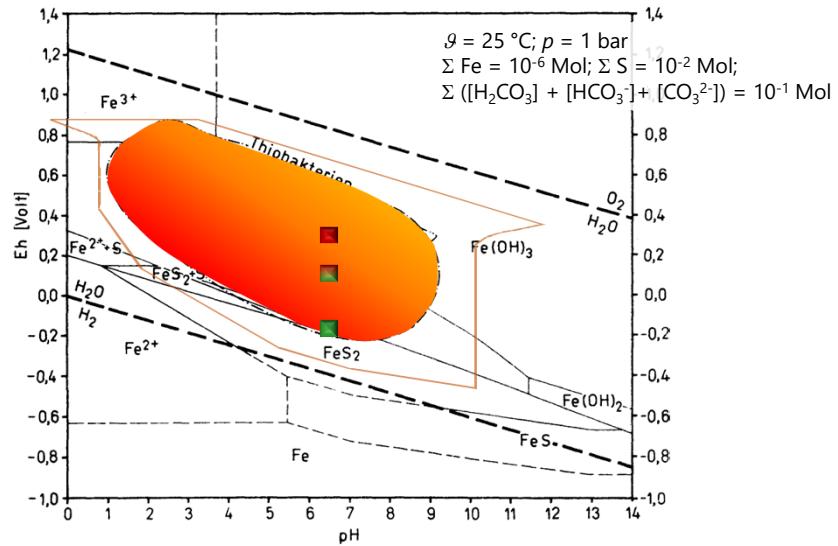


Mine Water Chemistry

52

6

Pourbaix-diagramm Fe-S-CO₂-H₂O



Tischendorf & Ungethüm 1965

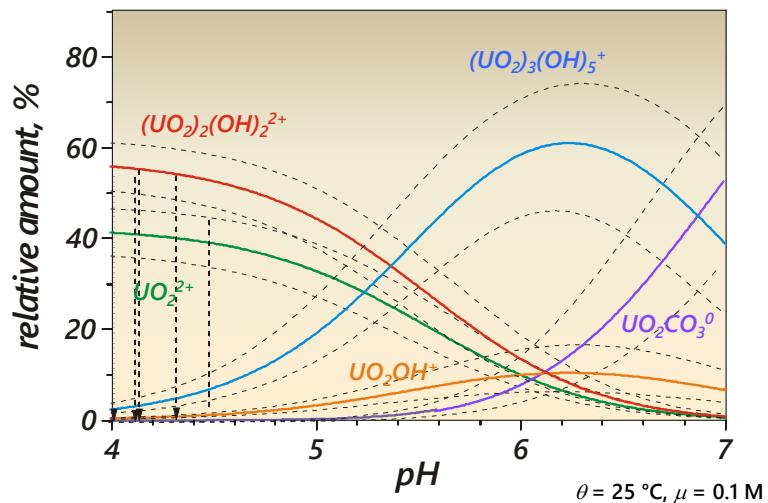


53

53

6

Uranium Speciation (U⁶⁺)



Meinrath 1998



54

6

Weathering Processes (1/4)

- The weathering of minerals (except di-sulfides such as pyrite) produces alkalinity and, therefore, buffers the acid

- Carbonates
- Feldspars
- Micas

	mineral	formula	pH-buffer range
Calcite	CaCO_3	6.5 ... 7.5	
Dolomite	$\text{CaMg}[\text{CO}_3]_2$	6.5 ... 7.5	
Siderite	FeCO_3	4.8 ... 6.3	
Mix carbonates	$(\text{Ca, Mg, Fe, Mn})\text{CO}_3$	4.8 ... 6.3	
Gibbsite	Al(OH)_3	4.0 ... 4.3	
Ferrhydrite	Fe(OH)_3	< 3.5	
Goethite	$\alpha\text{-FeOOH}$	1.3 ... 1.8	
K-Jarosite	$\text{KFe}_3[(\text{OH})_6](\text{SO}_4)_2$	1 ... 2 (laboratory experiments)	
Alumosilicates (feldspars, zeolites)		1 ... 2 (laboratory experiments)	

Mine Water Chemistry

55



55

6

Weathering Processes (2/4)

Carbonates

- Calcite (buffers at pH 6.5...7.5)
 - $\text{CaCO}_3 + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^-$
- Dolomite (buffers at pH 6.5...7.5)
 - $\text{CaMg}[\text{CO}_3]_2 + 2 \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{Mg}^{2+} + 2 \text{HCO}_3^-$
- Siderite (buffers at pH 4.8 ...6.3)
 - $\text{FeCO}_3 + \text{H}^+ \leftrightarrow \text{Fe}^{2+} + \text{HCO}_3^-$
 - $\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 + \frac{5}{2} \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2 \text{H}^+$

Mine Water Chemistry

56



6

Weathering Processes ($^{3/4}$)

Feldspar

- K-Feldspar
 - $KAlSi_3O_8 + H^+ + \frac{1}{2}H_2O \rightarrow K^+ + 2 H_4[SiO_4] + \frac{1}{2} Al_2Si_2O_5(OH)_4$
- Anorthite
 - $CaAl_2Si_2O_8 + H^+ + H_2O \rightarrow Ca^{2+} + 2 H_4[SiO_4] + \frac{1}{2} Al_2Si_2O_5(OH)_4$
- Albite
 - $NaAlSi_3O_8 + H^+ + \frac{1}{2}H_2O \rightarrow Na^+ + 2 H_4[SiO_4] + \frac{1}{2} Al_2Si_2O_5(OH)_4$

6

Weathering Processes ($^{4/4}$)

Mica

- Biotite

$$KMg_{3/2}Fe_{3/2}[AlSi_3O_{10}](OH)_2 + 7 H^+ + \frac{1}{2} H_2O \rightarrow K^+ + \frac{3}{2} Mg^{2+} + \frac{3}{2} Fe^{2+} + 2 H_4[SiO_4] + \frac{1}{2} Al_2Si_2O_5(OH)_4$$
- Muscovite

$$KAl_2[AlSi_3O_{10}](OH)_2 + H^+ + \frac{3}{2} H_2O \rightarrow K^+ + \frac{3}{2} Al_2Si_2O_5(OH)_4$$

6

Keep in Mind Mineralogy and Kinetics

- Disulfides are abundant in nearly all rocks as trace minerals
- Other minerals, for example silicates, are far more abundant
- Pyrite weathers more rapidly than silicates and therefore causes acid mine water (AMD)
- Already small amounts of di-sulfide cause severe problems due to different weathering kinetics of the minerals

Mine Water Chemistry

59

59



6

Secondary Minerals (1/3)

- Metal oxides and -hydroxides

Gibbsite



Iron hydroxide



Zinc hydroxide

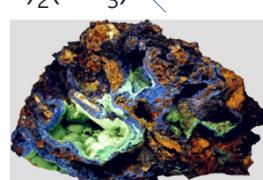


- Metal carbonates and hydroxy-carbonates

Cerrusite



Malachite



Mine Water Chemistry

60

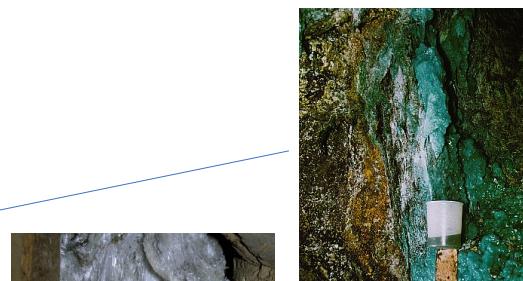


6

Secondary Minerals ($\frac{2}{3}$)

- Metal sulfates and -hydroxy-sulfates

Jarosite	$KFe_3(SO_4)_2(OH)_6$
Melanterite	$FeSO_4 \cdot 7H_2O$
Szomolnokite	$FeSO_4 \cdot H_2O$
Epsomite	$MgSO_4 \cdot 7H_2O$
Alunite	$KAl_3(SO_4)_2(OH)_6$
Jurbanite	$AlSO_4(OH) \cdot 5H_2O$
Basaluminite	$Al_4SO_4(OH)_{10} \cdot 5H_2O$
Schwertmannite	$Fe_{16}[O_{16}](OH)_{10}[(SO_4)_3] \cdot 10H_2O$
Anglesite	$PbSO_4$



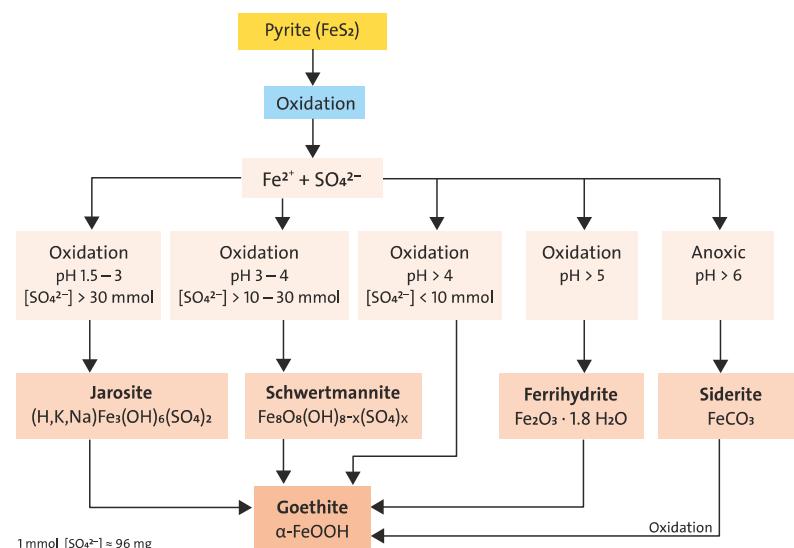
Mine Water Chemistry

61

61

6

Secondary Minerals ($\frac{3}{3}$)



after Bingham et al. 1992, Höglund et al. 2004

62

6

Control of Contamination Source

- Contaminant load (e.g. metals, acidity, sulfate) depends on:
 - Red-Ox conditions (does O₂ exist)
 - Weathering rate
 - Oxygen transport (diffusion)
 - Dissolving (transport remain in mine or transport to ecosphere)
 - Bacteria

Mine Water Chemistry

63

63

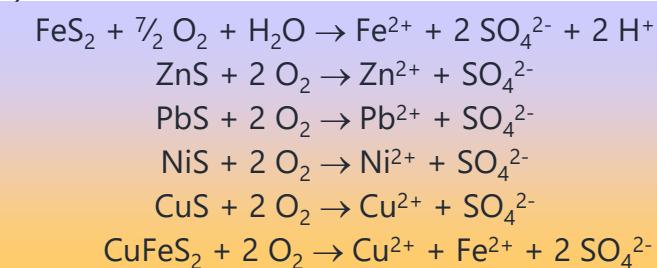


6

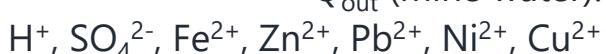
First Estimation

Metal loads released from a mine (or dump) reflect the weathering reactions involved

Q_{in} (Infiltration):



Q_{out} (mine water):



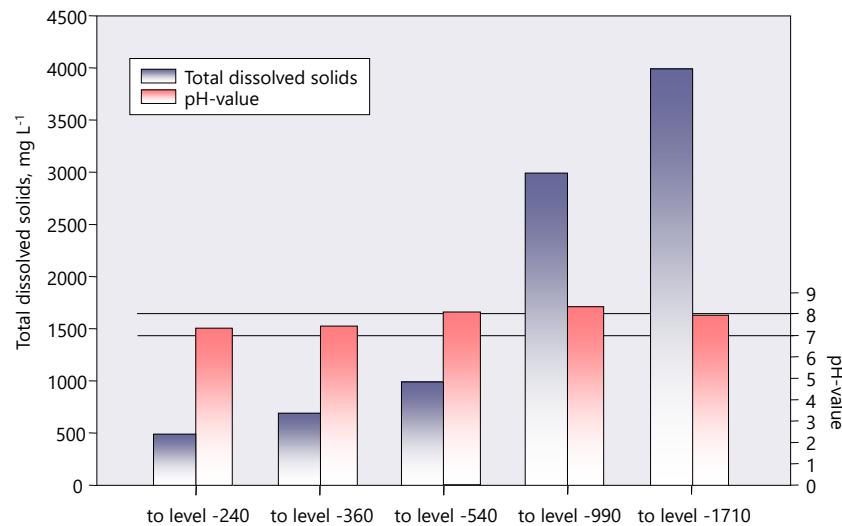
Mine Water Chemistry

64

64

6

Niederschlema Uranium Mine



Mine Water Chemistry

65

65

6

Acidity – Alkalinity

- Acidity of mine water is due to the mixing of infiltration waters that are
 - in contact with pyrite and produce acidity
 - in contact with carbonates or silicates and produce alkalinity
- Weathering rate acidity > alkalinity \Rightarrow **mine water is acidic**
- Weathering rate alkalinity > acidity \Rightarrow **mine water is alkaline**
- Acidity "base capacity" k_B
Alkalinity "acid capacity" k_A

Mine Water Chemistry

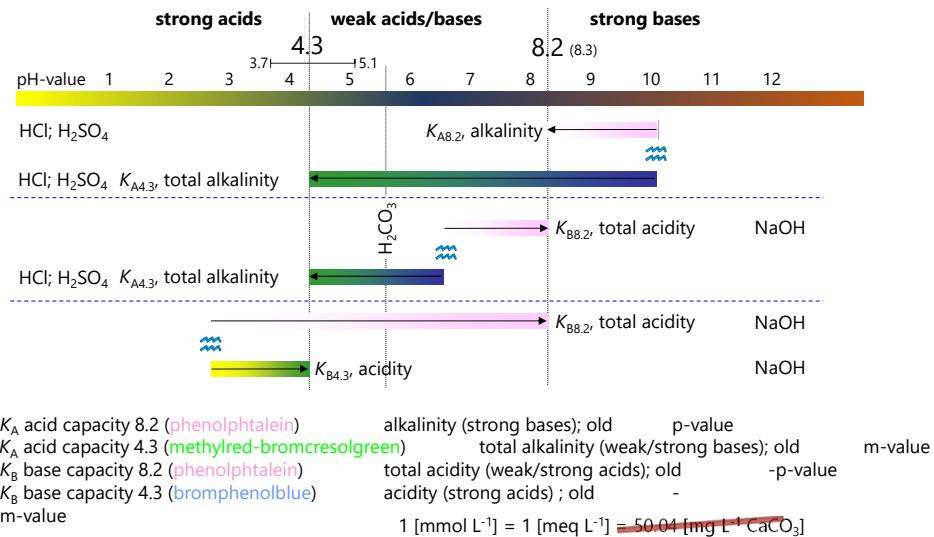
66

66



6

Acidity – Alkalinity



Mine Water Chemistry

67

67

6

Acidity – Alkalinity

- Acidic waters have a pH-value < 5.6
- Alkaline waters have a pH-value > 5.6
boundary is due to the end point of carbon acid titration
(use of buffer capacity)
- Acidic waters mobilize metal ions in a greater extend than alkaline ones
- Neutralisation of acidity also demobilizes metal loads (attenuation of metal contamination *Natural Attenuation*)

Mine Water Chemistry

68

68

6

Acidity – Alkalinity

- Relationship between alkalinity and acidity is of complex nature and results mainly from interplay of
 - Strong acids and bases
 - Weak acids and corresponding bases
 - Thermodynamic laws (mass action law, conservation of matter)
 - Mass and charge balance in aquatic systems
 - pH-value ("master variable")
- Microorganisms *speed up* chemical reactions, but they never enable reactions that are thermodynamically impossible!
- Alkalinity excess of strong base over strong acid in a natural water

6

Definitions

- "***I found at least 20 different definitions of alkalinity!***"
An ocean carbon cycle modeller from Hamburg.
- "... ***alkalinity, one of the most central but perhaps not the best understood concept in aquatic chemistry.***"
Morel & Hering (1993, p. 157)
- "***Alkalinity is an important and very useful concept in the context of the carbonate system in seawater. It is also called total alkalinity or titration alkalinity and is denoted by TA.***"
Zeebe & Gladrow-Wolf (2003, p. 27)

6

Strong Acids and Bases

- Complete dissociation
- Strong **bases** (base cation + OH⁻)
 - NaOH \leftrightarrow Na⁺ + OH⁻
 - Mg(OH)₂ \leftrightarrow Mg²⁺ + 2 OH⁻
- Strong **acids** (acid anion + H⁺)
 - HCl \leftrightarrow Cl⁻ + H⁺
 - H₂SO₄ \leftrightarrow SO₄²⁻ + 2 H⁺
- [Aci] = " Σ [H⁺] – Σ [OH⁻]" = 2 [SO₄²⁻] + [Cl⁻] – [Na⁺] – 2 [Mg²⁺]
- [Alk] = –[Aci] = [Na⁺] + 2 [Mg²⁺] – 2 [SO₄²⁻] – [Cl⁻]
- [Aci]_{calculated} = 2 [Fe²⁺]/56 + 3 [Fe³⁺]/56 + 3 [Al]/27 + 2 [Mn]/55 + 2 [Zn]/65 + 1000 (10^{-pH}), mol L⁻¹

6

Weak Acids and Bases

- Carbon acid is a weak acid resulting from the dissolution of CO₂ in water
- Stepwise dissociation
- Partly protonated, partly deprotonated species:
 - CO₂ (g) + H₂O \leftrightarrow H₂CO₃ log K_H = –1.27
 - H₂CO₃ \leftrightarrow HCO₃⁻ + H⁺ log K₁ = –6.35
 - HCO₃⁻ \leftrightarrow CO₃²⁻ + H⁺ log K₂ = –10.3
 - H₂O \leftrightarrow H⁺ + OH⁻ log K_W = –14.0

for all K $\vartheta = 25^\circ\text{C}; I = 0 \text{ mol}$
- at pH 5.6 [HCO₃⁻] substantially increases (\nearrow titration curve)



6

Thermodynamic Laws

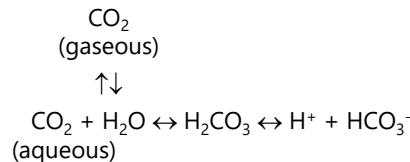
- Carbon acid balance (mass action law)

$$K_H = 10^{-1.27} = \frac{[\text{H}_2\text{CO}_3]}{[\text{H}_2\text{O}] p\text{CO}_2(\text{g})} \quad (\vartheta = 25^\circ\text{C}; I = 0 \text{ mol}; p\text{CO}_2 = 10^{-3.5} \text{ atm})$$

$$K_1 = 10^{-6.35} = \frac{[\text{HCO}_3^-][\text{H}^+]}{[\text{H}_2\text{CO}_3]} \quad (\vartheta = 25^\circ\text{C}; I = 0 \text{ mol})$$

$$K_2 = 10^{-10.3} = \frac{[\text{CO}_3^{2-}][\text{H}^+]}{[\text{HCO}_3^-]} \quad (\vartheta = 25^\circ\text{C}; I = 0 \text{ mol})$$

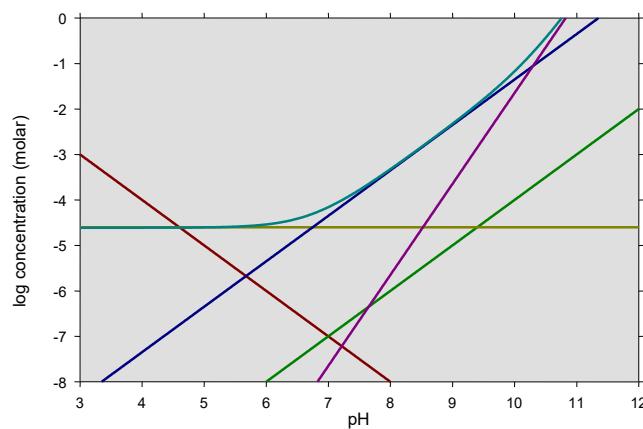
$$K_W = 10^{-14} = [\text{H}^+][\text{OH}^-] \quad (\vartheta = 25^\circ\text{C}; I = 0 \text{ mol})$$



6

Distribution of Carbon Species

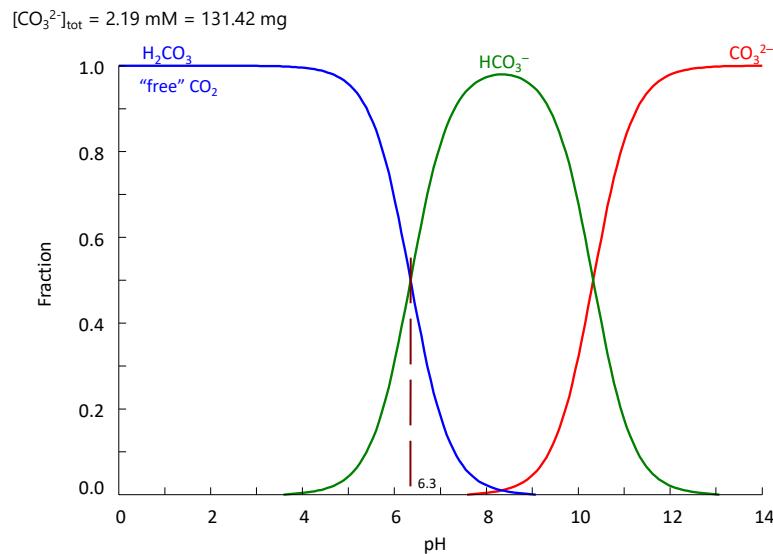
— $\log[\text{H}^+]$
 — $\log[\text{OH}^-]$
 — $\log[\text{H}_2\text{CO}_3]$
 — $\log[\text{HCO}_3^-]$
 — $\log[\text{CO}_3^{2-}]$
 — ΣC



- $\log[\text{H}^+] = -\text{pH}$
- $\log[\text{OH}^-] = -14 + \text{pH}$
- $\log[\text{H}_2\text{CO}_3] = -1.27 - \log p\text{CO}_2 \quad p\text{CO}_2 = -\log P = -\log 0.00045 = 3.347$
- $\log[\text{HCO}_3^-] = -6.35 + \log[\text{H}_2\text{CO}_3] + \text{pH}$
- $\log[\text{CO}_3^{2-}] = -10.3 + \log[\text{HCO}_3^-] + \text{pH}$

6

BJERRUM plot of Inorganic Carbon Species



Medusa Hydra Geochemical Software; Ignasi Puigdomenech

2010 – 2013



75

75

6

Mass and charge balance

- Ground water is always electro-neutral:

$$\sum_{\text{eq}} [\text{positive charged ions}] = \sum_{\text{eq}} [\text{negative charged ions}]$$
- Charge balance results of the summation of all cations and anions of all strong and weak acids and bases:

$$[\text{H}^+] + [\text{Na}^+] + [\text{K}^+] + 2 [\text{Ca}^{2+}] + 2 [\text{Mg}^{2+}] = \\ = [\text{OH}^-] + [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{Cl}^-] + [\text{NO}_3^-] + 2 [\text{SO}_4^{2-}]$$
- Rearranging results in (strong acids and bases to the left side):

$$[\text{Na}^+] + [\text{K}^+] + 2 [\text{Ca}^{2+}] + 2 [\text{Mg}^{2+}] - [\text{Cl}^-] - [\text{NO}_3^-] - 2 [\text{SO}_4^{2-}] = \\ = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$
- And, finally, expressed as a term of the bicarbonate buffer system:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

Mine Water Chemistry

76

6

Bicarbonate Buffer System

- Alkalinity in relation to the bicarbonate buffer system:

$$[\text{Alk}] = [\text{HCO}_3^-] + 2 [\text{CO}_3^{2-}] + [\text{OH}^-] - [\text{H}^+]$$

- Conservation of matter for HCO_3^- , CO_3^{2-} , OH^- results in a relation between **alkalinity** and **pH-value**:

$$[\text{Alk}] = \frac{p\text{CO}_2(\text{g}) K_1}{[\text{H}^+]} + \frac{[\text{HCO}_3^-] K_2}{[\text{H}^+]} + \frac{K_w}{[\text{H}^+]} - [\text{H}^+]$$

- for $6 < \text{pH} < 9$ the following simplification applies

$$[\text{CO}_3^{2-}], [\text{OH}^-], [\text{H}^+] \ll [\text{HCO}_3^-]$$

- consequently

$$[\text{Alk}] = [\text{HCO}_3^-] \text{ for most } \textit{natural waters}$$

6

Relation to the pH-value

- Within certain pH ranges, the relation between alkalinity and pH-value can be simplified. In the case of acidic mine water the following simplification can be applied to:

$$[\text{Alk}] \approx \frac{[\text{H}_2\text{CO}_3] K_1}{[\text{H}^+]} - [\text{H}^+] \text{ mol L}^{-1} \quad (\text{pH} < 8.3)$$

- solving the equation for $[\text{H}^+]$:

$$[\text{H}^+] = \frac{-[\text{Alk}] + \sqrt{[\text{Alk}]^2 + 4 [\text{H}_2\text{CO}_3] K_1}}{2}$$

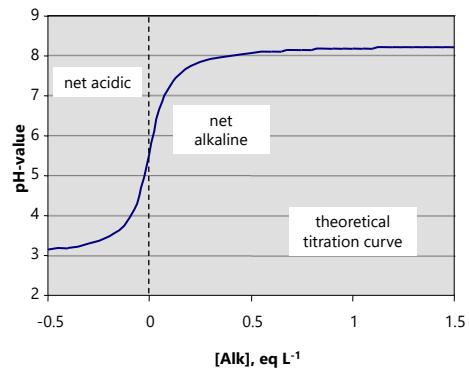
6

pH-Value and Alkalinity

- Water usually between pH 7 and 8
- Within broad pH-ranges water is of good quality and consequently good bioactivity
- Acidic water consumes alkalinity and results in low pH-values
- Under acidic conditions, that means at pH < 5.6, the pH-decreases rapidly and metals will dissolve
- High mobility and bioavailability

Mine Water Chemistry

79



Younger et al. 2002, p. 90



79

6

Mixing of Mine and Surface Waters

- The mixing of mine water with ground or surface water is conservative, because cations and anions won't interact with each other (no chemical interactions):

$$[\text{Alk}]_M = \frac{V_M (-[\text{Aci}]_M) + V_R ([\text{Alk}]_R)}{V_M + V_R}$$

V_M quantity of mine water, $\text{m}^3 \text{s}^{-1}$

V_R quantity of surface water, $\text{m}^3 \text{s}^{-1}$

$[\text{Aci}]_M$ = acidity of mine water, mmol L^{-1}

$[\text{Alk}]_M$ = alkalinity downstream of mine water discharge

$[\text{Alk}]_R$ = alkalinity of surface water, mmol L^{-1}

Mine Water Chemistry

80



Chemical-Thermodynamic ("Geochemical") Models

- A large number of models available
 - PHREEQC
 - WATEQ4F
 - MINTEQA2
 - CE-QUAL-W2
 - EPA-NET
 - GOLDSIM
 - KYBL-7
 - NETPATH
 - SOLMINEQ
 - Geochemists Workbench (GWB)

Temperature =	25.0 C	Pressure =	1.013 bars
pH =	8.341	log fO2 =	-0.699
Eh =	0.7255 volts	pe =	12.2638
Ionic strength =	0.652142		
Charge imbalance =	0.000117 eq/kg (0.01027% error)		
Activity of water =	0.982034		
Solvent mass =	1.0000 kg		
Solution mass =	1.0364 kg		
Mineral mass =	0.00000 kg		
Solution density =	1.029 g/cm ³		
Solution viscosity =	0.010 poise		
Chlorinity =	0.565633 molal		
Dissolved solids =	35075 mg/kg sol'n		
Hardness =	6338.64 mg/kg sol'n as CaCO ₃		
carbonate =	119.70 mg/kg sol'n as CaCO ₃		
non-carbonate =	6218.94 mg/kg sol'n as CaCO ₃		
Carbonate alkalinity =	119.70 mg/kg sol'n as CaCO ₃		
Water type =	Na-Cl		
Bulk volume =	1.01e+03 cm ³		
Fluid volume =	1.01e+03 cm ³		
Mineral volume =	0.000 cm ³		
Inert volume =	0.000 cm ³		
Porosity =	100. %		
Permeability =	98.7 cm ²		

Example (1/5)

Working example

The following mine water analyses in mg/L shows, that sulfate and copper are abundant. Both are a result of pyrite (FeS₂) and copper pyrite (CuFeS₂) weathering. Assumed, that no natural attenuation takes place ("no buffering"), the number of protons originating for the weathering shall be equal to the pH-value. Calculate the acidity due to the di-sulfide weathering and determine the degree of neutralization.

pH	7.6	SO ₄ ²⁻	1350	Ca	271	Mg	180
Al	0.5	Cu	0.2	Fe	7	Mn	4
Na	511	K	43	Si	30	Cl	142

analyses Niederschlema/Alberoda (Wismut GmbH) 11.8.1994:
366b (m-331). Also 4.3 mg L⁻¹ U and 4.2 mg L⁻¹ As

6

Example (2/5)

- Calculation of sulfate and copper molecular weight

element	S	O	Cu
molar mass	32.065	15.9994	63.546, g mol ⁻¹

$$M_{\text{SO}_4^{2-}} = 32.065 + 4 \cdot 15.9994 = 96.063 \text{ g mol}^{-1}$$

- Molar concentration of sulfate and copper in the mine water

$$[\text{SO}_4^{2-}] = 1350 / 96.063 = 14.05 \text{ mmol L}^{-1}$$

$$[\text{Cu}] = 0.2 / 63.546 = 0.003 \text{ mmol L}^{-1}$$

- Release of sulfate from pyrite ($S_{\text{Py}} - S_{\text{CuPy}}$)

$$[\text{SO}_4^{2-}]_{\text{Py}} = [\text{SO}_4^{2-}]_{\text{T}} - 2 [\text{Cu}^{2+}]$$

$$[\text{SO}_4^{2-}]_{\text{Py}} = 14.05 - 2 \cdot 0.003 = 14.04 \text{ mmol L}^{-1}$$



6

Example (3/5)

- Protons from pyrite weathering 2 protons per mole of Fe, assumed that pyrite weathers to sulfate and ochre

$$[\text{H}^+] = [\text{SO}_4^{2-}]_{\text{Py}} = 14.04 \text{ mmol L}^{-1}$$

Annotation the 7 mg L⁻¹ of iron (0.13 mmol L⁻¹) prove, that nearly all Fe²⁺ from pyrite (7.02 mmol L⁻¹ = 392 mg L⁻¹) precipitates as ochre

6

Example (4₅)

5. pH-value from proton activity

$$\text{pH} = -\log[\text{H}^+] = -\log[1.404 \cdot 10^{-2}] = 1.9$$

The pH-value measured is 7.6 and therefore ≈ 6 "units" above the pH calculated. Therefore, buffering must be assumed, resulting from the carbonate and silicate weathering. These reactions can be proved by the existence of "base cations" (Na^+ , Ca^{2+} , K^+ , Mg^{2+}).

$$\begin{aligned} [\text{Aci}]_{\text{calculated}} &= 23 \text{ mg CaCO}_3 (0.5 \text{ mmol}) \\ [\text{Alk}]_{\text{calculated}} &= 308 \text{ mg CaCO}_3 (6.2 \text{ mmol}) \end{aligned}$$

$$[\text{Aci}]_{\text{calculated}} = 50 \{2 [\text{Fe}^{2+}]/56 + 3 [\text{Fe}^{3+}]/56 + 3 [\text{Al}]/27 + 2 [\text{Mn}]/55 + 2 [\text{Zn}]/65 + 1000 (10^{-\text{pH}})\}$$

$$[\text{Alk}] \approx \frac{[\text{H}_2\text{CO}_3^-]K_1}{[\text{H}^+]} - [\text{H}^+] \text{ mol L}^{-1} \quad (\text{pH} < 8.3)$$

6

Example (5₅)

6. Calculate the annual sulfate and calcite flux from the mine discharge with a quantity $Q = 220 \text{ L s}^{-1}$

$$[\text{SO}_4^{2-}]_{\text{Py}} = 0.014 \text{ mol L}^{-1}$$

$$[\text{Ca}^{2+}] = 0.271 \text{ g L}^{-1} = (0.271/40.078) \text{ mol L}^{-1} = 6.76 \cdot 10^{-3} \text{ mol L}^{-1}$$

7. Multiply concentration with mine water make

$$F_S = Q \cdot [\text{SO}_4^{2-}]_{\text{Py}} = 220 \text{ L s}^{-1} \cdot 0.014 \text{ mol L}^{-1} = 3.08 \text{ mol s}^{-1}$$

$$F_{\text{Ca}} = Q \cdot [\text{Ca}^{2+}] = 220 \text{ L s}^{-1} \cdot 6.76 \cdot 10^{-3} \text{ mol L}^{-1} = 1.49 \text{ mol s}^{-1}$$

8. Annual weathering rate pyrite and calcite ($1 \text{ a} = 3.16 \cdot 10^7 \text{ s}$)

$$R_{\text{Py}} = \frac{1}{2} F_S = 1.54 \text{ mol s}^{-1} = 4.86 \cdot 10^7 \text{ mol y}^{-1} = 5850 \text{ t FeS}_2$$

$$R_{\text{Calcit}} = F_{\text{Ca}} = 1.49 \text{ mol s}^{-1} = 4.70 \cdot 10^7 \text{ mol y}^{-1} = 4700 \text{ t CaCO}_3$$

Literature

- Nordstrom, D. K. (1977) Hydrogeochemical and microbiological factors affecting the heavy metal chemistry of an acid mine drainage system. – 230 p.; United States (Degree Doctoral).
- Parizek, R. R. & Tarr, E. G. (1972) Mine drainage pollution prevention and abatement using hydrogeological and geochemical systems. Paper presented at the 4th Symposium on Coal Mine Drainage Research, Pittsburgh. – p. 56–82; Pittsburgh (Bituminous Coal Res. Inc.).
- Strömborg, B. & Banwart, S. (1994) Kinetic modelling of geo-chemical processes at the Aitik mining waste rock site in northern Sweden. – Applied Geochemistry, 9 583–595; Oxford.
- Stumm, W. & Morgan, J. I. (1996) Aquatic chemistry – Chemical Equilibria and Rates in Natural Waters. – 3rd edn., 1022 p.; New York (Wiley & Sons).
- Wolkersdorfer, Ch. (2008) Water Management at Abandoned Flooded Underground Mines – Fundamentals, Tracer Tests, Modelling, Water Treatment. – 466 p.; Heidelberg (Springer).
- www.wolkersdorfer.info/helpful-lines.html