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From Ground Water to Mine Water

Environmental Hydrogeology in Mining

Mine Water Geochemistry

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South African Research Chair for Acid Mine Drainage Treatment

From Ground Water to Mine Water

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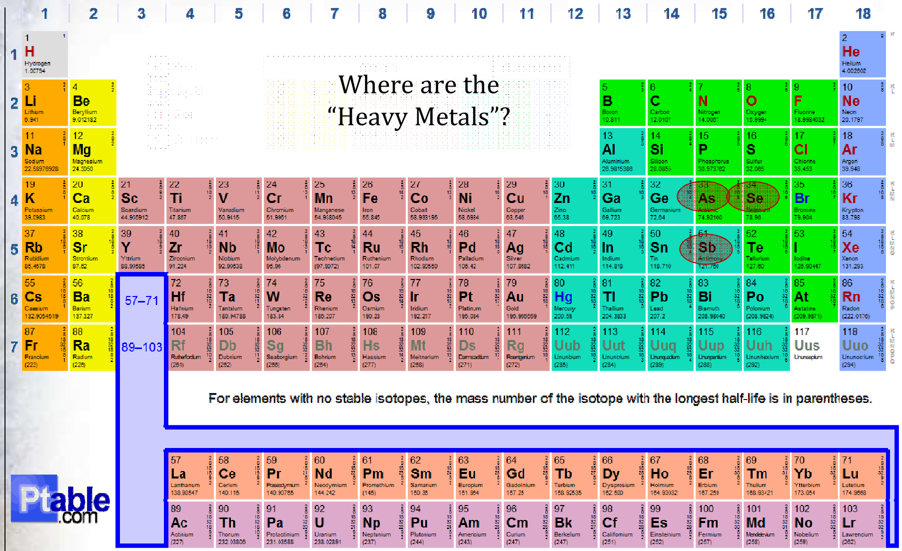
From Ground Water to Mine Water

Periodic Table of the Elements



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From Ground Water to Mine Water

Periodic Table of the Elements

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Black Sabbath – live evil: LP Cover (1982) | Iron Man (1970)

Mine Water Geochemistry

Why to deal with mine water chemistry?

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Cape Breton Island/Canada: Mine Water Outfall

Mine Water Geochemistry

Why to deal with mine water chemistry?

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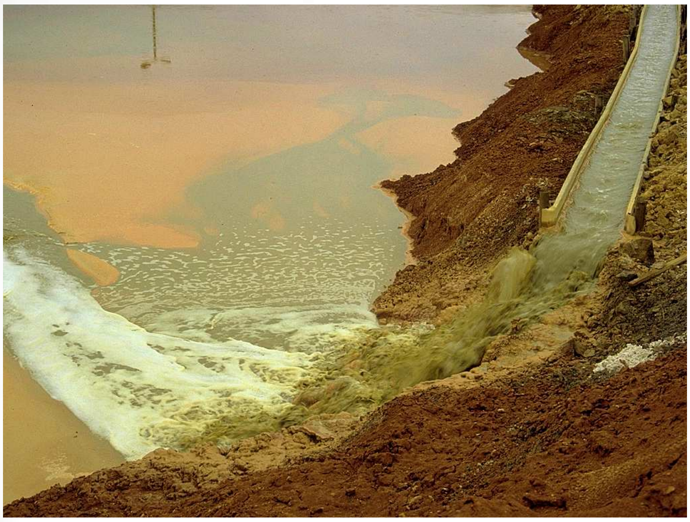
Eagle Picher Superfund Site/USA: Mark R. Boardman

Mine Water Geochemistry

Why to deal with mine water chemistry?



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Former Königstein Uranium Mine / Saxony

Mine Water Geochemistry

Why to deal with mine water chemistry?

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Pfunderer Berg/Southern Tyrol: Armin Hanneberg

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Georgi Unterbau / Tyrol

Mine Water Geochemistry

Why to deal with mine water chemistry?

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

Mine Water Geochemistry

Factors to be taken into Account

- Source — Pathway — Target-Concept
- Type of mine water
  - AMD: acid mine drainage (< ≈ pH 6)
  - circumneutral mine drainage (> ≈ pH 6 – 8)
  - SD: saline mine drainage (> ≈ 1000 mgL^{-1})
- Pyrite (di-sulphide) weathering
  - pH-dependence of metal dissolution
- 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

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Mine Water Geochemistry

What affects Mobility and Bioavailability

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

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Source—Pathway—Target-Concept

- Sources of contamination
  - Acidity: pyrite (“di-sulphide”) weathering
  - Metal ions: sulphide weathering
  - Chemical reactants (ore processing)
  - Organic substances (*e.g.* timber impregnation)
- Pathways
  - Alkalinity (calcite, alumosilicate weathering)
  - Precipitation, sorption of metal ions
  - ochre precipitation
- “Targets”
  - Surface water
  - Ground water

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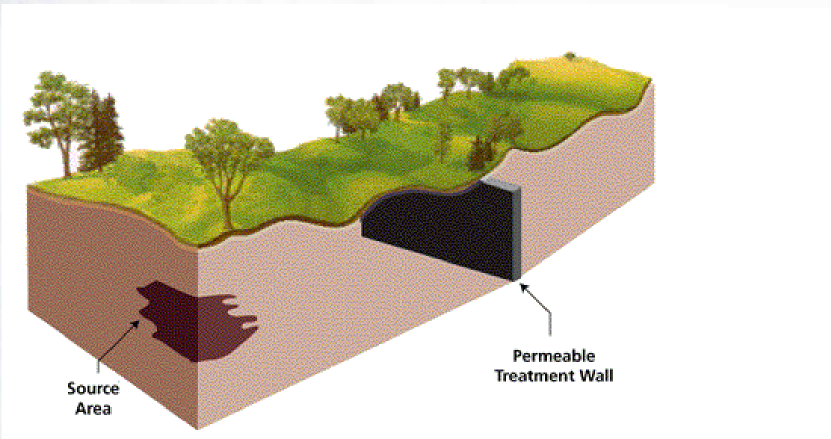
Mine Water Geochemistry

Source—Pathway—Target-Concept



Source → Pathway → Target

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From US EPA

Mine Water Geochemistry

Source—Pathway—Target-Concept

Sources

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

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

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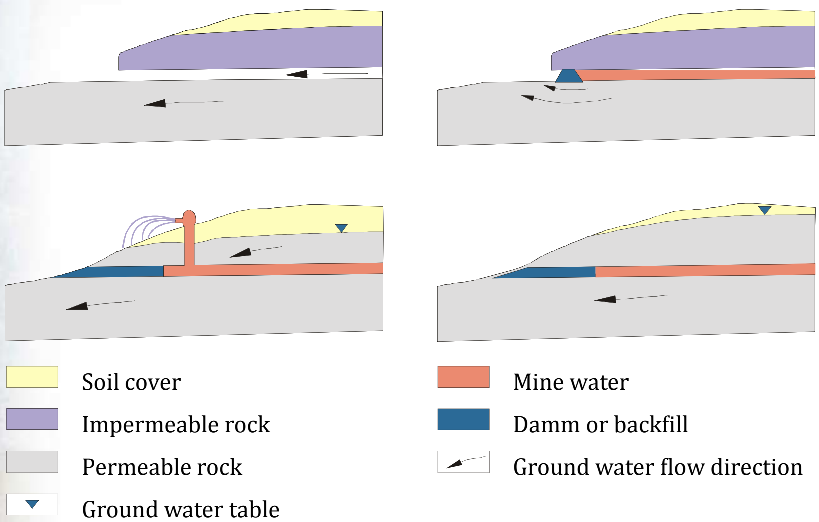
modified from GARD guide

Mine Water Geochemistry

Mine Closure Systems



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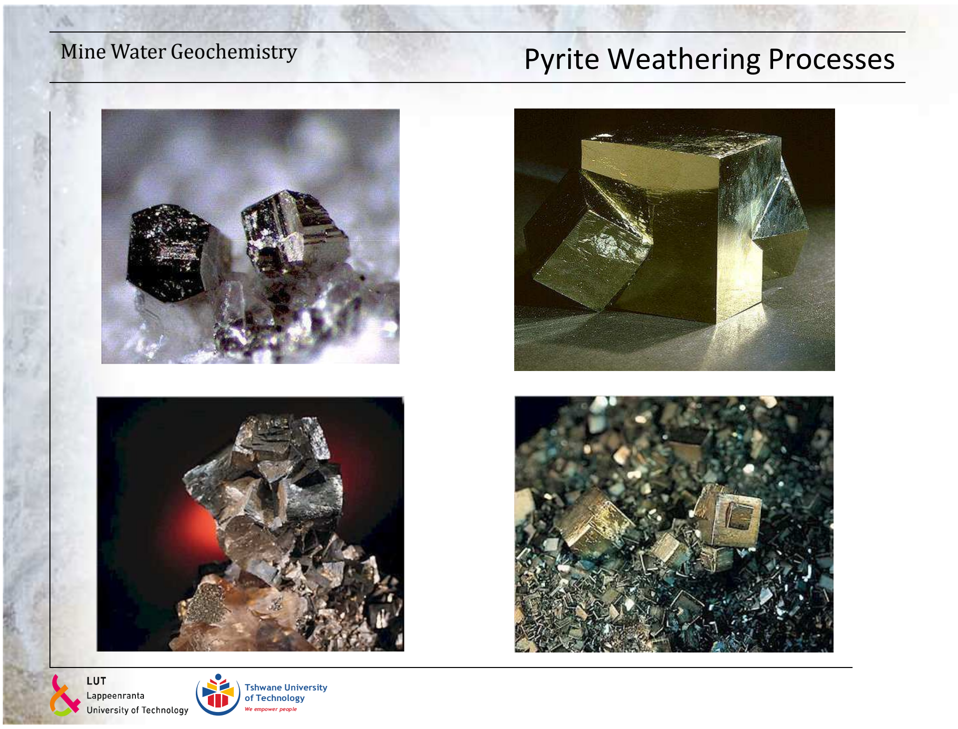
Fernandez-Rubio 1987


Mine Water Geochemistry
Pyrite Weathering Processes
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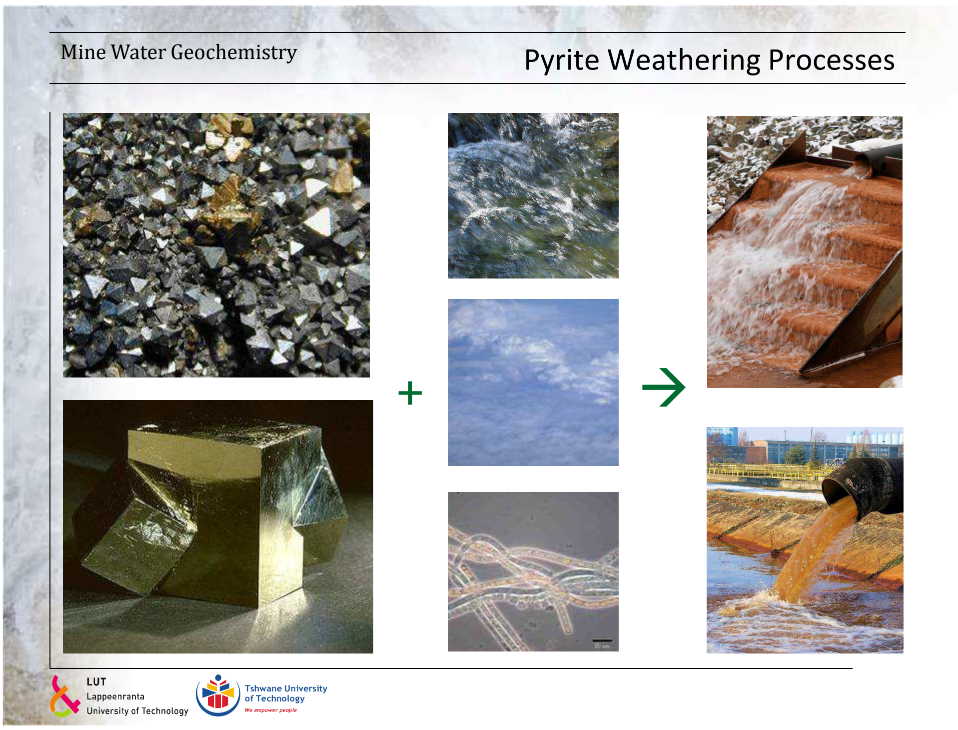
Mine Water Geochemistry
Pyrite Weathering Processes
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What to measure? On-site parameters …

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

Mine Water Geochemistry

Naming of parameters

- Physico-chemical parameters
  - Temperature
  - Electrical conductivity
  - pH
  - Redox-potential
  - Turbidity
- Chemical parameters
  - k_A, k_B, Oxygen content
  - Main ions
    - Cations: Na^+, K^+, Ca^{2+}, Mg^{2+}
    - Anions: Cl^-, NO_3^-, SO_4^{2-}, 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

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"master variables" in mine water

- pH
  - Proton-activity
  - pH = –log $\{H^+\}$
  - $FeS_2 + 3\frac{1}{2} O_2 + H_2O \rightarrow Fe^{2+} + SO_4^{2-} + 2\,H^+$
  - measurement
    - pH-meter
    - no units
    - no conversion
- E_h
  - Redox potential or
  - oxidation-reduction potential (ORP)
  - Electron-activity
  - pE = –log $\{e^-\}$
  - $U^{4+} \rightarrow U^{6+} + 2\,e^-$
  - $Fe^{2+} \rightarrow Fe^{3+} + 1\,e^-$
  - measurement
    - Redox-probe
    - mV (or V)
    - conversion to SHE

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Mine Water Geochemistry

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.*

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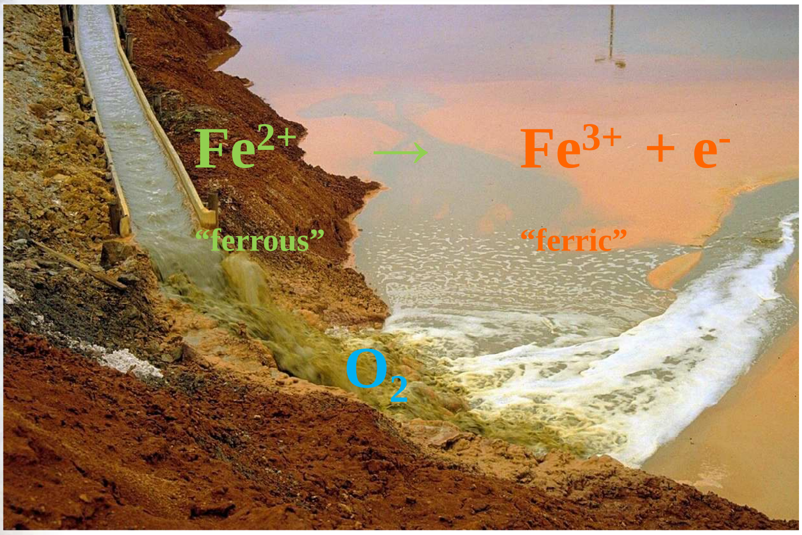
Mine Water Geochemistry

Redox Process



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Königstein uranium mine, Germany

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Redox potential – Nernst equation

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

with

E_h^0	reference condition, mV
R	gas constant, 8.3144621 J mol^{-1}K^{-1}
T	temperature, K
n	number of electrons involved, –
F	Faraday constant, 6 485.3365 C mol^{-1}

$$E_h = \frac{2.303RT}{nF}\text{pE}$$

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

$$Fe^{2+} \rightarrow Fe^{3+} + e\text{-}$$

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

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Mine Water Geochemistry

Redox potential – Correction to SHE

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

with

$E_{0(25\ °C)}$	redox potential corrected to SHE, mV
E_t	measured potential of secondary electrode, mV
T	temperature, °C
a, b	coefficient

Sensor Type	Coefficient *a*	Coefficient *b*
Mercury calomel KCl	67798	324
Ag/AgCl KCl 1 mol L^{-1}	62612	279
Ag/AgCl KCl 3 mol L^{-1}	50230	295

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Wolkersdorfer, 2008

Mine Water Geochemistry

Redox potential – Correction to SHE: Example

- Measured values (Ag/AgCl KCl 3 mol L^{-1}–electrode)
  - ORP -44 mV
  - Temp. 23.4 °C

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

$$0.198 \times (23.4 - 25) + \sqrt{50230 - 295 \times 23.4} =$$

$$0.198 \times (-1.6) + \sqrt{43327} =$$

$$-0.3168 + 208.1514 =$$

$$E_{0(25\ °C)} = -44\ \text{mV} + 208\ \text{mV} = 164\ \text{mV}$$

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

Sensor Type	Coefficient *a*	Coefficient *b*
Ag/AgCl KCl 3 mol L^{-1}	50230	295

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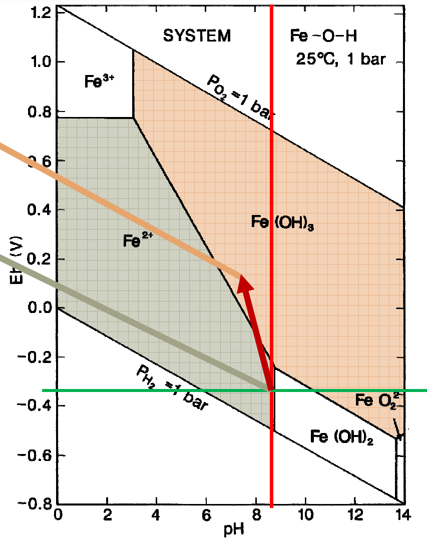
Redox Process



$Fe^{2+} \rightarrow Fe^{3+} + e^-$

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Brookins, 1988

Pyrite Weathering Processes (⅓)

(1) $2\ FeS_{2\,(s)} + 7\ O_{2(aq)} + 2\ H_2O \rightarrow 2\ Fe^{2+} + 4\ SO_4^{2-} + \boldsymbol{4\ H^+}$

(2) $2\ Fe^{2+} + ½\ O_2 + \boldsymbol{2\ H^+} \rightarrow 2\ Fe^{3+} + H_2O$

(3) $2\ Fe^{3+} + 6\ H_2O \leftrightarrow 2\ Fe(OH)_{3(s)} + \boldsymbol{6\ H^+}$

(4) $14\ Fe^{3+} + FeS_2 + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + \boldsymbol{16\ H^+}$

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

(1) and (2) are catalysed by bacteria: *e.g.*

Acidithiobacillus thiooxidans, Gallionella

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Pyrite Weathering Processes (2/3)

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Reiche Zeche shaft, Germany

Mine Water Geochemistry

Pyrite Weathering Processes (3/3)

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Straßberg silver mine, Germany

Mine Water Geochemistry

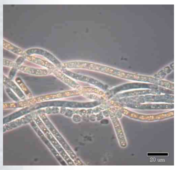
Bacterial Processes

Acidithiobacillus thiooxidans, Gallionella, Beggiatoa and *Thiothrix* increase the reaction speed 10^6-fold

$$ADP + P^- \leftrightarrow ATP \qquad \Delta G°' = +32\ kJ$$

$$2\ S^{2-} + 4\ H_3O^+ + O_2 \leftrightarrow 2\ S + 6\ H_2O$$

$$2\ S + 6\ H_2O + 3\ O_2 \leftrightarrow 2\ SO_4^{2-} + 4\ H_3O^+ \qquad \Delta G°' = -498\ kJ$$



	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

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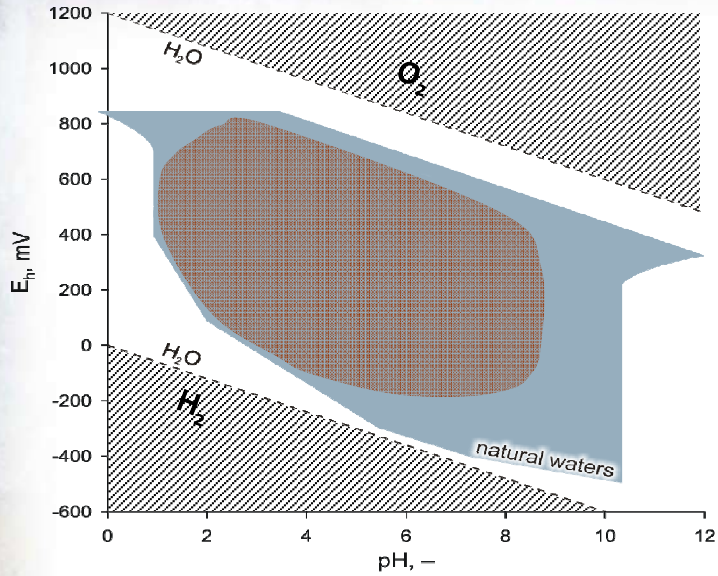
Bacterial Processes



Baas-Becking *et al.* 1960

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Sulphide Weathering

sphalerite	$ZnS_{(s)} + 2\ O_{2(aq)} \rightarrow Zn^{2+} + SO_4^{2-}$
galena	$PbS_{(s)} + 2\ O_{2(aq)} \rightarrow Pb^{2+} + SO_4^{2-}$
millerite	$NiS_{(s)} + 2\ O_{2(aq)} \rightarrow Ni^{2+} + SO_4^{2-}$
greenockite	$CdS_{(s)} + 2\ O_{2(aq)} \rightarrow Cd^{2+} + SO_4^{2-}$
covellin	$CuS_{(s)} + 2\ O_{2(aq)} \rightarrow Cu^{2+} + SO_4^{2-}$
copper pyrite	$CuFeS_{(s)} + 4\ O_{2(aq)} \rightarrow Cu^{2+} + Fe^{2+} + 2\ SO_4^{2-}$

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

Mine Water Geochemistry

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

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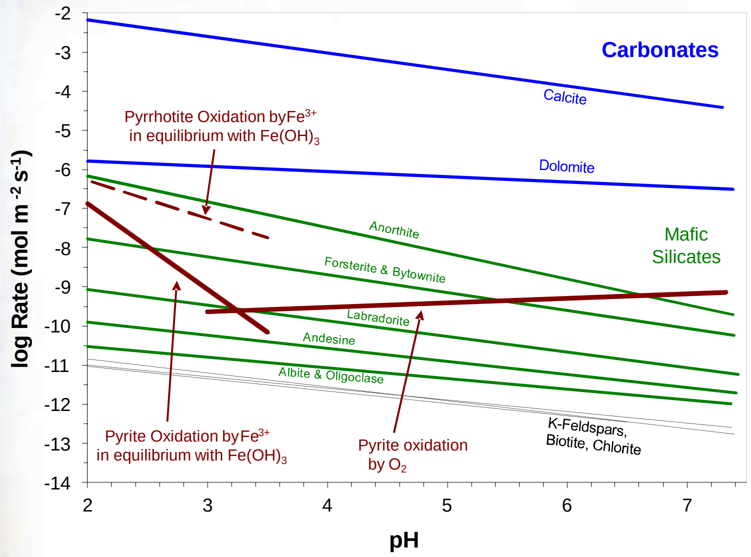
Prediction of Mine Flooding

Weathering Kinetics



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

Mine Water Geochemistry

pH-Values and Metal Concentrations

lokality	pH	$[SO_4^{2-}]$	[Fe]	[Al]	[Mn]	[Zn]	[Cu]
Iron Mountain, Cal (copper)	0.4	108000	18600	2320		2060	290
Iron Mountain, Cal (copper)	1.1	41000	7820	1410	11	1860	360
Pyrite mine	2.5	5110	1460	84	3	1	0.2
abandoned coal mine	3.6	1044	101	17	4	0.2	0.007
abandoned coal mine	4.2	1554	180	< 0.5	6	0.06	
waste rock dump (coal)	5.5	146	287	1	5	0.05	< 0.007
Straßberg Germany	6.3	359	31		6	0.9	0.08
abandoned coal mine	6.3	210	11	< 0.05	2	< 0.007	
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	1138	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}

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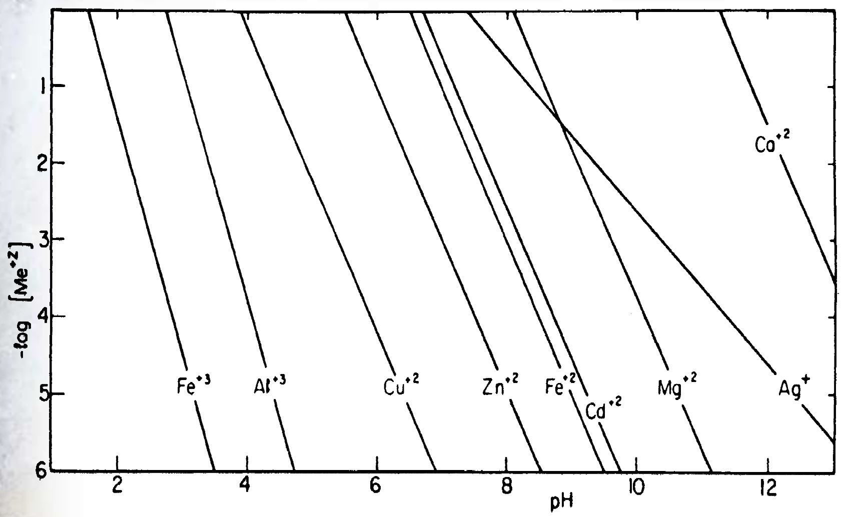
pH-Dependency of Metal Solubility



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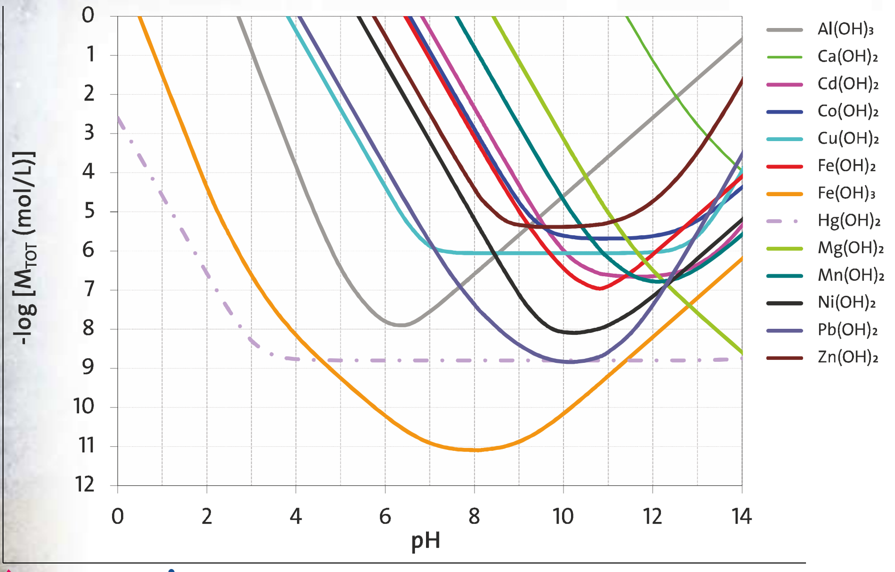
Stumm & Morgan 1996

Mine Water Treatment

pH-dependence of Me-oxide solubility



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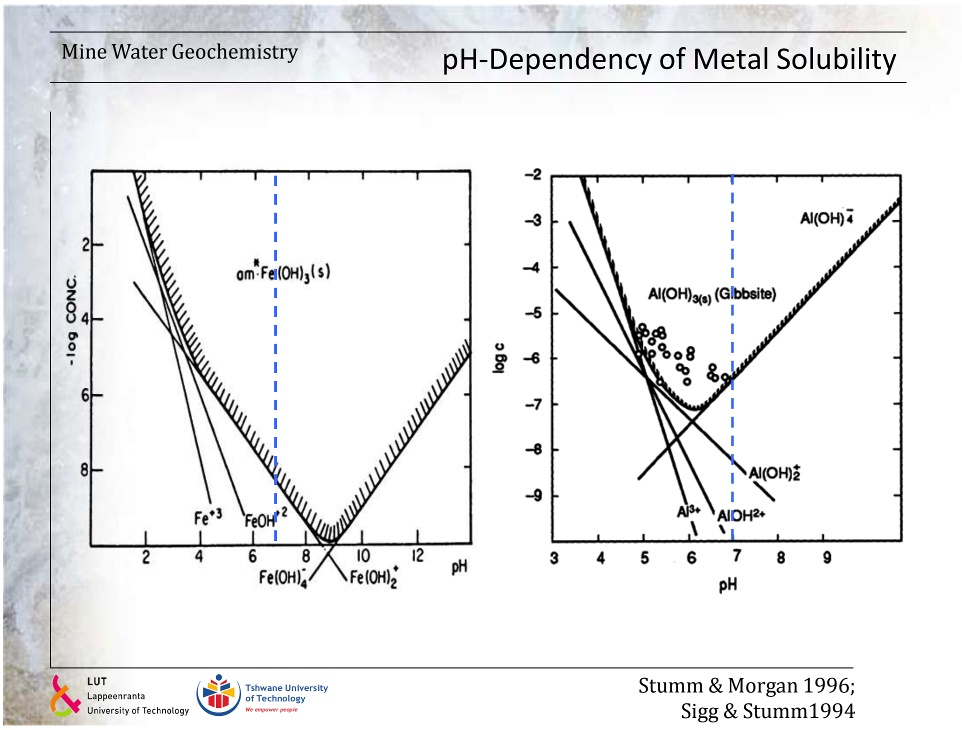
from Wolkersdorfer 2014, after Cravotta pers. comm.


Mine Water Geochemistry
pH-Dependency of Metal Solubility
am-Fe(OH)$_3$(s)
-log CONC.
Fe^{+3}
FeOH^{+2}
Fe(OH)$_4^-$
Fe(OH)$_2^+$
pH
Al(OH)$_4^-$
Al(OH)$_{3(s)}$ (Gibbsite)
log c
Al(OH)$_2^+$
Al^{3+}
AlOH^{2+}
pH
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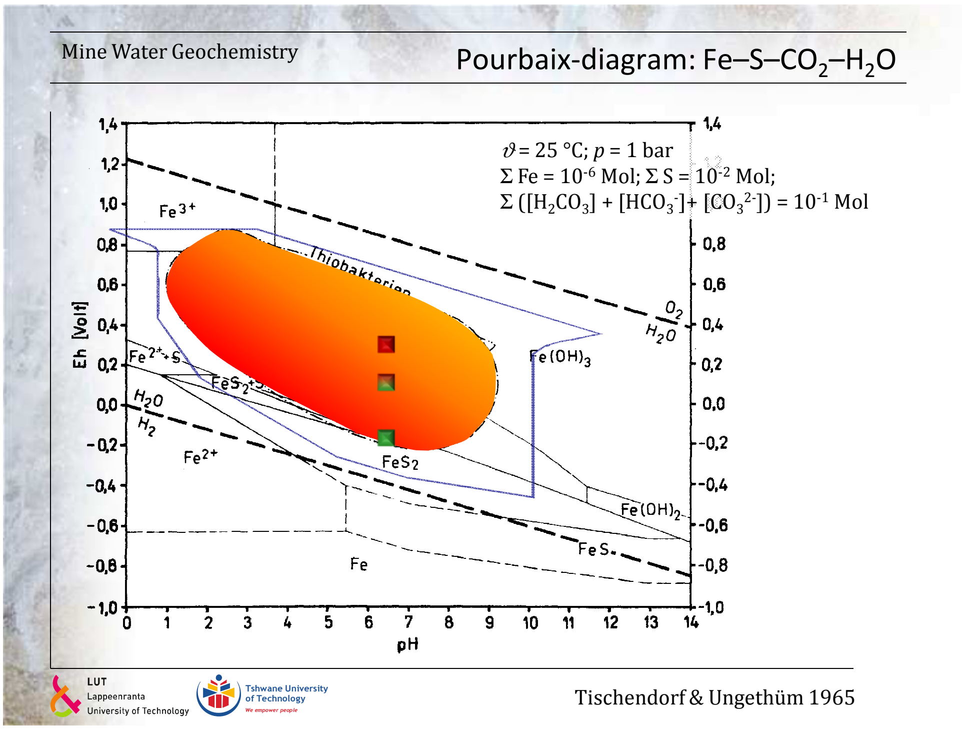
Stumm & Morgan 1996;
Sigg & Stumm1994


Mine Water Geochemistry
Pourbaix-diagram: Fe–S–CO$_2$–H$_2$O
ϑ = 25 °C; p = 1 bar
Σ Fe = 10^{-6} Mol; Σ S = 10^{-2} Mol;
Σ ([H$_2$CO$_3$] + [HCO$_3^-$]+ [CO$_3^{2-}$]) = 10^{-1} Mol
Fe^{3+}
Thiobakterien
O$_2$
H$_2$O
Fe(OH)$_3$
Fe^{2+}+S
FeS$_2$
H$_2$O
H$_2$
Fe^{2+}
FeS$_2$
Fe(OH)$_2$
FeS
Fe
Eh [Volt]
pH
LUT Lappeenranta University of Technology
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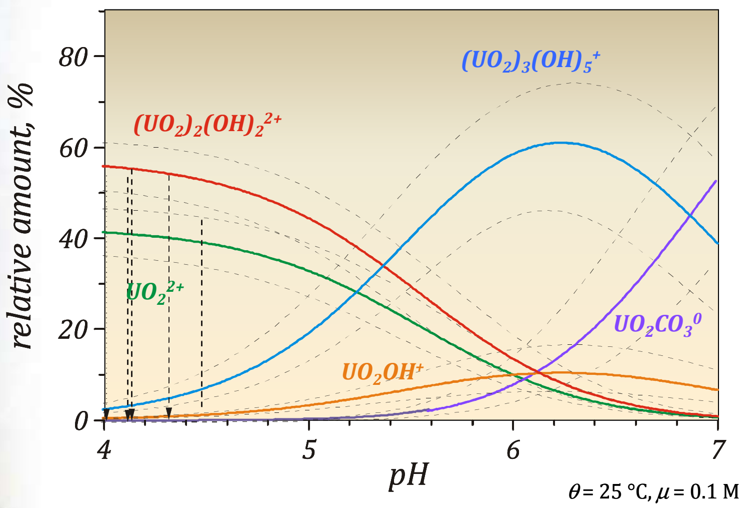
Tischendorf & Ungethüm 1965

Mine Water Geochemistry

Uranium Speciation (U^{6+})



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Meinrath 1998

Natural Attenuation

Weathering Processes

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

- Carbonates
- Feldspar
- Mica

mineral	formula	pH-buffer range
Calcite	$CaCO_3$	6.5 … 7.5
Dolomite	$CaMg[CO_3]_2$	6.5 … 7.5
Siderite	$FeCO_3$	4.8 … 6.3
Mix carbonates	$(Ca, Mg, Fe, Mn)CO_3$	4.8 … 6.3
Gibbsite	$Al(OH)_3$	4.0 … 4.3
Ferrihydrite	$Fe(OH)_3$	< 3.5
Goethite	α-FeOOH	1.3 … 1.8
K-Jarosite	$KFe_3[(OH)_6|(SO_4)_2]$	1 … 2 (laboritory experiments)
Alumino-silikates		1 … 2 (laboritory experiments)

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Natural Attenuation — Weathering Processes

- *Carbonates*
- Calcite (buffers at pH 6.5…7.5)
  - $CaCO_3 + \boldsymbol{H^+} \leftrightarrow Ca^{2+} + HCO_3^-$
- Dolomite (buffers at pH 6.5…7.5)
  - $CaMg[CO_3]_2 + 2\ \boldsymbol{H^+} \leftrightarrow Ca^{2+} + Mg^{2+} + 2\ HCO_3^-$
- Siderite (buffers at pH 4.8 …6.3)
  - $FeCO_3 + \boldsymbol{H^+} \leftrightarrow Fe^{2+} + HCO_3^-$
  - $Fe^{2+} + \frac{1}{4}\ O_2 + {}^5/_2\ H_2O \rightarrow Fe(OH)_3 + 2\ H^+$

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Natural Attenuation — Weathering Processes

- *Feldspar*
- K-Feldspar

  $KAlSi_3O_8 + \boldsymbol{H^+} + {}^9/_2\ H_2O \rightarrow 2\ H_4[SiO_4] + \frac{1}{2}\ Al_2Si_2O_5(OH)_4$
- Anorthite

  $CaAl_2Si_2O_8 + \boldsymbol{H^+} + H_2O \rightarrow Ca^{2+} + 2\ H_4[SiO_4] + \frac{1}{2}\ Al_2Si_2O_5(OH)_4$
- Albite

  $NaAlSi_3O_8 + \boldsymbol{H^+} + {}^9/_2\ H_2O \rightarrow Na^+ + 2\ H_4[SiO_4] + \frac{1}{2}\ Al_2Si_2O_5(OH)_4$

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Weathering Processes

- *Mica*
- Biotite

  $KMg_{3/2}Fe_{3/2}[AlSi_3O_{10}](OH)_2 + 7\ H^+ + ½\ H_2O \rightarrow$
  $K^+ + {}^3/_2\ Mg^{2+} + {}^3/_2\ Fe^{2+} + 2\ H_4[SiO_4] + ½\ Al_2Si_2O_5(OH)_4$
- Muscovite

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

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Keep in Mind: Mineralogy and Kinetics

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

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Secondary Minerals (1/2)

- Metal oxides and -hydroxides

Gibbsite	$Al(OH)_3$
Iron hydroxide	$Fe(OH)_3$
Zinc hydroxide	$Zn(OH)_2$

- Metal carbonates and hydroxy-carbonates

Cerrusite	$PbCO_3$
Malachite	$Cu_2(OH)_2(CO_3)$

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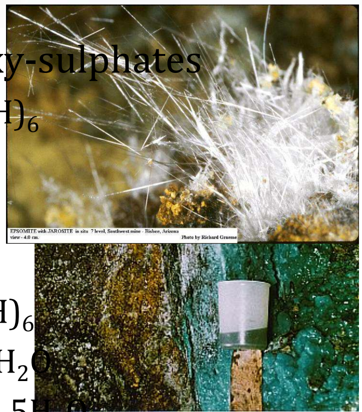
Immobilisation of Metals

Secondary Minerals (2/2)

- Metal sulphates and -hydroxy-sulphates

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	$Al_4SO_4(OH)_{10} \cdot 5H_2O$
Anglesite	$PbSO_4$



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Alpers; Graeme

Control of Contamination Source

- Contaminant load (*e.g.* metals, acidity, sulphate) depends on:
  - Red-Ox conditions (does O_2 exist)
  - Weathering rate
  - Oxygen transport (diffusion)
  - Dissolving (transport: remain in mine or transport to ecosphere)
  - Bacteria

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Mine Water Geochemistry

First Estimation

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

Q_{in} (Infiltration):

$$FeS_2 + {}^7/_2\, O_2 + H_2O \rightarrow Fe^{2+} + 2\, SO_4^{2-} + 2\, H^+$$
$$ZnS + 2\, O_2 \rightarrow Zn^{2+} + SO_4^{2-}$$
$$PbS + 2\, O_2 \rightarrow Pb^{2+} + SO_4^{2-}$$
$$NiS + 2\, O_2 \rightarrow Ni^{2+} + SO_4^{2-}$$
$$CuS + 2\, O_2 \rightarrow Cu^{2+} + SO_4^{2-}$$
$$CuFeS_2 + 2\, O_2 \rightarrow Cu^{2+} + Fe^{2+} + 2\, SO_4^{2-}$$

Q_{out} (mine water):

H^+, SO_4^{2-}, Fe^{2+}, Zn^{2+}, Pb^{2+}, Ni^{2+}, Cu^{2+}

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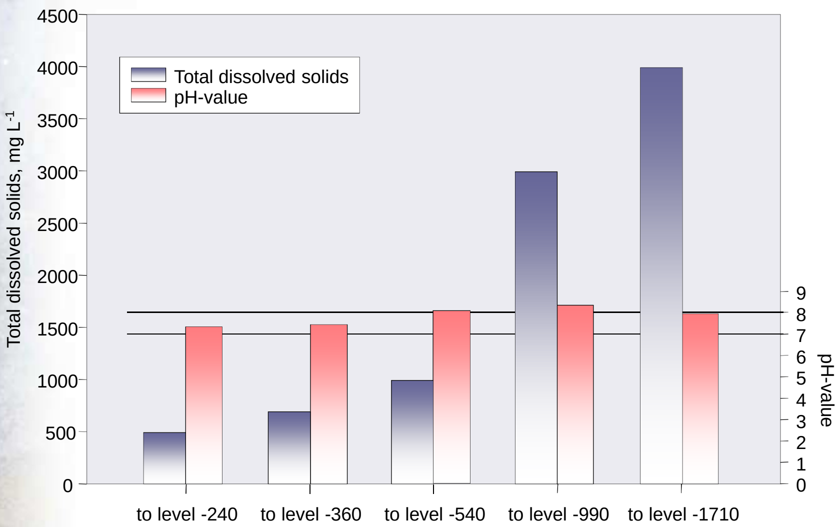
Mine Water Geochemistry

Niederschlema Uranium Mine



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Mine Water Geochemistry

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 ⇒ mine water is acidic
- Weathering rate alkalinity > acidity ⇒ mine water is alkaline
- Acidity: “base capacity” k_B
  Alkalinity: “acid capacity” k_A

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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*)

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

Strong Acids and Bases

- Complete dissociation
- Strong bases (base cation + OH^-)
  - $NaOH \leftrightarrow Na^+ + OH^-$
  - $Mg(OH)_2 \leftrightarrow Mg^{2+} + 2\ OH^-$
- Strong acids (acid anion + H^+)
  - $HCl \leftrightarrow Cl^- + H^+$
  - $H_2SO_4 \leftrightarrow SO_4^{2-} + 2\ H^+$
- [Aci] = "Σ [H^+] - Σ [OH^-]" = 2 [SO_4^{2-}] + [Cl^-] - [Na^+] – 2 [Mg^{2+}]
- [Alk] = -[Aci] = [Na^+] + 2 [Mg^{2+}] - 2 [SO_4^{2-}] - [Cl^-]
- $[Aci]_{calculated}$ = 2 [Fe^{2+}]/56 + 3 [Fe^{3+}]/56 + 3 [Al]/27 + 2 [Mn]/55 + 2 [Zn]/65 + 1000 (10^{-pH}), mol L^{-1}

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Acidity – Alkalinity

Weak Acids and Bases

- Carbon acid is a weak acid resulting from the dissolution of CO_2 in water
- Stepwise dissociation
- Partly protonated, partly deprotonated species:
  - $CO_2\ (g) + H_2O \leftrightarrow H_2CO_3$ $\log K_H = -1.27$
  - $H_2CO_3 \leftrightarrow HCO_3^- + H^+$ $\log K_1 = -6.35$
  - $HCO_3^- \leftrightarrow CO_3^{2-} + H^+$ $\log K_2 = -10.3$
  - $H_2O \leftrightarrow H^+ + OH^-$ $\log K_W = -14.0$

  for all K: ϑ = 25 °C; I = 0 mol

- at pH 5.6 [HCO_3^-] substantially increases (↗ titration curve)

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Acidity – Alkalinity

Thermodynamic Laws

- Carbon acid balance (mass action law)

$$K_H = 10^{-1.27} = \frac{[H_2CO_3]}{[H_2O]\ pCO_2(g)} \quad (\vartheta = 25\,°C;\ I = 0\ \text{mol};\ pCO_2 = 10^{-3.5}\ atm)$$

$$K_1 = 10^{-6.35} = \frac{[HCO_3^-][H^+]}{[H_2CO_3]} \quad (\vartheta = 25\,°C;\ I = 0\ \text{mol})$$

$$K_2 = 10^{-10.3} = \frac{[CO_3^{2-}][H^+]}{[HCO^{3-}]} \quad (\vartheta = 25\,°C;\ I = 0\ \text{mol})$$

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

CO_2
(gaseous)
↑↓
$CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-$
(aqueous)

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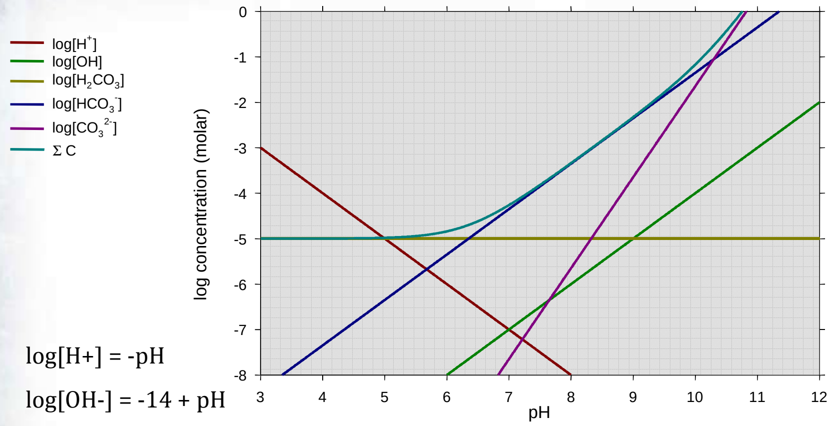
Acidity – Alkalinity

Distribution of Carbon Species



- log[H+] = -pH
- log[OH-] = -14 + pH
- $\log[H_2CO_3] = -1.27 + \log pCO_2$
- $\log[HCO_3^-] = -6.35 + \log[H_2CO_3] + pH$
- $\log[CO_3^{2-}] = -10.3 + \log[HCO_3^-] + pH$

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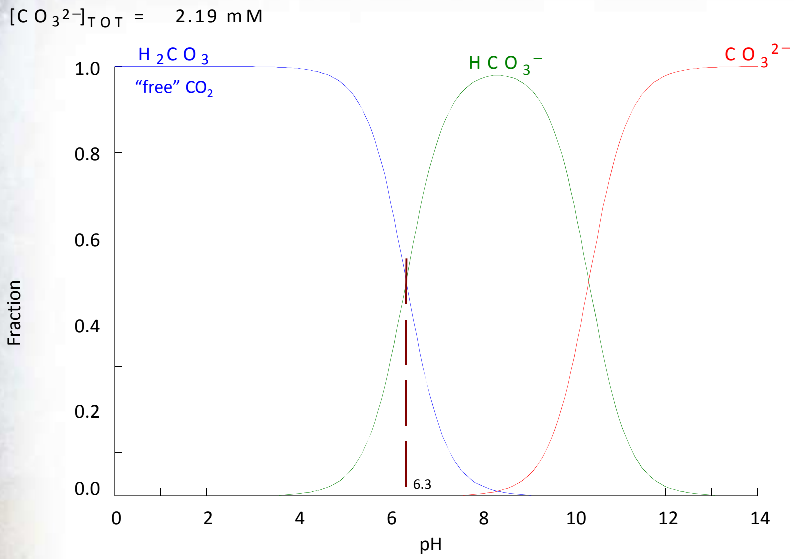
Acidity – Alkalinity

Distribution of Carbon Species



Medusa Hydra Geochemical Software; Ignasi Puigdomenech: 2010 – 2013

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Aqueous Solutions

Mass and charge balance

- Ground water is always electro-neutral:

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

  $[H^+] + [Na^+] + [K^+] + 2\ [Ca^{2+}] + 2\ [Mg^{2+}] =$
  $= [OH^-] + [HCO_3^-] + 2\ [CO_3^{2-}] + [Cl^-] + [NO_3^-] + 2\ [SO_4^{2-}]$
- Rearranging results in (strong acids and bases to the left side):

  $[Na^+] + [K^+] + 2\ [Ca^{2+}] + 2\ [Mg^{2+}] - [Cl^-] - [NO_3^-] - 2\ [SO_4^{2-}] =$
  $= [HCO_3^-] + 2\ [CO_3^{2-}] + [OH^-] - [H^+]$
- And, finally, expressed as a term of the bicarbonate buffer system:

  $[Alk] = [HCO_3^-] + 2\ [CO_3^{2-}] + [OH^-] - [H^+]$

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Acidity – Alkalinity

Bicarbonate Buffer System

- Alkalinity in relation to the bicarbonate buffer system:

  $[Alk] = [HCO_3^-] + 2\,[CO_3^{2-}] + [OH^-] - [H^+]$

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

$$[Alk] = \frac{pCO_2\,(g)\,K_1}{[H^+]} + \frac{[HCO_3^-]K_2}{[H^+]} + \frac{K_W}{[H^+]} - [H^+]$$

- for 6 < pH < 9 the following simplification applies

  $[CO_3^{2-}], [OH^-], [H^+] \ll [HCO_3^-]$

- consequently:

  $[Alk] = [HCO_3^-]$ for most *natural waters*

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Acidity – Alkalinity

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 waters the following simplification can be applied to:

$$[Alk] \cong \frac{[H_2CO_3]K_1}{[H^+]} - [H^+] \quad \text{mol L}^{-1} \quad (pH < 8.3)$$

- solving the equation for $[H^+]$:

$$[H^+] = \frac{-[Alk] + \sqrt{[Alk]^2 + 4\,[H_2CO_3]K_1}}{2}$$

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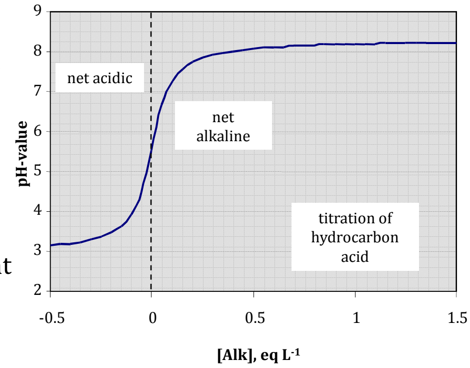
Acidity – Alkalinity

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



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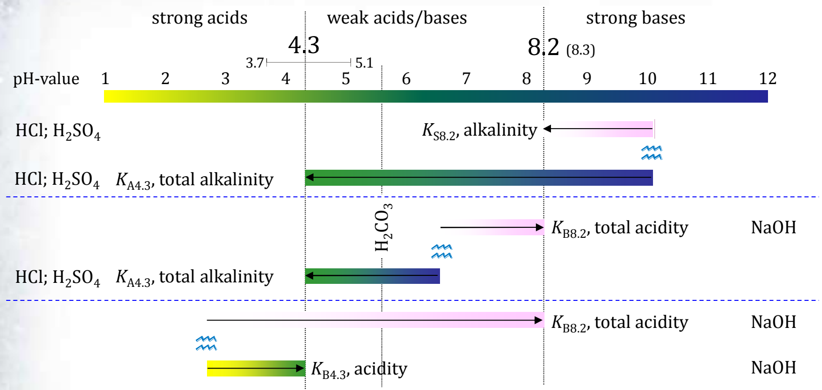
Acidity – Alkalinity

Acidity – Alkalinity



K_A acid capacity 8.2 (phenolphtalein): alkalinity (strong bases); old: p-value
K_A acid capacity 4.3 (methylred-bromcresolgreen): total alkalinity (weak/strong bases); old: m-value
K_B base capacity 8.2 (phenolphtalein): total acidity (weak/strong acids); old: -p-value
K_B base capacity 4.3 (bromphenolblue): acidity (strong acids) ; old: -m-value

1 [mmol L^{-1}] = 1 [meq L^{-1}] = ~~50.04 [mg L^{-1} CaCO$_3$]~~

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Acidity – Alkalinity

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):

$$[\mathrm{Alk}]_\mathrm{M} = \frac{V_\mathrm{M}(-[\mathrm{Aci}]_\mathrm{M}) + V_\mathrm{R}[\mathrm{Alk}]_\mathrm{R}}{V_\mathrm{M} + V_\mathrm{R}}$$

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

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

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

$[Alk]_M$= alkalinity downstream of mine water discharge

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

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Models

Chemical-Thermodynamic ("Geochemical") Models

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

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Example (1⁄4)

Working example

The following mine water analyses shows, that sulphate and copper are abundant. Both are a result of pyrite (FeS_2) and copper pyrite ($CuFeS_2$) 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-sulphide weathering and determine the degree of neutralization.

pH	7.6	SO_4^{2-}	1350	Ca	271	Mg	180
Al	0.5	Cu	0.02	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

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Mine Water Geochemistry

Example (2⁄4)

1. Calculation of sulphate and copper molecular weight

element	S	O	Cu
atomical mass	32.066	15.9994	63.546, g mol^{-1}

$M_{SO_4^{2-}}$ = 32.066 + 4· 15.9994 = 96.064 g mol^{-1}

2. Molar concentration of sulphate and copper in the mine water

$[SO_4^{2-}]$ = 1350 / 96.064 = 14.05 mmol L^{-1}

$[Cu]$ = 0.02 / 63.546 = 0.003 mmol L^{-1}

3. Release of sulphate from pyrite

$[SO_4^{2-}]_{Py} = [SO_4^{2-}]_T - 2\,[Cu^{2+}]$

$[SO_4^{2-}]_{Py}$ = 14.05 - 2· 0.003 = 14.04 mmol L^{-1}

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Mine Water Geochemistry

Example (3⁄4)

4. Protons from pyrite weathering: 2 protons, assumed that pyrite weathers to sulphate and ochre

   $[H^+] = 2\ [SO_4^{2-}]_{Py} = 2 \cdot 14.04$ mmol L^{-1} = 28.08 mmol L^{-1}

   Annotation: the 7 mg L^{-1} of iron (0.13 mmol L^{-1}) prove, that nearly all Fe^{2+} (14.04 mmol L^{-1} = 784 mg L^{-1}) precipitates as ochre

5. pH-value from proton activity

   $pH = -\log[H^+] = -\log[2.808 \cdot 10^{-2}] = 1.6$

   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+}). $[Aci]_{calculated}$ = 23 mg $CaCO_3$; $[Alk]_{calculated}$ = 308 mg $CaCO_3$

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

$$[Alk] \cong \frac{[H_2CO_3^-]K_1}{[H^+]} - [H^+] \quad \text{mol } L^{-1} \quad (pH < 8.3)$$

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Mine Water Geochemistry

Example (4⁄4)

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

   $[SO_4^{2-}]_{Py}$ = 0.014 mol L^{-1}

   $[Ca^{2+}]$ = 0.271 g L^{-1} = (0.271/40.08) mol L^{-1} = $6.76 \cdot 10^{-3}$ mol L^{-1}

7. Multiply concentration with mine water make

   $F_S = Q \cdot [SO_4^{2-}]_{Py}$ = 220 L $s^{-1} \cdot$ 0.014 mol L^{-1} = 3.08 mol s^{-1}

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

8. Annual weathering rate pyrite and calcite (1 y = $3.15 \cdot 10^7$ s)

   $R_{Py} = ½\ F_S$ = 1.54 mol s^{-1} = $4.85 \cdot 10^7$ mol y^{-1} = 5500 t FeS_2

   $R_{Calcit} = F_{Ca}$ = 1.49 mol s^{-1} = $4.69 \cdot 10^7$ mol y^{-1} = 4700 t $CaCO_3$

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Mine Water Geochemistry

Literature

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