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Geología
FACULTAD DE CIENCIAS
FÍSICAS Y MATEMÁTICAS
UNIVERSIDAD DE CHILE

GL5213 Hidrogeología
(hidrogeología = hidrodinámica, hidrogeoquímica y contaminación)

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Programa Semestre 2011/2012

- GL5230 Hidrogeología:
Flujo en medio poroso,
hidrogeoquímica y contaminación

Semestre 2012
Electivo: Aguas ácidas: Formación, control, remediación y prevención

Yanacocha
Chañaral
Pascua-Lama
Grasberg-Freeport
Sandoz – Schweizerhalle
Baia Mare - Rumanie
Bopal - Bophal
Bangladesh - arsenic
Aználcollar - Doñana
Seveso - Dioxine
Wismut – Uranium
Guarani
Runge
Petorca
Chernobyl
Ajka, Hungria
Madre de Dios, Peru-Bolivia

Web of Knowledge (solo ISI:
http://portal.isiknowledge.com/portal.cgi/wos?Init=Yes&SID=W2mI6AcA6553KhG6Bgk

Georef:
http://web5s.silverplatter.com/webspirs/start.ws?customer=udl&language=fr&databases=GE,NP,SJ
(tambien abstractos)

ScienceDirect (Elsevier): www.sciencedirect.com

Springer: www.springer.com

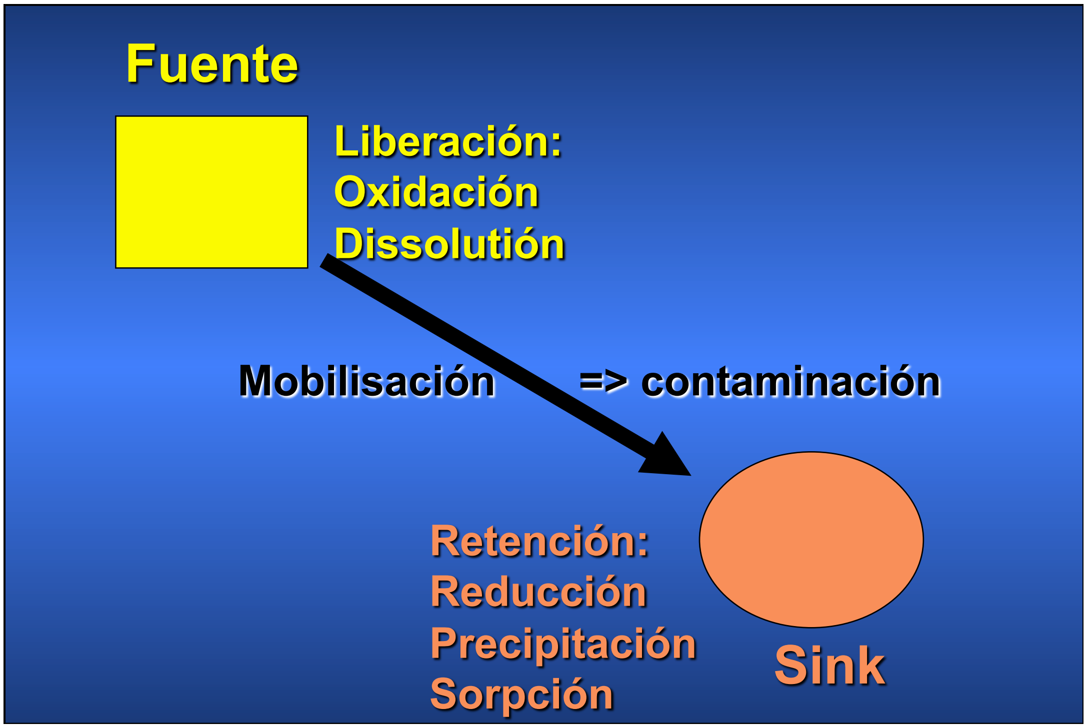
- Para entender el ciclo hidráulico hay que entender lo siguiente:

  - Evaporación y evapotranspiración
  - Meteorología
  - Procesos de escurrimiento y infiltración
  - Flujo de aguas subterráneas
  - Procesos geoquímicos

- Agua subterráneo: un recurso vulnerable?

  En Alemania y Europa no se creía hasta los años 60.
  - aumento de nitratos en acuíferos pocos profundos después de la II Guerra Mundial
  - aumento de pesticidas en acuíferos pocos profundos desde los 1960
  - Contaminación debido a basurales y depósitos químicos clandestinos
  - Contaminación por accidentes (Schweizerhalle, Seveso, Baia Mare, Chernobyl etc…)
  - Contaminación debido a la minería

  Y en Chile?



Fuente

Liberación:
Oxidación
Dissolutión

Mobilisación => contaminación

Retención:
Reducción
Precipitación
Sorpción

Sink

Tailings Dam failure
Aznalcóllar 25.4.1998, Spain

Baia Mare, Romania

Spread of the cyanide spill from Baia Mare - cyanide concentration values

Area of the ecological disaster

Date of cyanide spill 01.30.2000

	Measurement place:	Date:	Max. concentration:
1.	Szamos at Csenger	02.01.	32.6 mg/l cyanide
2.	Tisza at Lónya	02.03.	13.5 mg/l cyanide
3.	Tisza at Tiszalök	02.05.	3.7 mg/l cyanide
4.	Tisza at Kisköre	02.08.	3.8 mg/l cyanide
5.	Tisza at Szolnok	02.09.	3.2 mg/l cyanide
6.	Tisza at Tápé	02.11.	2.2 mg/l cyanide
7.	Tisza at Tiszasziget	02.11.	1.49 mg/l cyanide

Sanitary level: 0.1 mg/l cyanide

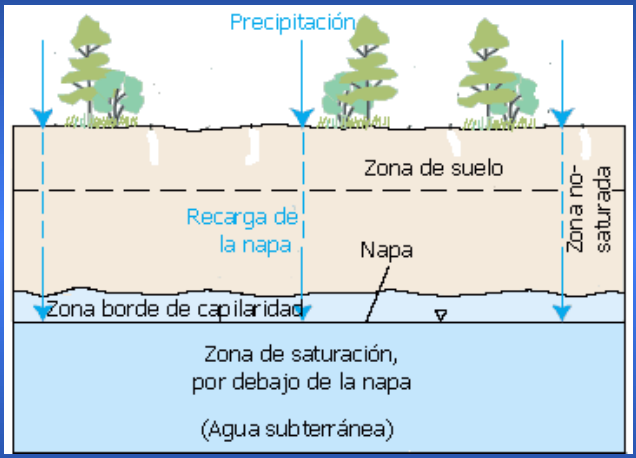
Source:
Ministry for Environmental Protection (Hungary)
Environmental Inspectorates
MTI Co. Media Data Bank

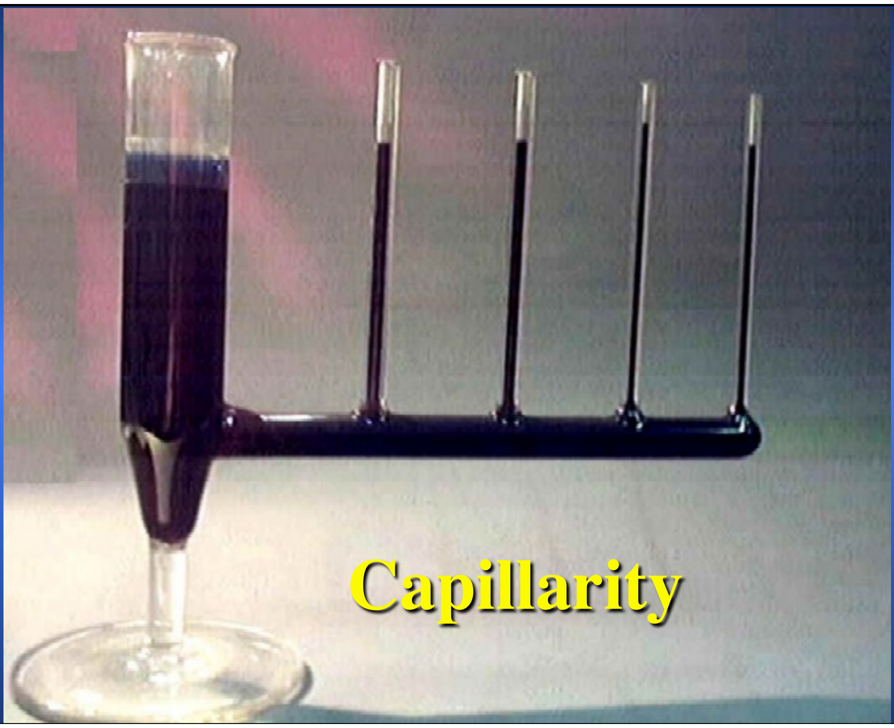
The spill reached Belgrade: 02.14.2000

Aguas Acidas de Roca
Acid Rock Drainage
(ARD)

Aguas Acidas Mineras
Acid Mine Drainage
(AMD)


6000 µg/L As





Capillarity

Ley de Jurin

La ley de Jurin define la altura que se alcanza cuando se equilibra el peso de la columna de líquido y la fuerza de ascensión por capilaridad. La altura h en metros de una columna líquida está dada por la ecuación:

$$h = \frac{2\gamma\cos\theta}{\rho g r}$$

Ángulo de contacto.

donde:

= tensión superficial interfacial (N/m)

θ = ángulo de contacto

ρ = densidad del líquido (kg/m³)

g = aceleración debida a la gravedad (m/s²)

r = radio del tubo (m)

Para un tubo de vidrio en el aire a nivel del mar y lleno de agua,

= 0,0728 N/m a 20 °C

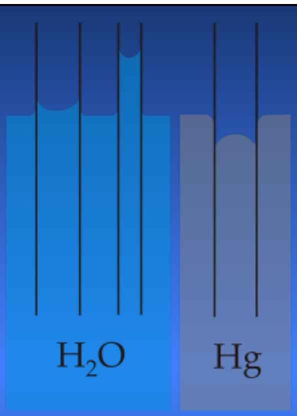
θ = 20°

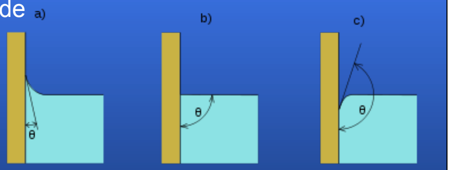
ρ = 1000 kg/m³

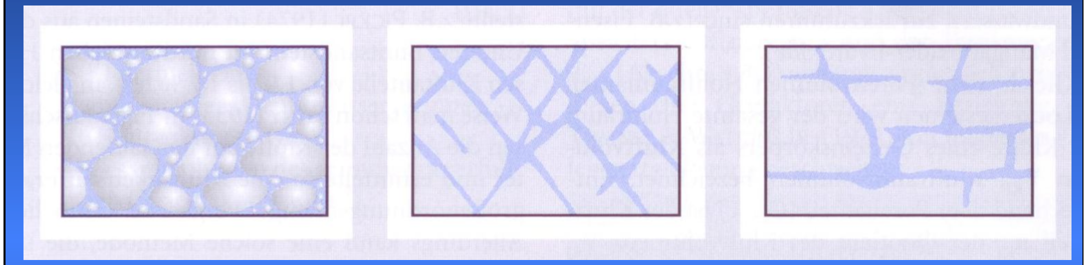
g = 9,80665 m/s²

entonces, la altura de la columna de agua, en metros, será:

Por ejemplo, en un tubo de 1 mm de radio, el agua ascenderá por capilaridad unos 14 mm.



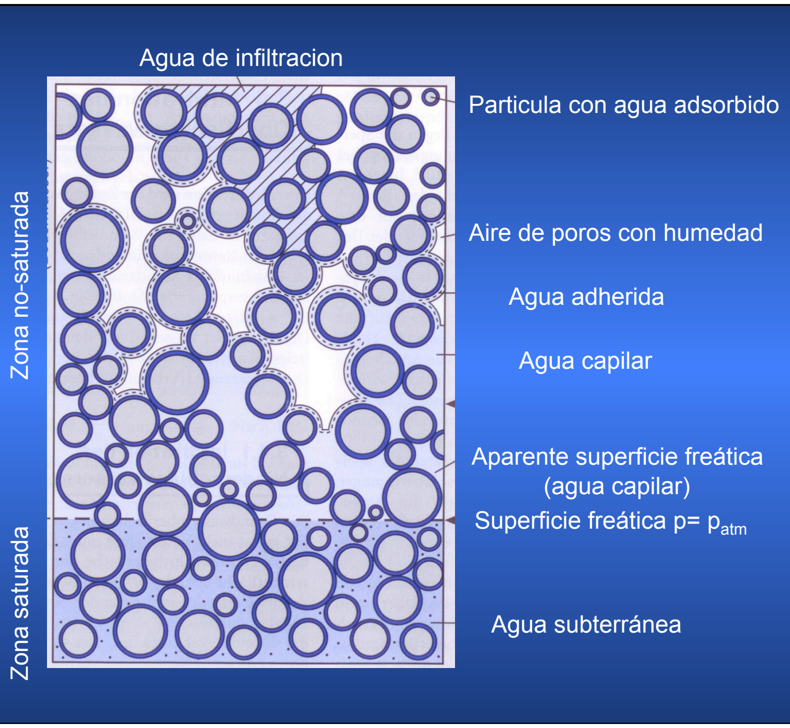




Poros
Arenas, gravas

Fracturas
Roca ignea

Cavidades
karst



- Tipos de Acuíferos:

  - relacionado al tipo de roca
  - hard rock -> fracturas (granita, andesita)
  - sedimentos -> poros (arena, gravas, limo)
  - porosidad doble -> fracturas y poros (areniscas)

- Definiciones:

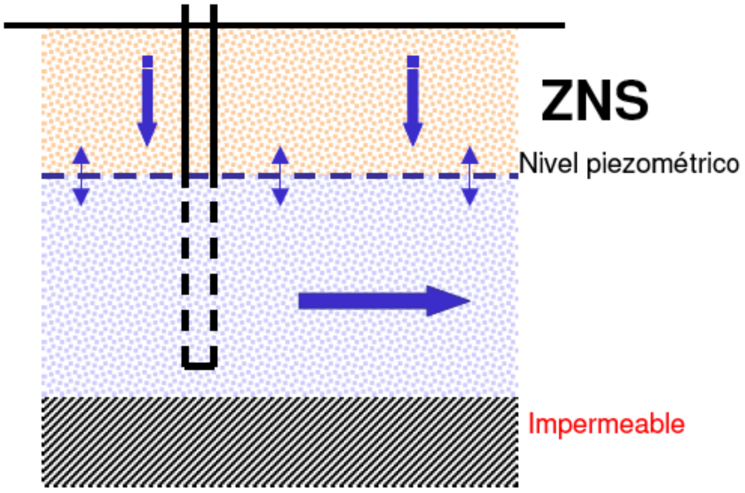
Acuifugo: No posee capacidad de circulación ni de retención de agua

Acuicludo: Contiene agua en su interior, incluso hasta la saturación, pero no la transmite

Acuitardo: Contiene agua y la transmite muy lentamente

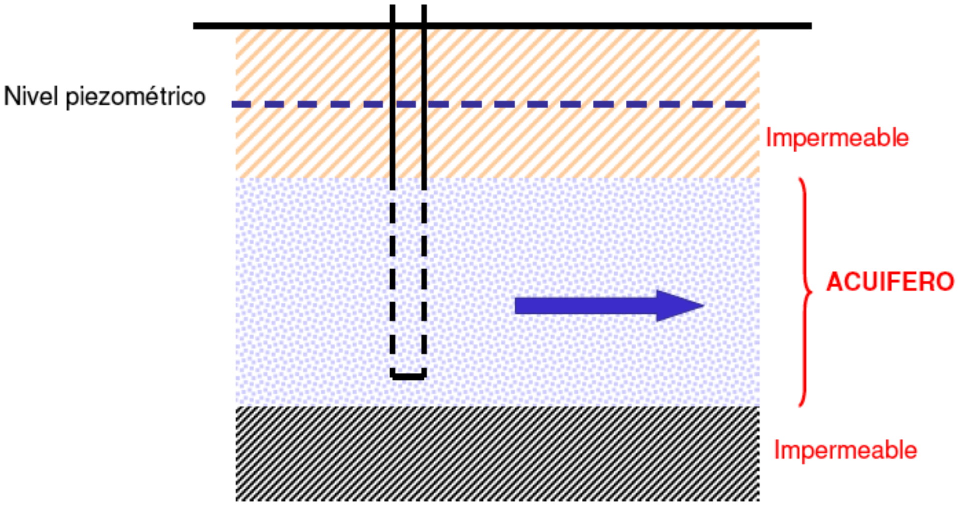
Acuífero: Almacena agua en los poros y circula con facilidad por ellos.

ACUIFEROS LIBRES



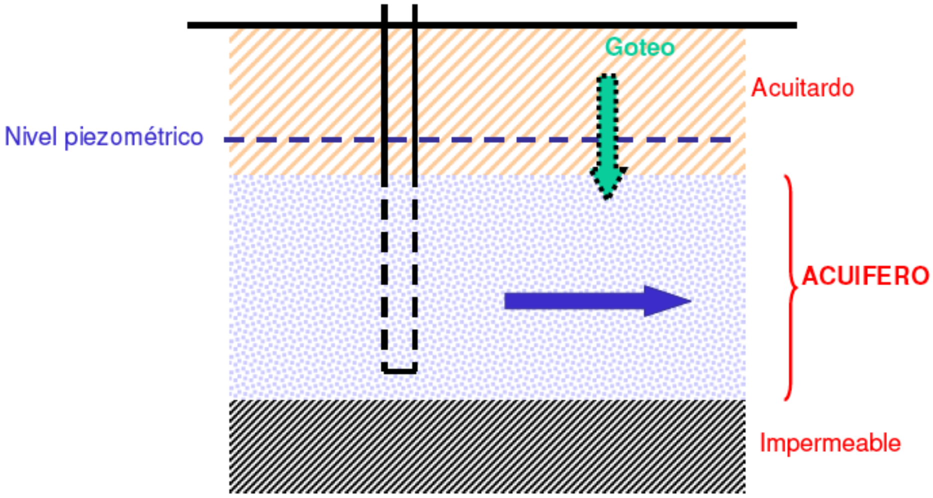
Existencia de zona no saturada
Nivel piezométrico real
Superficie libre de agua a presión atmosférica
Recarga directa

ACUIFEROS CONFINADOS



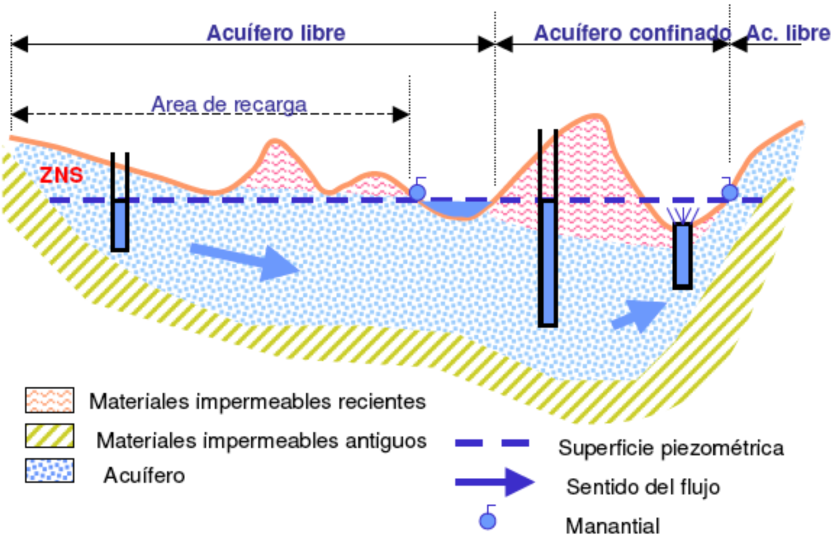
Ausencia de zona no saturada
Nivel piezométrico virtual

ACUIFEROS SEMICONFINADOS



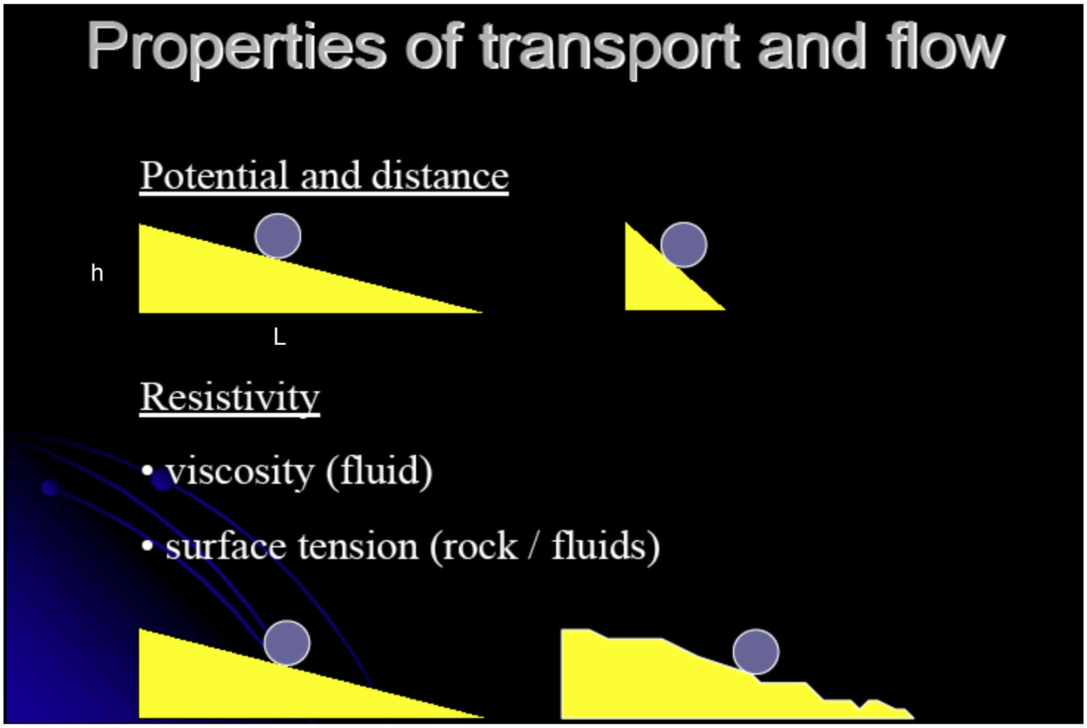
Ausencia de zona no saturada
Nivel piezométrico virtual
Superficie de agua a presión > atmosférica
Recarga diferida

RELACIONES ENTRE ACUIFEROS



Why does groundwater flow?

- Driving force: potential difference (pressure, gravity head, others….)
- Permeability of rock
- (porosity of rock [voids in hard rock])

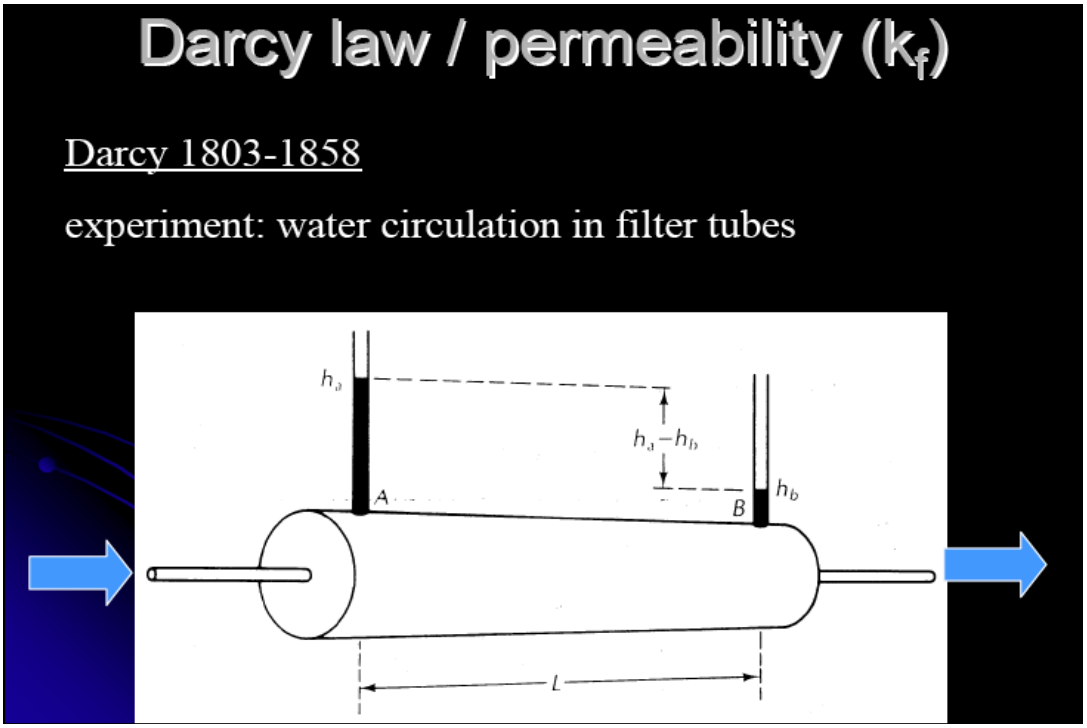


Properties of transport and flow

Potential and distance

Resistivity

- viscosity (fluid)
- surface tension (rock / fluids)



Darcy law / permeability (k_f)

Darcy 1803-1858

experiment: water circulation in filter tubes

Darcy law / permeability (k_f)

$v_f = k_f \cdot \Delta i$

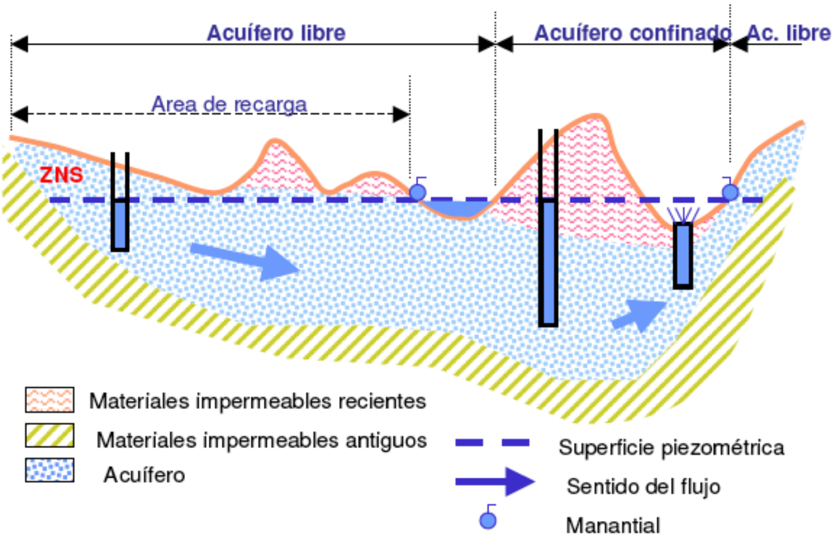
k_f = filtration coefficient
v_f = filtration velocity

$\Delta i = \Delta H / \Delta L$

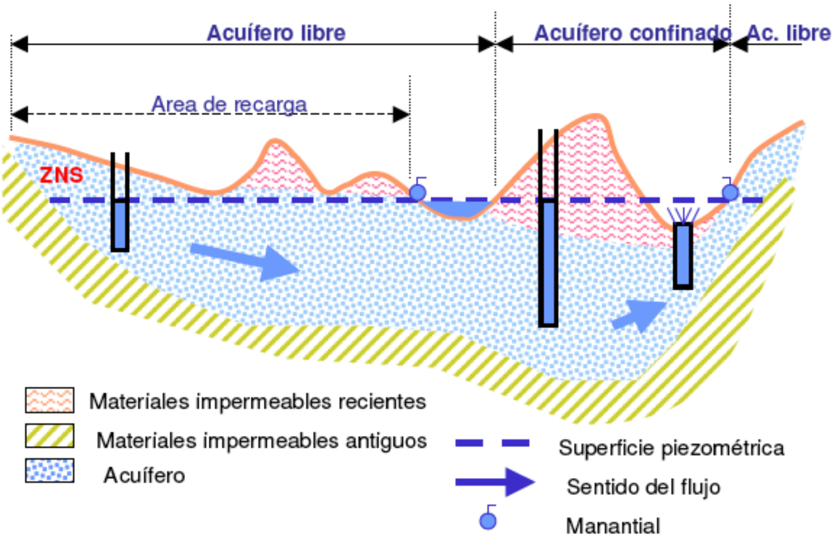
L = length, H = potential difference

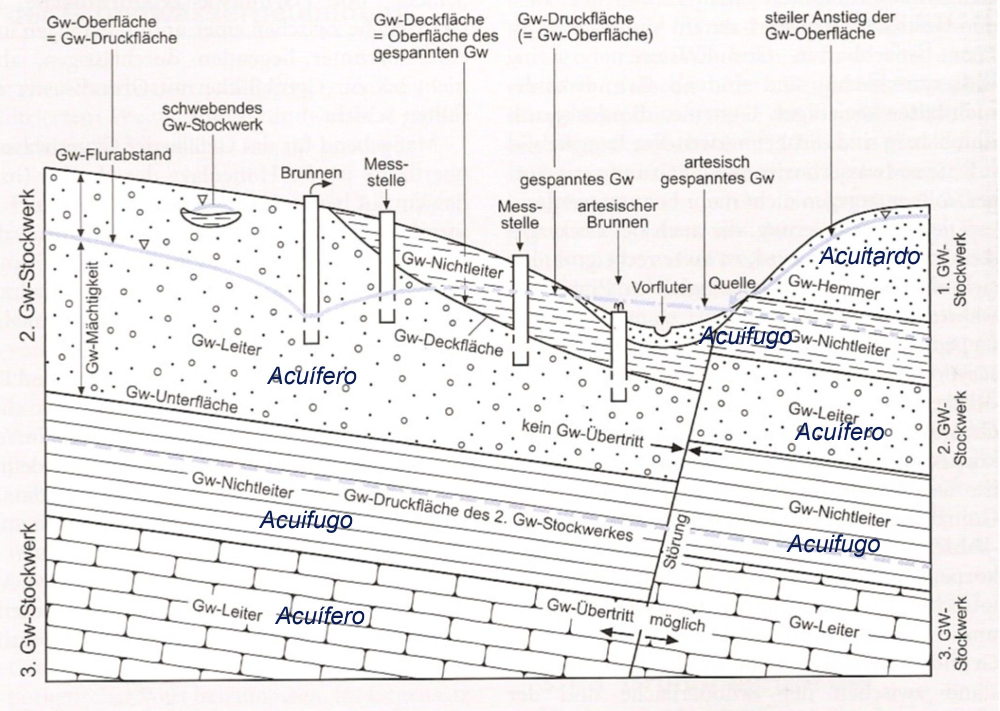
units: k_f = m/s velocity!

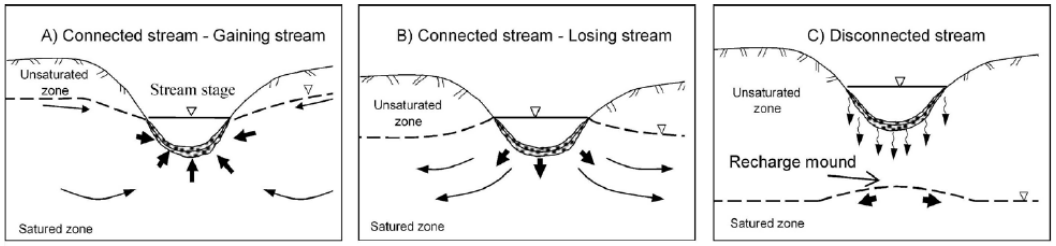
RELACIONES ENTRE ACUIFEROS



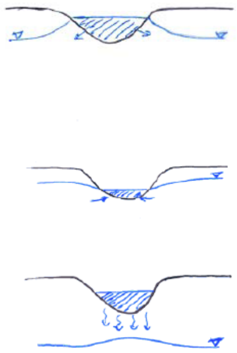
RELACIONES ENTRE ACUIFEROS



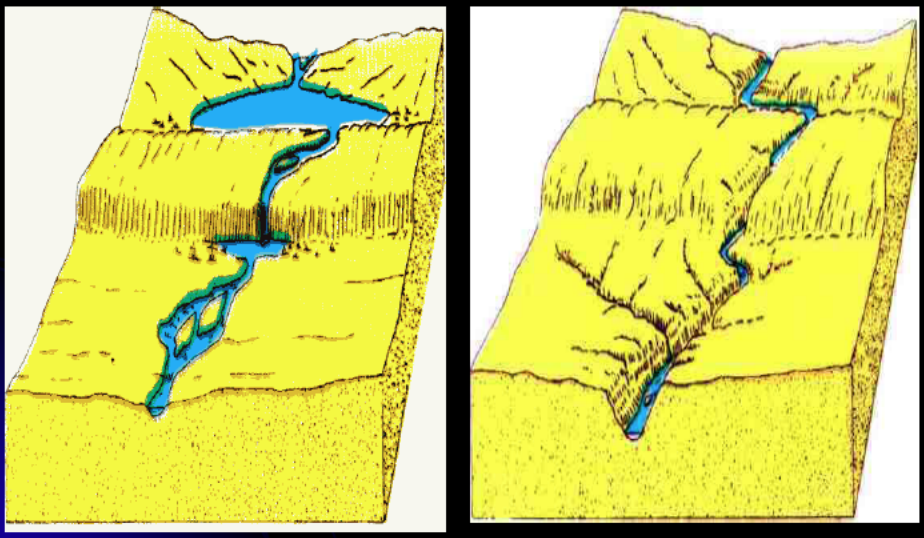




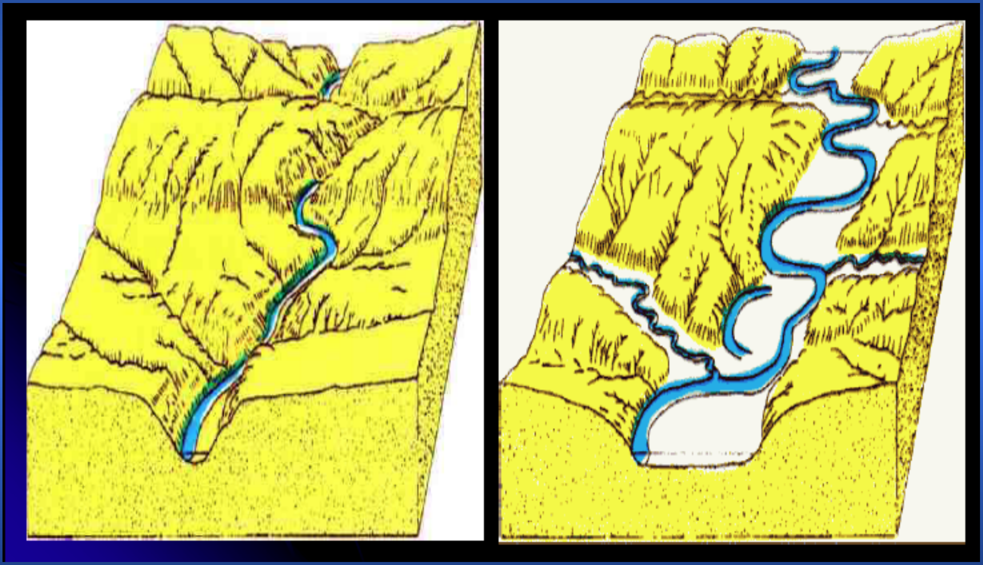
- Río influyente
  (perdedor)
- Río efluente
  (ganador)
- Río desconectado



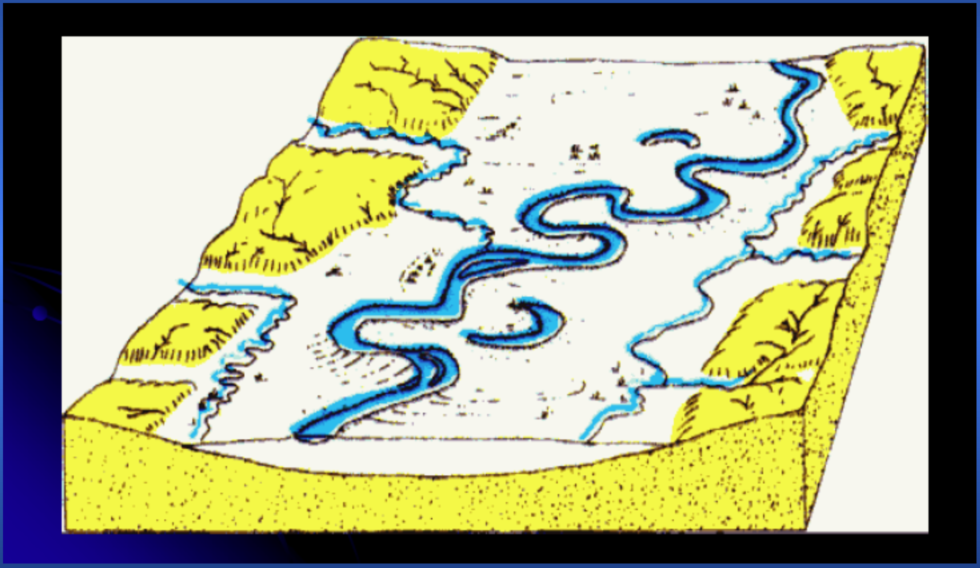
Depósitos fluviatiles



Depósitos fluviatiles

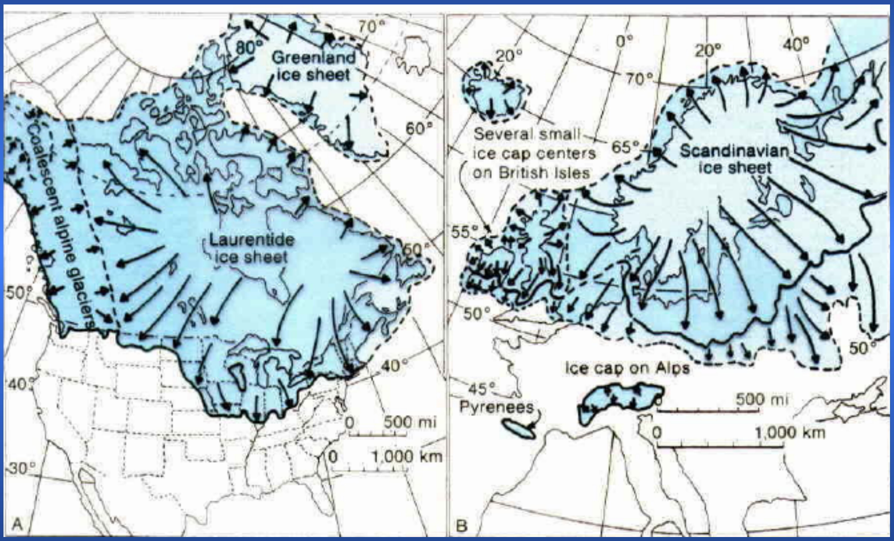


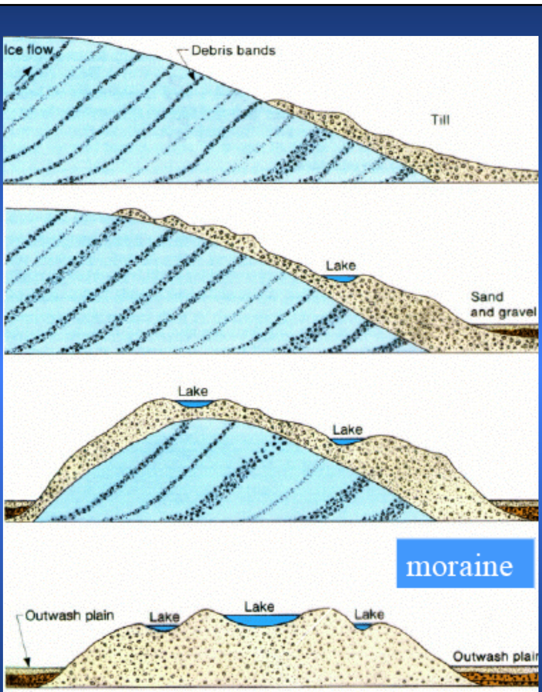
Depósitos fluviatiles



Gravas, arenas, limos, arcillas

Depósitos glaciares

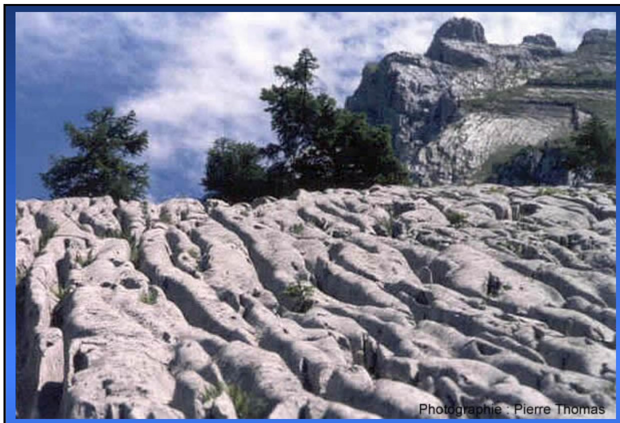




Como funcionan
Glaciares…
Rocas
Gravas
Arena
Limo
Arcillas

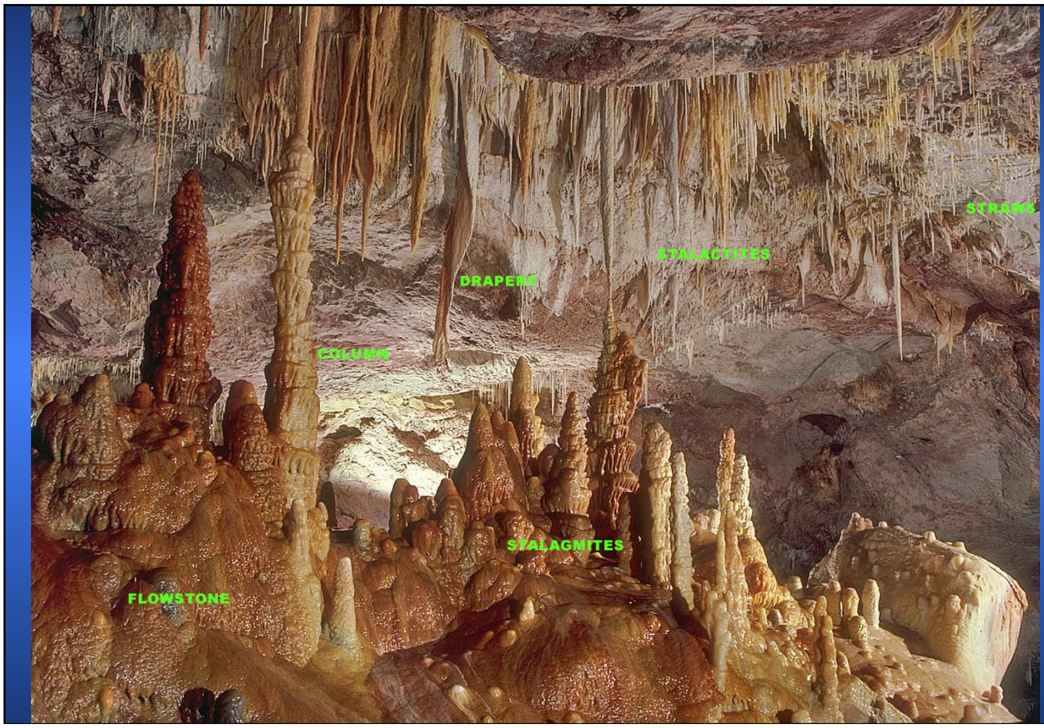
- Karst:

  - corosion quimica de la roca
  - carbonatos, dolomita, (calcita, dolomita, yeso, anhidrita, halita)
  - corosion de los carbonatos debido al CO_2 en agua y aire (clima!)
  - forma cuevas, “sinkholes” y ríos subterráneos

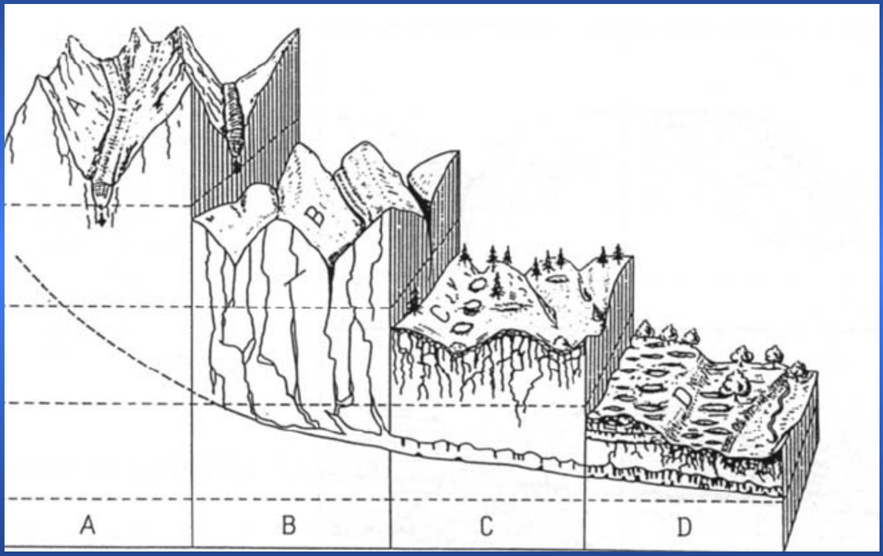


Photographie : Pierre Thomas

Karst erosión comienza en la superficie



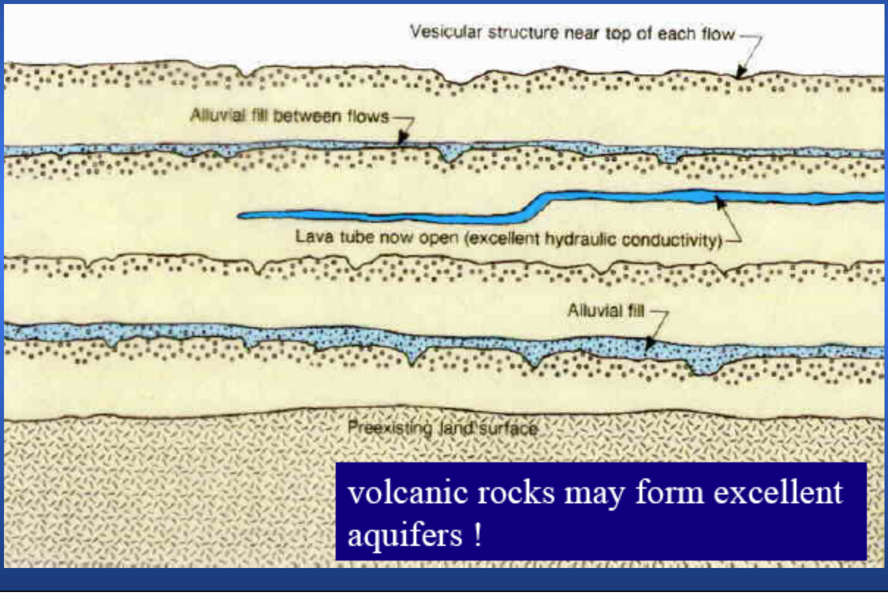
Evolución de un sistema de karst



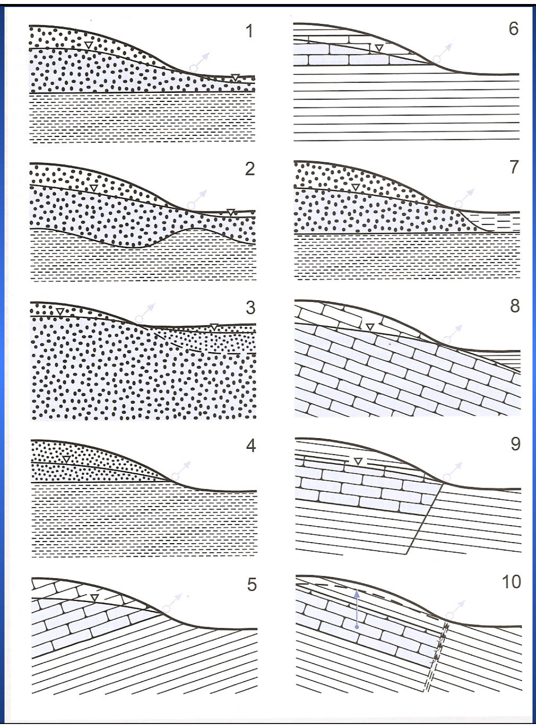
- Aguas subterráneas en karst:

  - un caso especifico como hay flujo preferencial
  - karst poco profundos tiene alto riesgo de contaminación
  - la capacidad de retención es poca
  - la velocidad de flujo es muy alto

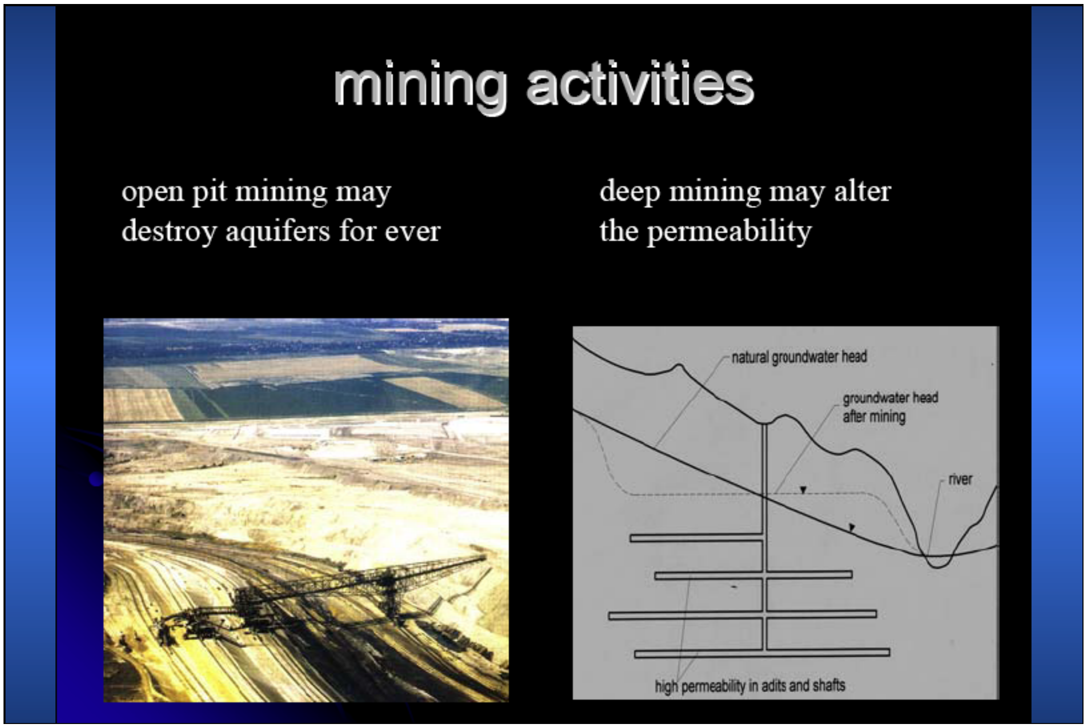
Flujos de lava



volcanic rocks may form excellent aquifers !



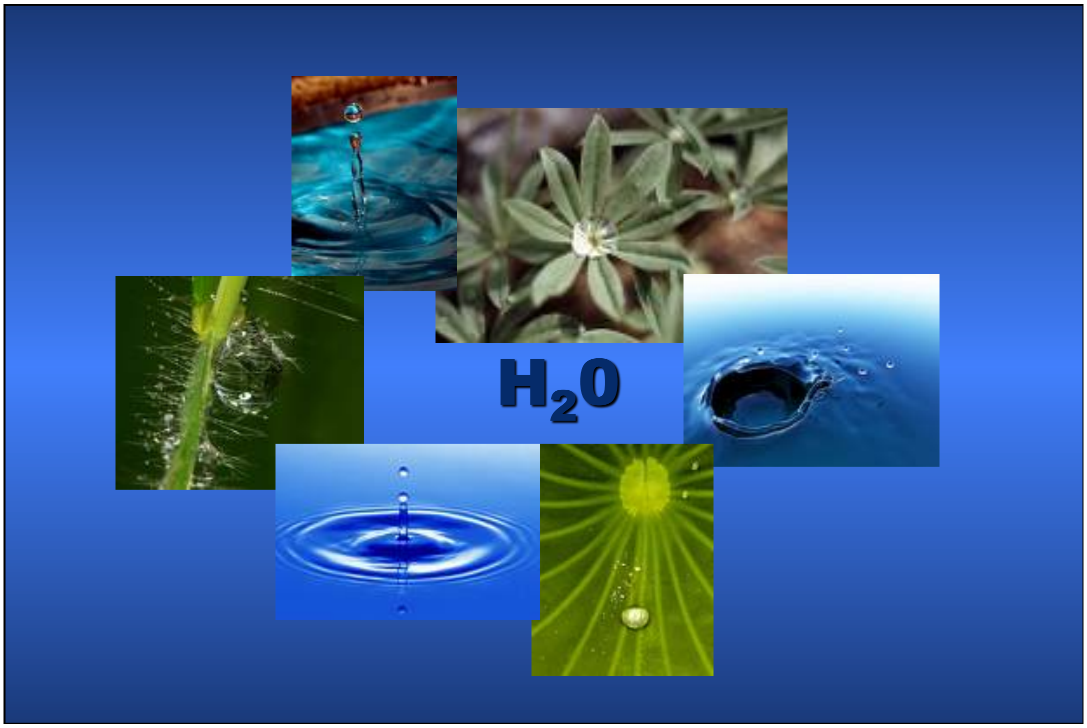
Surgencias,
fuentes



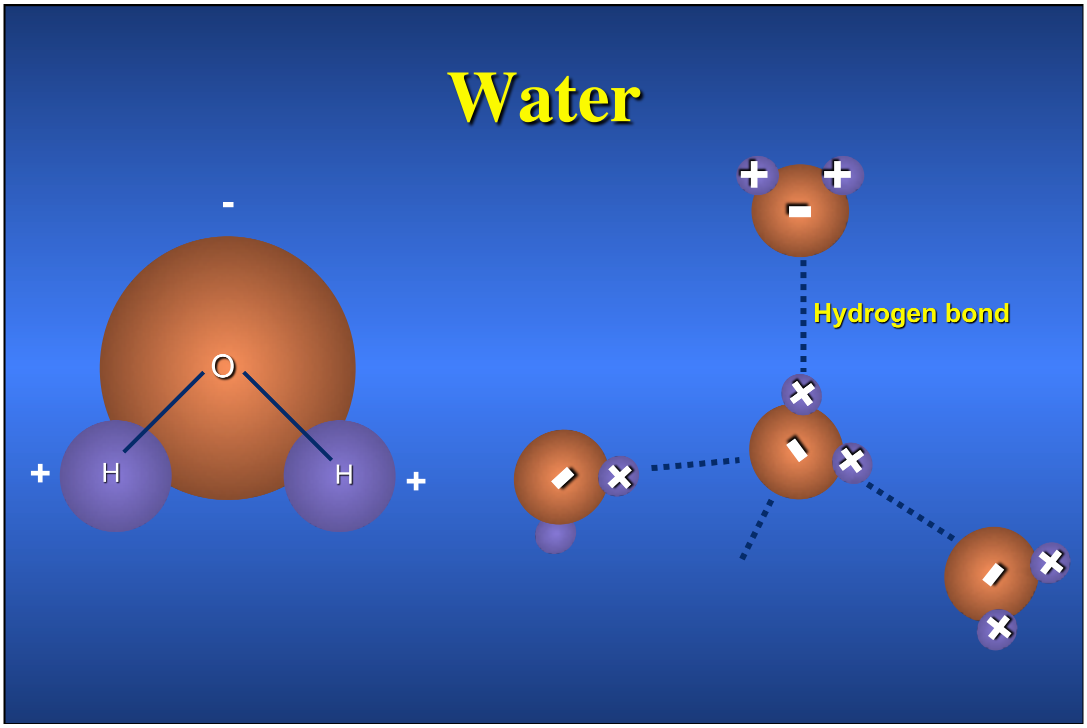
mining activities

open pit mining may destroy aquifers for ever

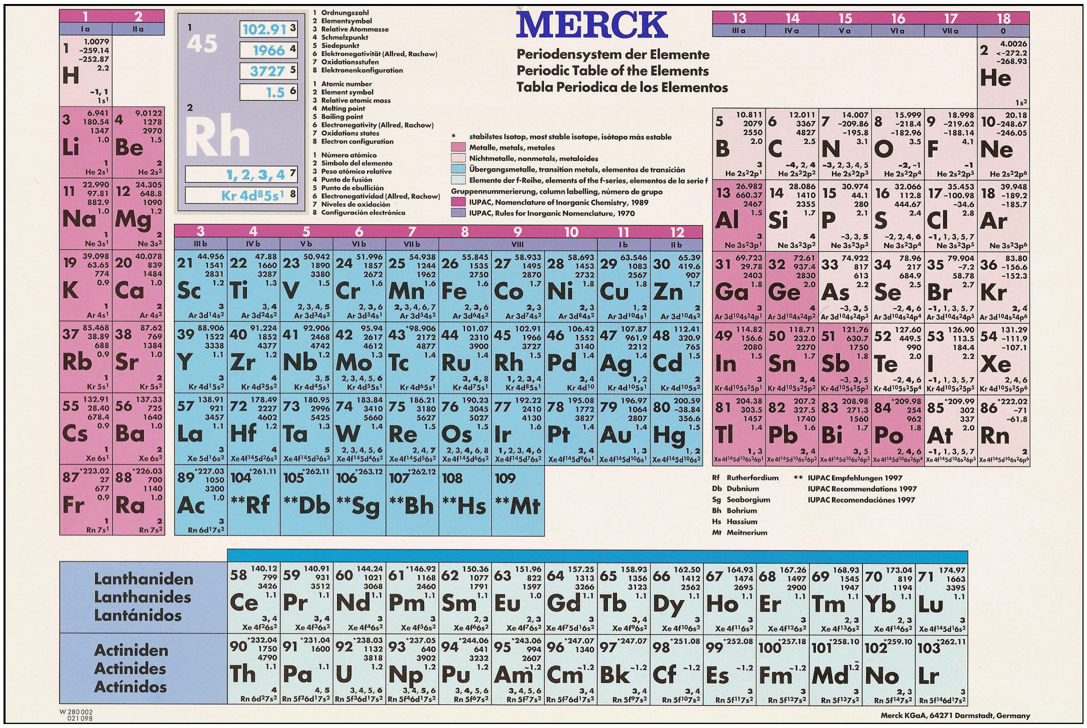
deep mining may alter the permeability



H_2O



Water



MERCK

Periodensystem der Elemente
Periodic Table of the Elements
Tabla Periodica de los Elementos

1 Ordnungszahl
2 Elementsymbol
3 Relative Atommasse
4 Schmelzpunkt
5 Siedepunkt
6 Elektronegativität (Allred, Rachow)
7 Oxidationsstufen
8 Elektronenkonfiguration

1 Atomic number
2 Element symbol
3 Relative atomic mass
4 Melting point
5 Boiling point
6 Electronegativity (Allred, Rachow)
7 Oxidations states
8 Electron configuration

1 Número atómico
2 Simbolo del elemento
3 Peso atómico relative
4 Punto de fusión
5 Punto de ebullición
6 Electronegatividad (Allred, Rachow)
7 Niveles de oxidación
8 Configuración electrónica

* stabilstes Isotop, most stable isotope, isótopo más estable
▨ Metalle, metals, metales
▨ Nichtmetalle, nonmetals, metaloides
▨ Übergangsmetalle, transition metals, elementos de transición
▨ Elemente der f-Reihe, elements of the f-series, elementos de la serie f

Gruppennummerierung, column labelling, número de grupo
▨ IUPAC, Nomenclature of Inorganic Chemistry, 1989
▨ IUPAC, Rules for Inorganic Nomenclature, 1970

Lanthaniden
Lanthanides
Lantánidos

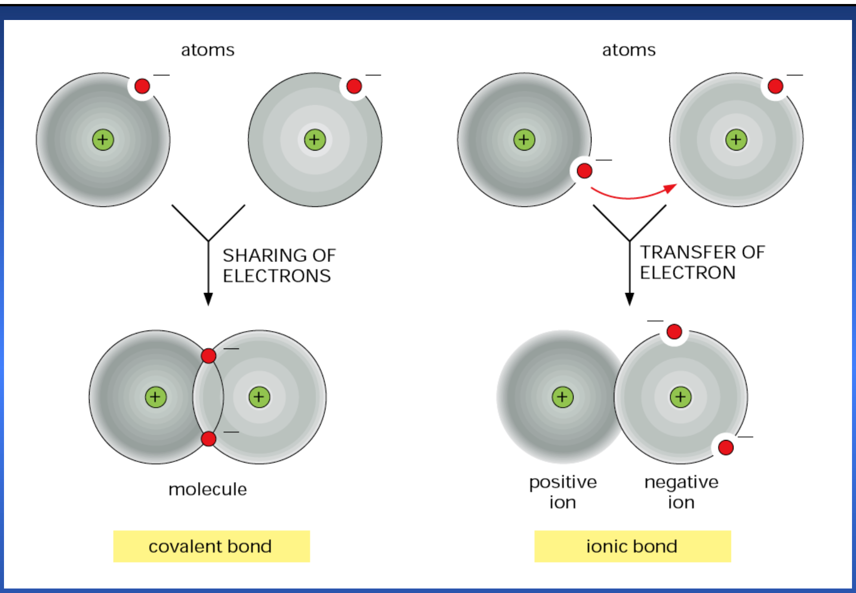
Actiniden
Actinides
Actínidos

Rf Rutherfordium
Db Dubnium
Sg Seaborgium
Bh Bohrium
Hs Hassium
Mt Meitnerium

** IUPAC Empfehlungen 1997
IUPAC Recommendations 1997
IUPAC Recomendaciónes 1997

W 280002
021098

Merck KGaA, 64271 Darmstadt, Germany

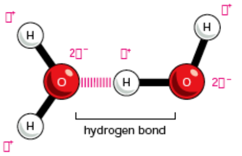


Legend: Atoms can attain a more stable arrangement of electrons in their outermost shell by interacting with one another. An ionic bond is formed when electrons are transferred from one atom to the other. A covalent bond is formed when electrons are shared between atoms. The two cases shown represent extremes; often, covalent bonds form with a partial transfer (unequal sharing of electrons), resulting in a polar covalent bond

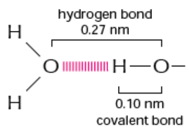
HYDROGEN BONDS

Because they are polarized, two adjacent H_2O molecules can form a linkage known as a hydrogen bond. Hydrogen bonds have only about 1/20 the strength of a covalent bond.

Hydrogen bonds are strongest when the three atoms lie in a straight line.

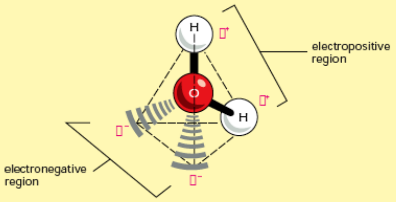


bond lengths



WATER

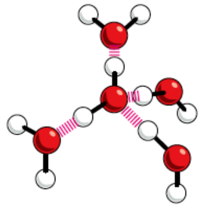
Two atoms, connected by a covalent bond, may exert different attractions for the electrons of the bond. In such cases the bond is polar, with one end slightly negatively charged (δ−) and the other slightly positively charged (δ+).



Although a water molecule has an overall neutral charge (having the same number of electrons and protons), the electrons are asymmetrically distributed, which makes the molecule polar. The oxygen nucleus draws electrons away from the hydrogen nuclei, leaving these nuclei with a small net positive charge. The excess of electron density on the oxygen atom creates weakly negative regions at the other two corners of an imaginary tetrahedron.

WATER STRUCTURE

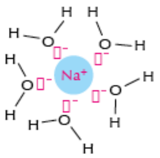
Molecules of water join together transiently in a hydrogen-bonded lattice. Even at 37°C, 15% of the water molecules are joined to four others in a short-lived assembly known as a "flickering cluster."

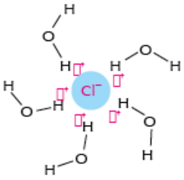


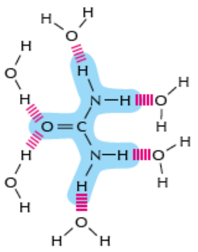
The cohesive nature of water is responsible for many of its unusual properties, such as high surface tension, specific heat, and heat of vaporization.

HYDROPHILIC MOLECULES

Substances that dissolve readily in water are termed hydrophilic. They are composed of ions or polar molecules that attract water molecules through electrical charge effects. Water molecules surround each ion or polar molecule on the surface of a solid substance and carry it into solution.





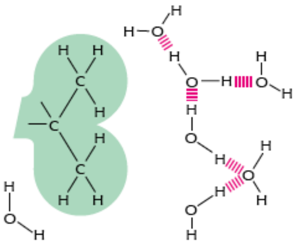


Ionic substances such as sodium chloride dissolve because water molecules are attracted to the positive (Na^+) or negative (Cl^-) charge of each ion.

Polar substances such as urea dissolve because their molecules form hydrogen bonds with the surrounding water molecules

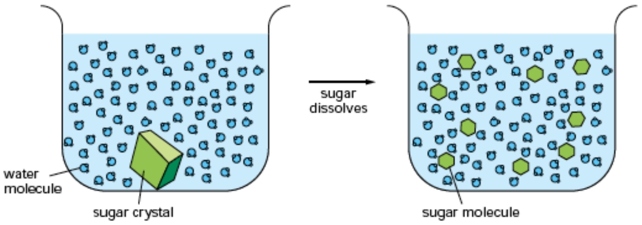
HYDROPHOBIC MOLECULES

Molecules that contain a preponderance of nonpolar bonds are usually insoluble in water and are termed hydrophobic. This is true, especially, of hydrocarbons, which contain many C–H bonds. Water molecules are not attracted to such molecules and so have little tendency to surround them and carry them into solution.



WATER AS A SOLVENT

Many substances, such as household sugar, dissolve in water. That is, their molecules separate from each other, each becoming surrounded by water molecules.



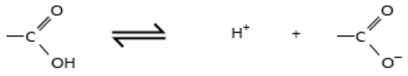
When a substance dissolves in a liquid, the mixture is termed a solution. The dissolved substance (in this case sugar) is the solute, and the liquid that does the dissolving (in this case water) is the solvent. Water is an excellent solvent for many substances because of its polar bonds.

ACIDS

Substances that release hydrogen ions into solution are called acids.

$$\underset{\text{hydrochloric acid (strong acid)}}{HCl} \longrightarrow \underset{\text{hydrogen ion}}{H^+} + \underset{\text{chloride ion}}{Cl^-}$$

Many of the acids important in the cell are only partially dissociated, and they are therefore weak acids—for example, the carboxyl group (–COOH), which dissociates to give a hydrogen ion in solution

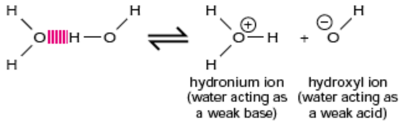


(weak acid)

Note that this is a reversible reaction.

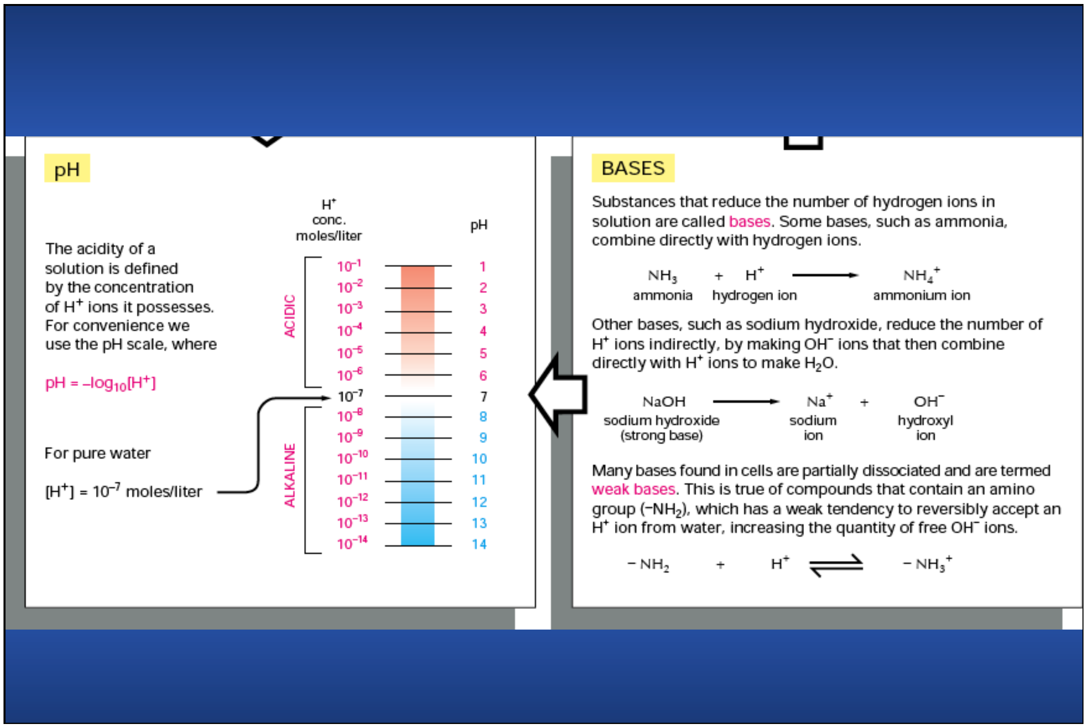
HYDROGEN ION EXCHANGE

Positively charged hydrogen ions (H^+) can spontaneously move from one water molecule to another, thereby creating two ionic species.



often written as: $H_2O \rightleftharpoons \underset{\text{hydrogen ion}}{H^+} + \underset{\text{hydroxyl ion}}{OH^-}$

Since the process is rapidly reversible, hydrogen ions are continually shuttling between water molecules. Pure water contains a steady state concentration of hydrogen ions and hydroxyl ions (both 10^{-7} M).



pH

The acidity of a solution is defined by the concentration of H^+ ions it possesses. For convenience we use the pH scale, where

$pH = -log_{10}[H^+]$

For pure water

$[H^+] = 10^{-7}$ moles/liter

H^+ conc. moles/liter	pH
10^{-1}	1
10^{-2}	2
10^{-3}	3
10^{-4}	4
10^{-5}	5
10^{-6}	6
10^{-7}	7
10^{-8}	8
10^{-9}	9
10^{-10}	10
10^{-11}	11
10^{-12}	12
10^{-13}	13
10^{-14}	14

BASES

Substances that reduce the number of hydrogen ions in solution are called bases. Some bases, such as ammonia, combine directly with hydrogen ions.

$$\underset{\text{ammonia}}{NH_3} + \underset{\text{hydrogen ion}}{H^+} \longrightarrow \underset{\text{ammonium ion}}{NH_4^+}$$

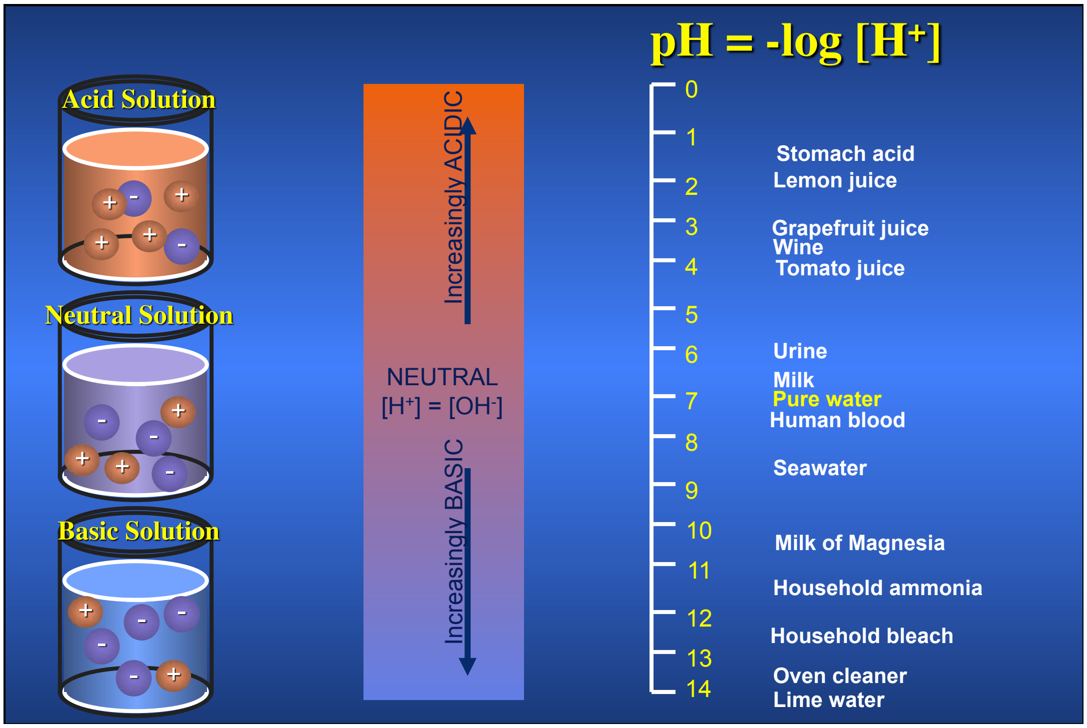
Other bases, such as sodium hydroxide, reduce the number of H^+ ions indirectly, by making OH^- ions that then combine directly with H^+ ions to make H_2O.

$$\underset{\substack{\text{sodium hydroxide}\\\text{(strong base)}}}{NaOH} \longrightarrow \underset{\substack{\text{sodium}\\\text{ion}}}{Na^+} + \underset{\substack{\text{hydroxyl}\\\text{ion}}}{OH^-}$$

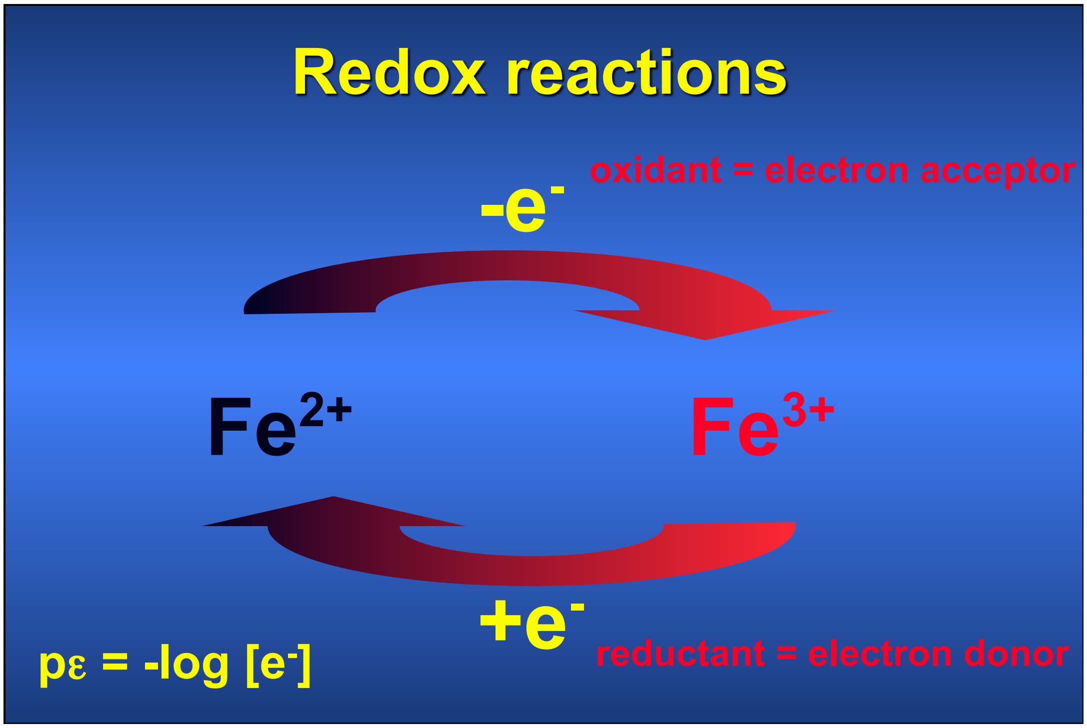
Many bases found in cells are partially dissociated and are termed weak bases. This is true of compounds that contain an amino group ($-NH_2$), which has a weak tendency to reversibly accept an H^+ ion from water, increasing the quantity of free OH^- ions.

$$-NH_2 + H^+ \rightleftharpoons -NH_3^+$$

$pH = -log [H^+]$



Stomach acid
Lemon juice
Grapefruit juice
Wine
Tomato juice
Urine
Milk
Pure water
Human blood
Seawater
Milk of Magnesia
Household ammonia
Household bleach
Oven cleaner
Lime water



Redox reactions

oxidant = electron acceptor

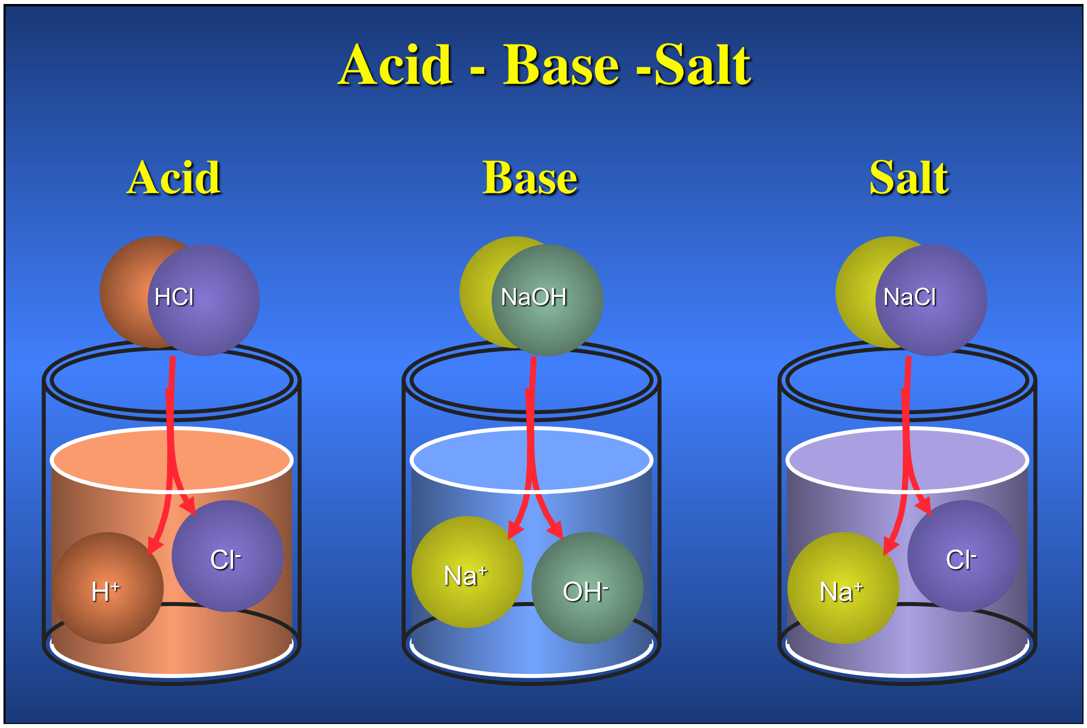
$-e^-$

Fe^{2+} Fe^{3+}

$+e^-$

reductant = electron donor

$p\varepsilon = -\log [e^-]$

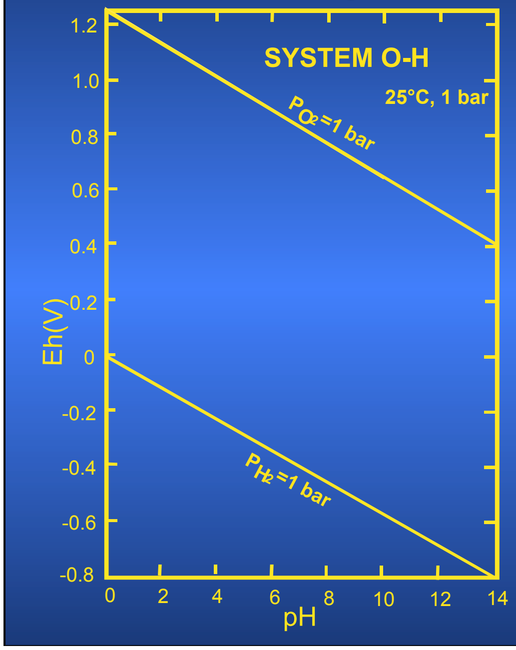


Acid - Base -Salt

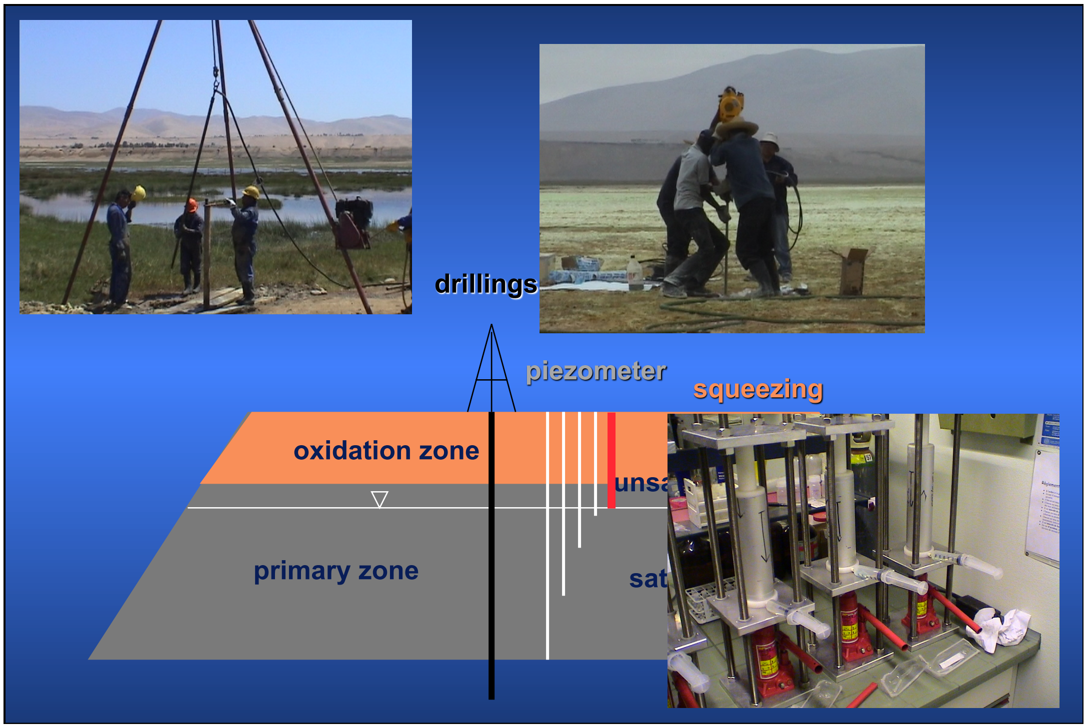
Definitions

- $pH = -\log[H^+]$ → low pH = high $[H^+]$ = acid
- $p\varepsilon = -\log [e^-]$ → low $p\varepsilon$ = high $[e^-]$ = reducing
- Eh = Redox Potential (volt) = $0.059 \times p\varepsilon$
- Acidity = capacity of water to donate protons
- Alkalinity = capacity of water to accept protons (Acid Neutralizing Capacity)
- Total Alkalinity = $[HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+]$
- Mol = 6.02205×10^{23} particles (Avogadro number)
- Molecular weight [g/mol]

Eh-pH diagram



Eh-pH diagram



drillings

piezometer

squeezing

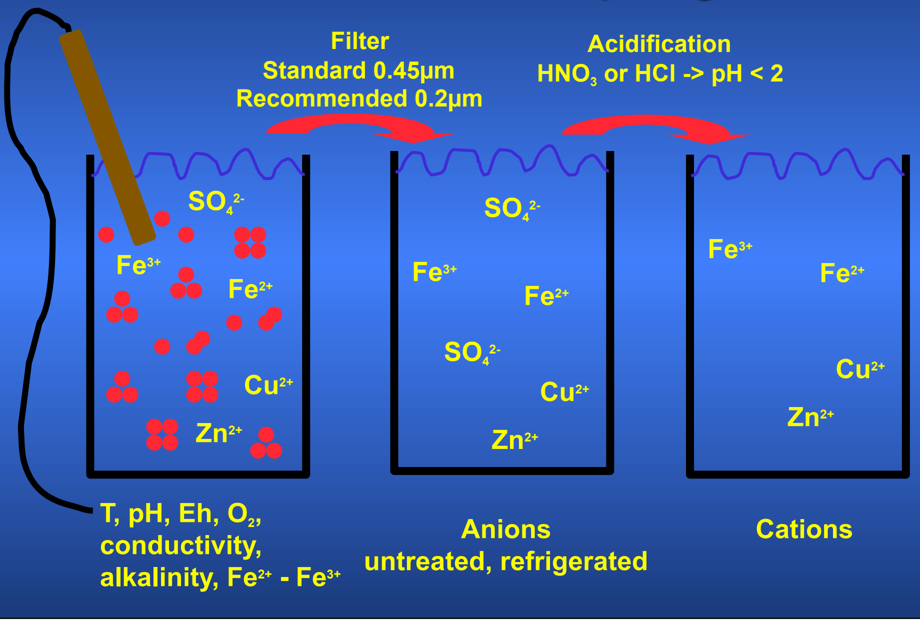
oxidation zone

unsa

primary zone

sat

Water sampling



Filter
Standard 0.45µm
Recommended 0.2µm

Acidification
HNO_3 or HCl -> pH < 2

T, pH, Eh, O_2, conductivity, alkalinity, Fe^{2+} - Fe^{3+}

Anions
untreated, refrigerated

Cations

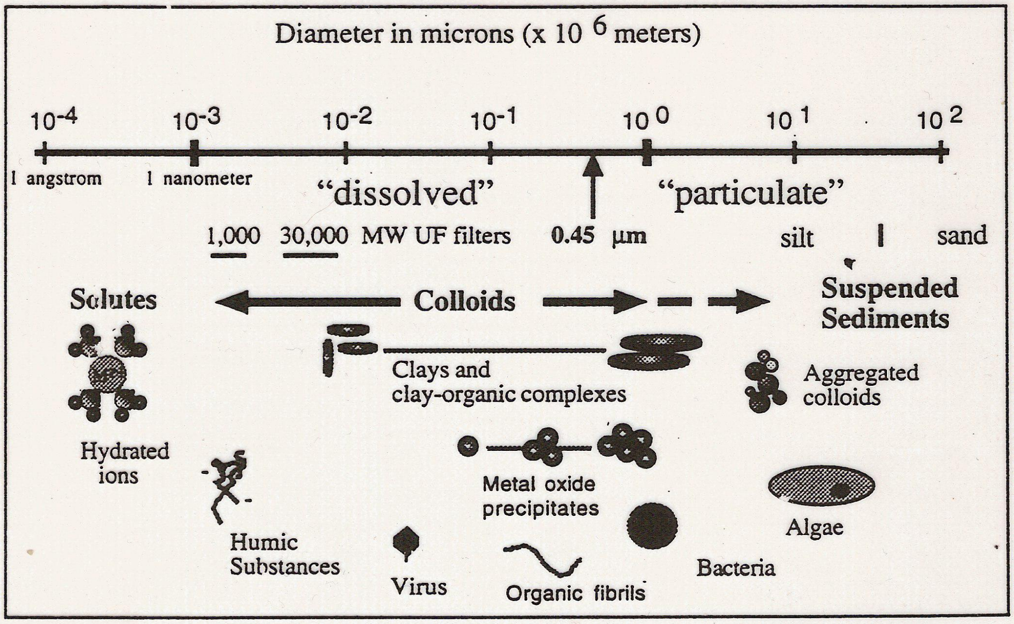


FIGURE 8.2—The solute/colloid/particle size continuum and examples of aquatic colloids.

Water analysis

- Atention with the Material of Filters (depends what you want analyse
- CATIONS:
- Atomic Absorption Spectroscopy (AAS) & IC
- Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES)
- Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) ATENTION!!! Many Interferences!!!
- ANIONS:
- Ion chromatography (IC, HPLC, GC, CE) ATENTION!!!
- Organic compounds (e.g. LMW organic acids)
- GC-MS

pH - pe (Eh) - pK

pH

$H_2O = H^+ + OH^-$

For wich at 25°C

$$K_w = \frac{[H^+][OH^-]}{[H_2O]} = 10^{-14}$$

pH = -log{H^+} *a* = 1 => -log[H^+] *a = activity*

low pH = high [H^+] = acid

Oxidation - Reduction pε (Eh)

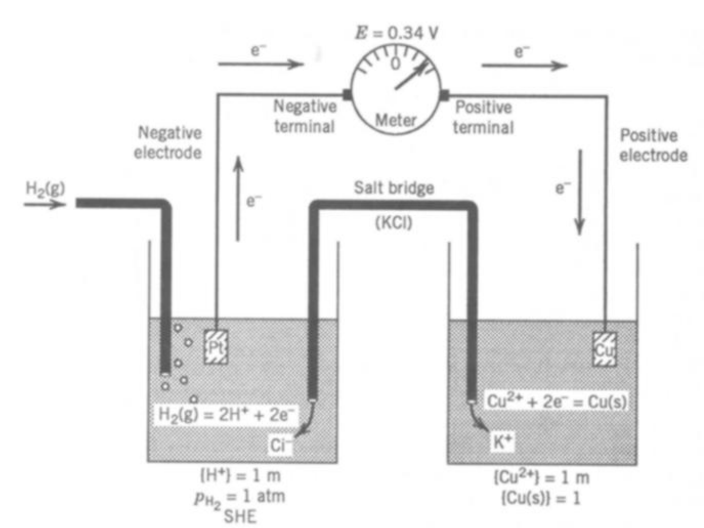
- Elements can occur in more than one oxidation state e.g. Fe(III)/Fe(II), As(V)/As(III)
- Major redox elements are H, O, C, S, N, and Fe (Mn)
- In ore deposit systems U, Cr, As, Mo, V, Se, Sb, W, Cu, Au, Ag, and Hg may be important
- Oxidation state controls the chemical and biological behavior as toxicity and mobility

pH - pE (pε − Eh)

pH	pE
•Free H^+ exists in water or as H_3O^+	•Free e^- do not exists in water
•Reversible	•irreversible
•Electrodes respond to H^+(aq) from solutes and solvents	•Electrodes respond to electron transfer from solutes
•H^+(aq) is a weak oxidizing agent; It can be reduced to $H_{2\,(g)}$ in solution	•e^-(aq) once formed, is a stronger reducing agent than metallic Na

---

Standard Hydrogene Electrode SHE



$H^+ + e^- = {}^1/_2H_{2(g)}$

$Cu^{2+} + 2e^- = Cu^o$

$Cu^{2+} + H_{2(g)} = 2H^+ + Cu^o$

Measurement by platinium or glassy carbon indicator electrode and a calomel (Hg_2Cl_2/Hg^o) or Ag/AgCl reference electrode of known potential
=> Correction to SHE !!!

From Stumm and Morgan, 1996

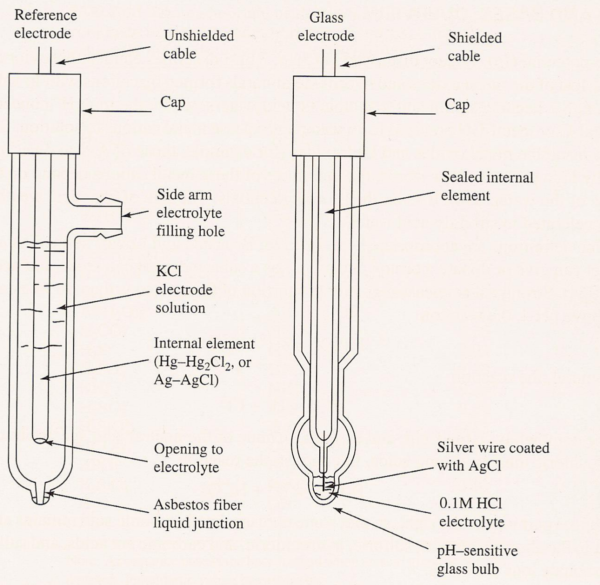


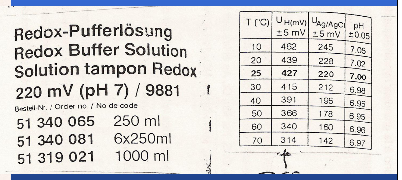
Figure 5.1 Basic design of a typical commercial reference electrode and glass electrode. After D. Langmuir, Eh-pH determination, in *Procedures in Sedimentary Petrology*, R. E. Carver, ed. Copyright © 1971 by John Wiley & Sons, Inc. Used by permission of John Wiley & Sons, Inc.

$$H^+ + e^- = {}^1/_2H_{2(g)}$$

$$Cu^{2+} + 2e^- = Cu^o$$

$$Cu^{2+} + H_{2(g)} = 2H^+ + Cu^o$$

Measurement by platinium or glassy carbon indicator electrode and a calomel (Hg_2Cl_2/Hg^o) or Ag/AgCl reference electrode of known potential
=> Correction to SHE !!!



Redox-Pufferlösung
Redox Buffer Solution
Solution tampon Redox
220 mV (pH 7) / 9881
Bestell-Nr. / Order no. / No de code
51 340 065 250 ml
51 340 081 6x250ml
51 319 021 1000 ml

T (°C)	$U_{H(mV)}$ ±5 mV	$U_{Ag/AgCl}$ ±5 mV	pH ±0.05
10	462	245	7.05
20	439	228	7.02
25	**427**	**220**	**7.00**
30	415	212	6.98
40	391	195	6.95
50	366	178	6.95
60	340	160	6.96
70	314	142	6.97

The Eh Probe

- Eh is not a comparative measurement. An absolute measurement of cell potential - reference electrode vs. reactions at a Pt surface
- The Eh probe is not adjusted to the value of known standards. It is compared to known standards.

  e.g. Zobell’s solution:

  An equi-molar solution of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ has an expected E_{meas} = +186 mV

Measurement

- Measured and calculated Eh are in good agreement for systems controlled by Fe, Mn, sulfide sulfur
- In bad agreement for C, N, O, H
- Mixed potentials:

  Fe(III)/Fe(II);

  As(V)/As(III) slow kinetics
- => Eh measurements not very stable and thermodinamically useful in surface waters, except acid waters e.g. acid mine drainage (AMD)

Aqueous Complexes

Aqueous Complexes

Complex = metal cation + ligand

Why is complexation important?

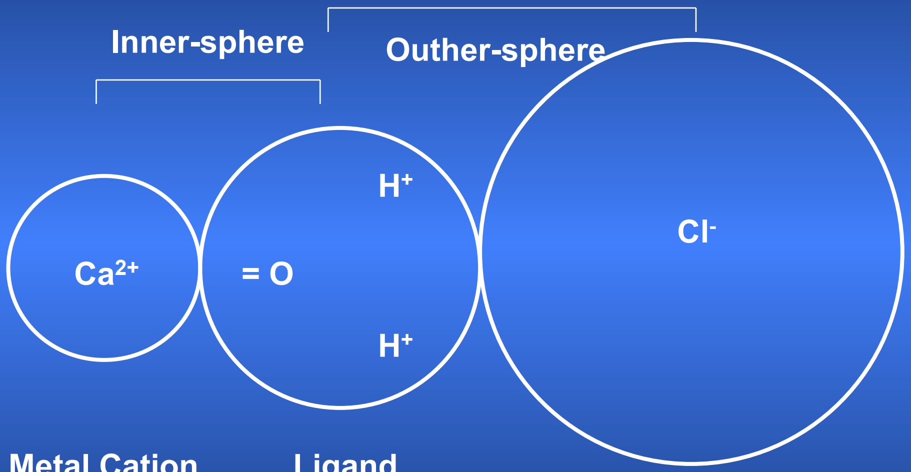
1.) increase of solubility => increase of mobility

2.) some elements are mainly as complexes present

3.) complexation changes sorption porperties

4.) Toxicity and bioavailability depends on speciation or complexation of the metals

Outer- and Inner-sphere Complexes



Inner-sphere

Outher-sphere

Ca^{2+}

= O

H^+

H^+

Cl^-

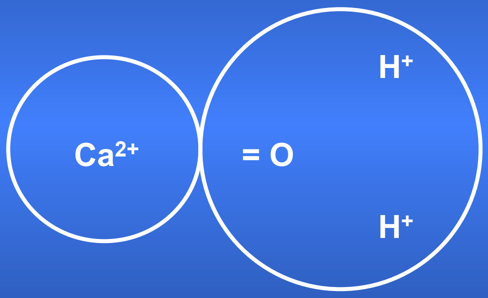
Metal Cation

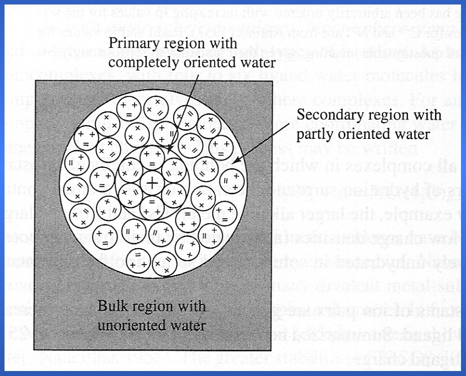
Ligand

Anion

Aquo-complex

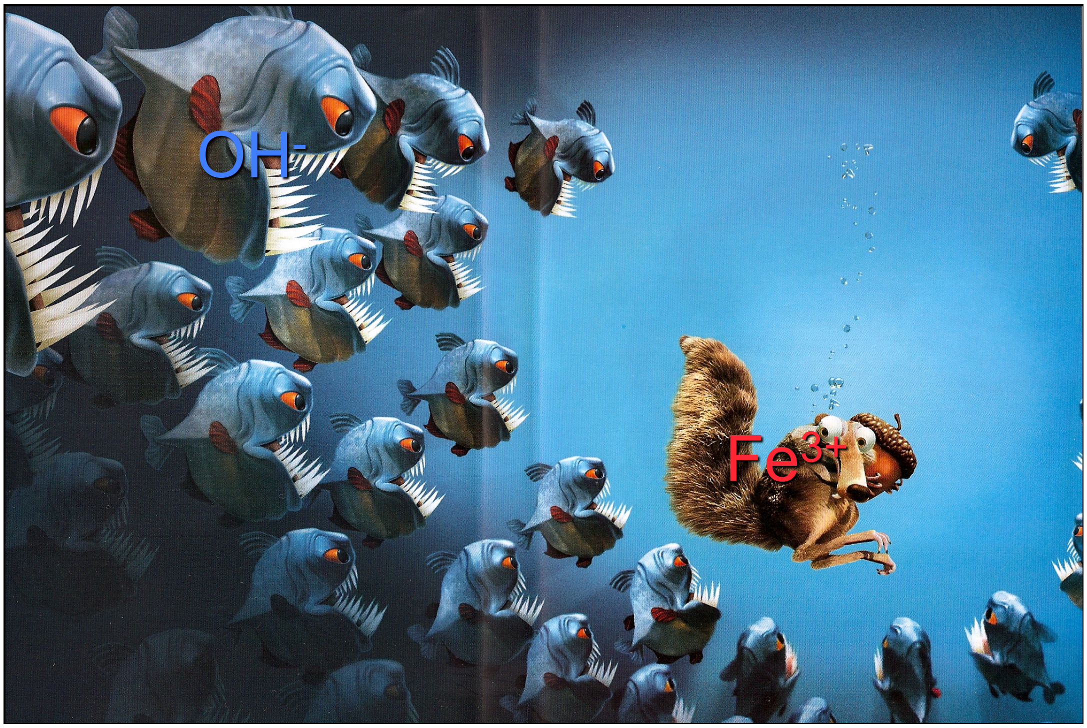
Outer- and Inner-sphere Complexes





Metal Cation **Ligand**

Aquo-complex



Charge density and ionic potential

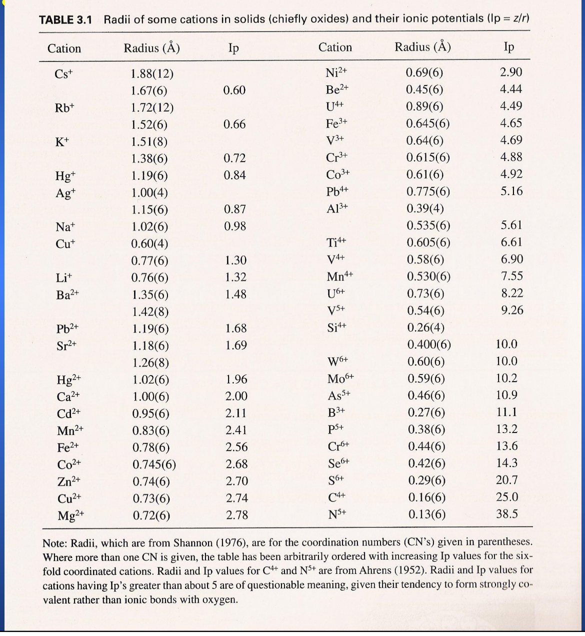


TABLE 3.1 Radii of some cations in solids (chiefly oxides) and their ionic potentials (Ip = z/r)

Cation	Radius (Å)	Ip	Cation	Radius (Å)	Ip
Cs^+	1.88(12)		Ni^{2+}	0.69(6)	2.90
	1.67(6)	0.60	Be^{2+}	0.45(6)	4.44
Rb^+	1.72(12)		U^{4+}	0.89(6)	4.49
	1.52(6)	0.66	Fe^{3+}	0.645(6)	4.65
K^+	1.51(8)		V^{3+}	0.64(6)	4.69
	1.38(6)	0.72	Cr^{3+}	0.615(6)	4.88
Hg^+	1.19(6)	0.84	Co^{3+}	0.61(6)	4.92
Ag^+	1.00(4)		Pb^{4+}	0.775(6)	5.16
	1.15(6)	0.87	Al^{3+}	0.39(4)	
Na^+	1.02(6)	0.98		0.535(6)	5.61
Cu^+	0.60(4)		Ti^{4+}	0.605(6)	6.61
	0.77(6)	1.30	V^{4+}	0.58(6)	6.90
Li^+	0.76(6)	1.32	Mn^{4+}	0.530(6)	7.55
Ba^{2+}	1.35(6)	1.48	U^{6+}	0.73(6)	8.22
	1.42(8)		V^{5+}	0.54(6)	9.26
Pb^{2+}	1.19(6)	1.68	Si^{4+}	0.26(4)	
Sr^{2+}	1.18(6)	1.69		0.400(6)	10.0
	1.26(8)		W^{6+}	0.60(6)	10.0
Hg^{2+}	1.02(6)	1.96	Mo^{6+}	0.59(6)	10.2
Ca^{2+}	1.00(6)	2.00	As^{5+}	0.46(6)	10.9
Cd^{2+}	0.95(6)	2.11	B^{3+}	0.27(6)	11.1
Mn^{2+}	0.83(6)	2.41	P^{5+}	0.38(6)	13.2
Fe^{2+}	0.78(6)	2.56	Cr^{6+}	0.44(6)	13.6
Co^{2+}	0.745(6)	2.68	Se^{6+}	0.42(6)	14.3
Zn^{2+}	0.74(6)	2.70	S^{6+}	0.29(6)	20.7
Cu^{2+}	0.73(6)	2.74	C^{4+}	0.16(6)	25.0
Mg^{2+}	0.72(6)	2.78	N^{5+}	0.13(6)	38.5

Note: Radii, which are from Shannon (1976), are for the coordination numbers (CN's) given in parentheses. Where more than one CN is given, the table has been arbitrarily ordered with increasing Ip values for the six-fold coordinated cations. Radii and Ip values for C^{4+} and N^{5+} are from Ahrens (1952). Radii and Ip values for cations having Ip's greater than about 5 are of questionable meaning, given their tendency to form strongly covalent rather than ionic bonds with oxygen.

Coordination chemistry of complexes

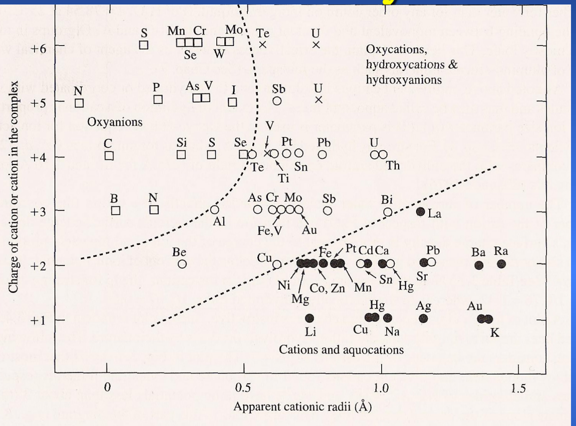
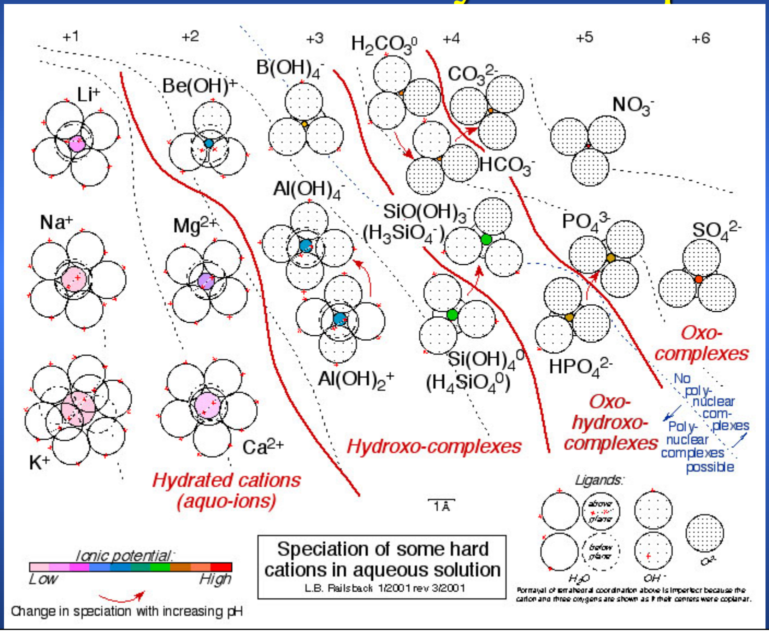


Figure 3.4 Charge of core cations in their aquocomplexes plotted against apparent crystal radii of the cations in solids (1 Å = 1 nm). The radii are mostly from Shannon and Prewitt (1969). Dashed curves roughly divide species by their behavior. Radii of the cations were computed assuming the radius of the oxygen atom equals 1.4 Å and is constant. However, it is less than 1.4 Å in the oxyanions because of strong covalent bonding between oxygen and multivalent cations of N, C, S, and B, for example. Consequently, the apparent radii of these cations shown in the figure are only qualitatively meaningful. (●) cations and aquocations; (○) hydroxycations and hydroxyanions; (×) oxycations; (□) oxyanions. Reprinted with permission from Techniques of estimating thermodynamic properties for some aqueous complexes of geochemical interest, D. Langmuir. In *Chemical modeling in aqueous systems,* ed. E. A. Jenne, Am. Chem. Soc. Symp. Ser. 93. Copyright 1979 American Chemical Society.

Coordination chemistry of complexes



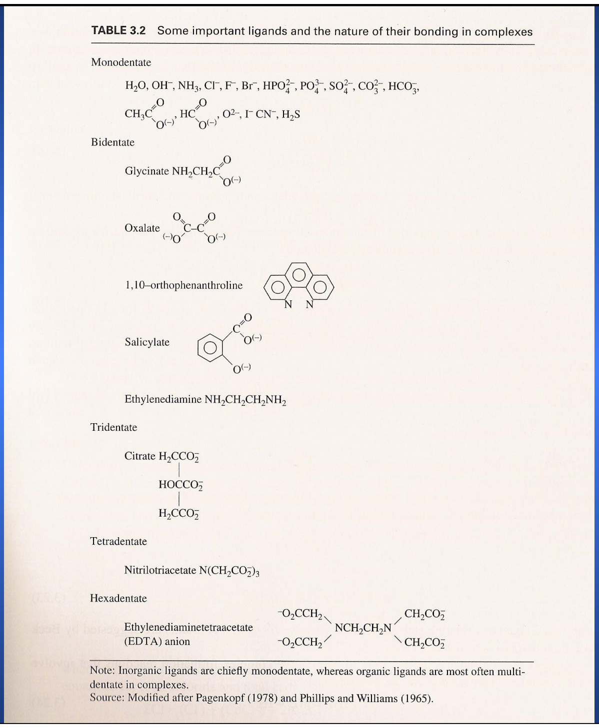


TABLE 3.2 Some important ligands and the nature of their bonding in complexes

Monodentate

H_2O, OH^-, NH_3, Cl^-, F^-, Br^-, HPO_4^{2-}, PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, HCO_3^-,

$CH_3C(=O)O^{(-)}$, $HC(=O)O^{(-)}$, O^{2-}, I^- CN^-, H_2S

Bidentate

Glycinate $NH_2CH_2C(=O)O^{(-)}$

Oxalate $^{(-)}O(O=)C{-}C(=O)O^{(-)}$

1,10–orthophenanthroline

Salicylate

Ethylenediamine $NH_2CH_2CH_2NH_2$

Tridentate

Citrate $H_2CCO_2^-$
$HOCCO_2^-$
$H_2CCO_2^-$

Tetradentate

Nitrilotriacetate $N(CH_2CO_2^-)_3$

Hexadentate

Ethylenediaminetetraacetate (EDTA) anion $(^-O_2CCH_2)_2NCH_2CH_2N(CH_2CO_2^-)_2$

Note: Inorganic ligands are chiefly monodentate, whereas organic ligands are most often multidentate in complexes.
Source: Modified after Pagenkopf (1978) and Phillips and Williams (1965).

Aqueous Complexes

General trends of Complexation

1.) The stability of complexes increases with increasing charge and/or decreasing cation for a given ligand, or ligand for a given cation. Ion pairs or outer-sphere complexes are weak and electrostatically bonded. Inner-sphere complexes involve covalent bonding between cation and ligand and are generally stronger.

2.) Cations and ligand that form strong complexes also tend to form minerals with low solubility

3.) Complexing tend to increase the solubility of minerals that contains the species being complexed. Complexing of a species may also enhance or inhibit its adsorption an will usually affect its toxicity and bioavailability.

4.) The more saline a water, the more ions in it exist as complexes

5.) The more saline a water, the more soluble minerals tend to be in it, both because of complex formation and activity-coefficient effects.

Hydrolysis

$$Fe^{3+} + xH_2O \Leftrightarrow Fe(OH)_3 + xH^+$$

Speciation of Fe^{2+} and Fe(II)-OH complexes as a function of pH

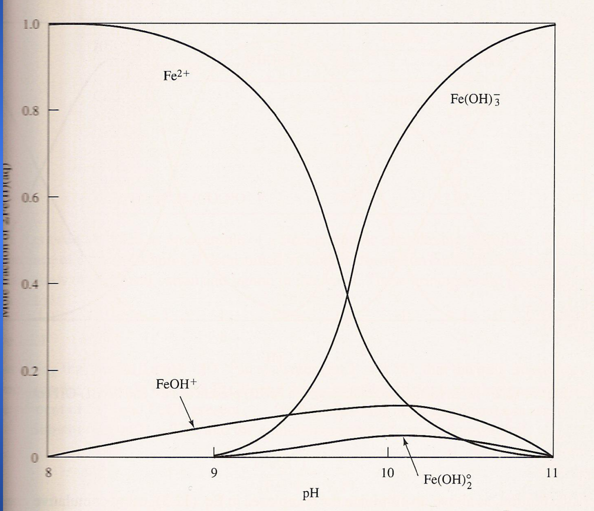
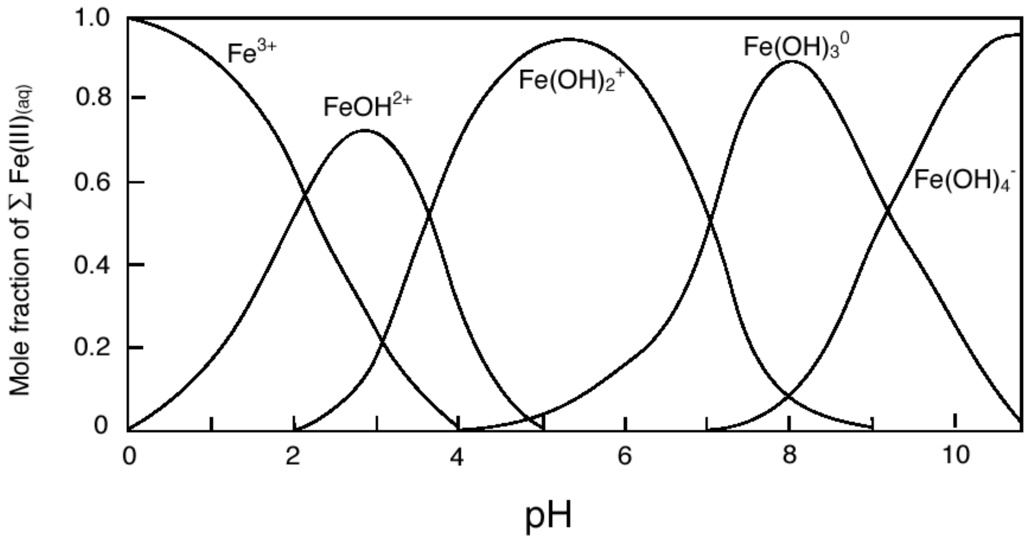


Figure 12.1 Mole fraction of total dissolved Fe(II) present as Fe^{2+} and Fe(II)-OH complexes as a function of pH in pure water at 25°C.

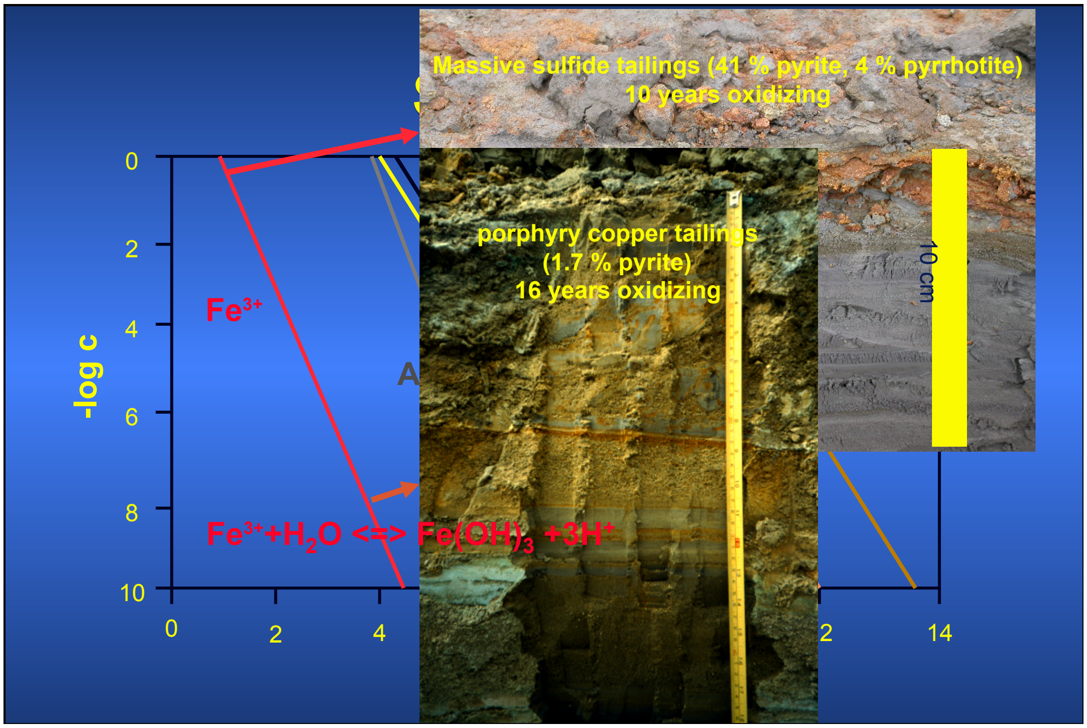
Speciation of Fe^{3+} and Fe(III)-OH complexes as a function of pH



Hydrolysis

Table 2: *Hydrolysis reactions of Fe(III) species and the associated protons produced (from Stumm and Morgan, 1996).*

Species	Equation	Fe^{3+}	H^+	log *K* (I = 3 M)
Fe^{3+}		1	0	0
$Fe(OH)^{2+}$	$Fe^{3+} + H_2O \Leftrightarrow Fe(OH)^{2+} + H^+$	1	-1	-3.05
$Fe(OH)_2^+$	$Fe^{3+} + 2H_2O \Leftrightarrow Fe(OH)_2^+ + 2H^+$	1	-2	-6.31
$Fe(OH)_{3\,(aq)}$	$Fe^{3+} + 3H_2O \Leftrightarrow Fe(OH)_{3\,(aq)} + 3H^+$	1	-3	-13.8
$Fe(OH)_4^-$	$Fe^{3+} + 4H_2O \Leftrightarrow Fe(OH)_4^- + 4H^+$	1	-4	-22.7
$Fe_2(OH)_2^{4+}$	$2Fe^{3+} + 2H_2O \Leftrightarrow Fe_2(OH)_2^{4+} + 2H^+$	2	-2	-2.91
$Fe_3(OH)_4^{5+}$	$3Fe^{3+} + 4H_2O \Leftrightarrow Fe_3(OH)_4^{5+} + 4H^+$	3	-4	-5.77

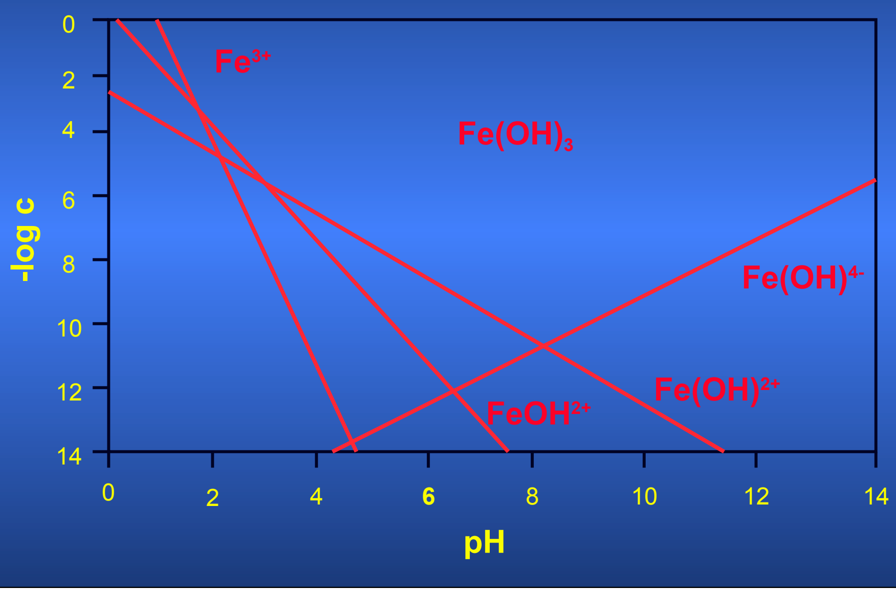


Massive sulfide tailings (41 % pyrite, 4 % pyrrhotite)
10 years oxidizing

porphyry copper tailings
(1.7 % pyrite)
16 years oxidizing

$Fe^{3+}+H_2O <=> Fe(OH)_3 +3H^+$

Solubility of $Fe(OH)_3$



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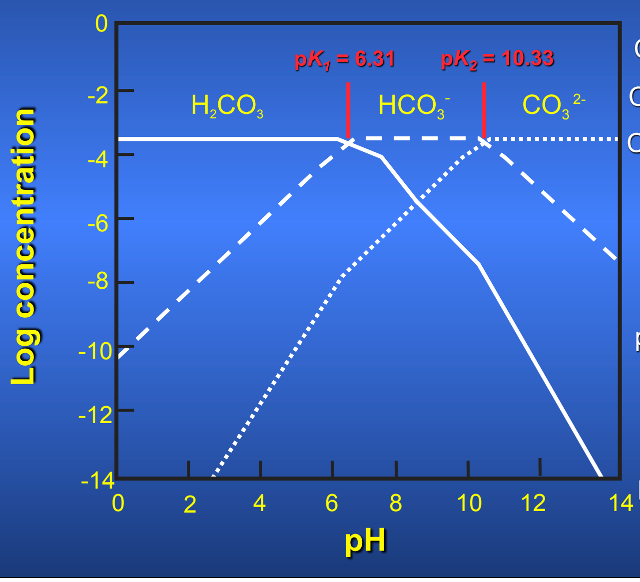
carbonate speciation



$CaCO_3 = Ca^{2+} + CO_3^{2-}$

$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$

$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3^o$

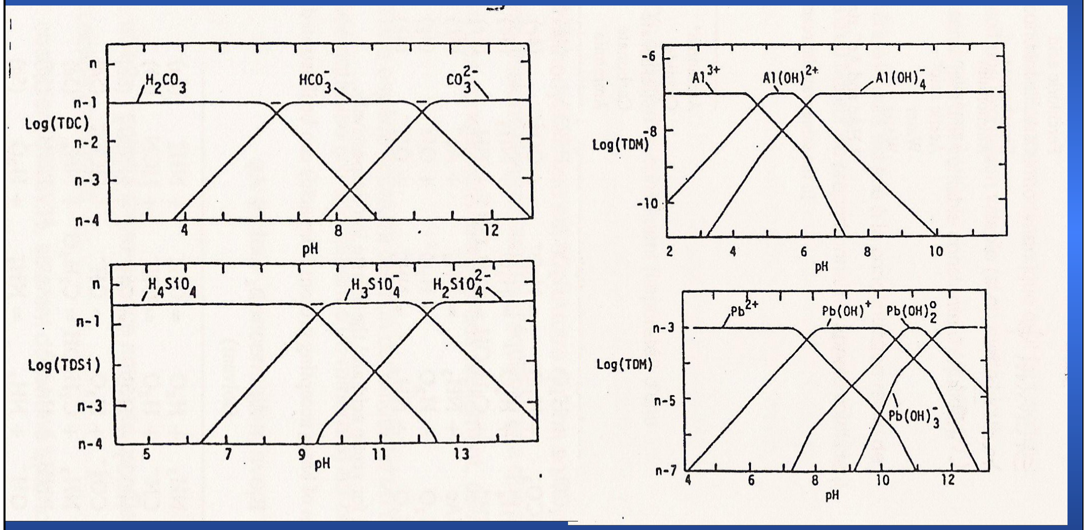
$H_2CO_3^o = HCO_3^- + H^+$

$$pK_1 = K_1 = \frac{[HCO_3^-] + [H^+]}{[\,H_2CO_3^o]} = 10^{-6.35}$$

$HCO_3^- = CO_3^{2-} + H^+$

$$pK_2 = K_2 = \frac{[CO_3^{2-}] + [H^+]}{[HCO_3^-]} = 10^{-10.33}$$

Speciation



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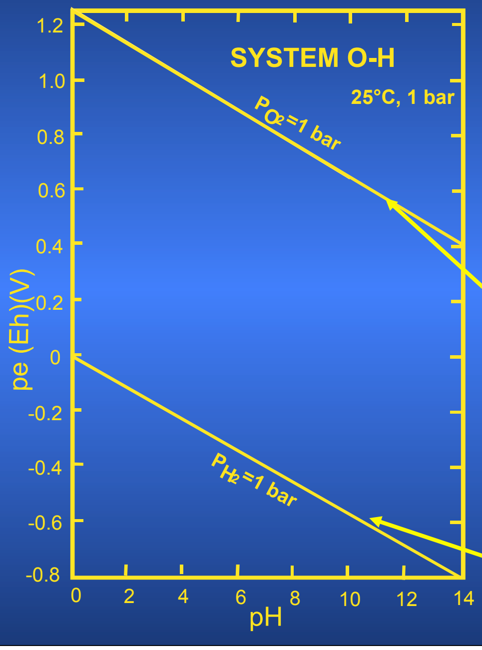
pe (Eh)-pH diagram



$1/4O_{2(g)} + H^+ + e^- = 1/2H_2O$ log K_1 = 20.75

$H^+ + e^- = 1/2H_{2(g)}$ log K_2 = 0

$$K_1 = \frac{1/2[H_2O]}{1/4pO_{2(g)} \bullet [H^+] \bullet [e^-]}$$

=> Log K_1 =-1/4 log P_{O2}+pe+pH

Pour P_{O2}=1 atm -> Log P_{O2} = 0

=> pe = 20.75-pH

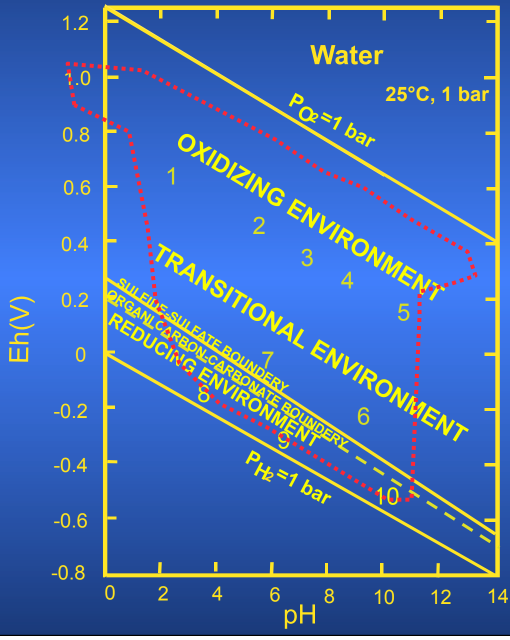
$$K_2 = \frac{1/2P_{H2}}{[H^+] \bullet [e^-]}$$

=> Log K_2 =1/2 log P_{H2}+pe+pH

Pour P_{H2}=1 atm

=> pe = -pH

Eh-pH diagrams



1 mine waters
2 rain
3 streams
4 normal ocean water
5 aerated saline water
6 ground water
7 bog water
8 water-logged soils
9 euxenic marine water
10 organic-rich saline waters

after Brookins (1988)

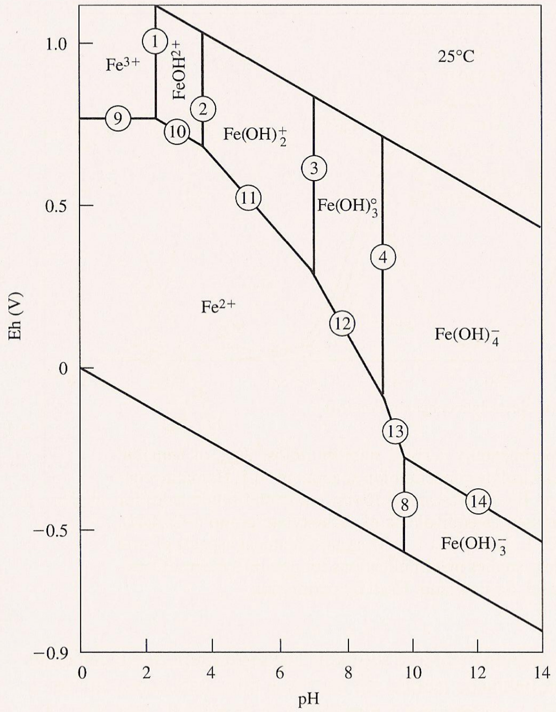
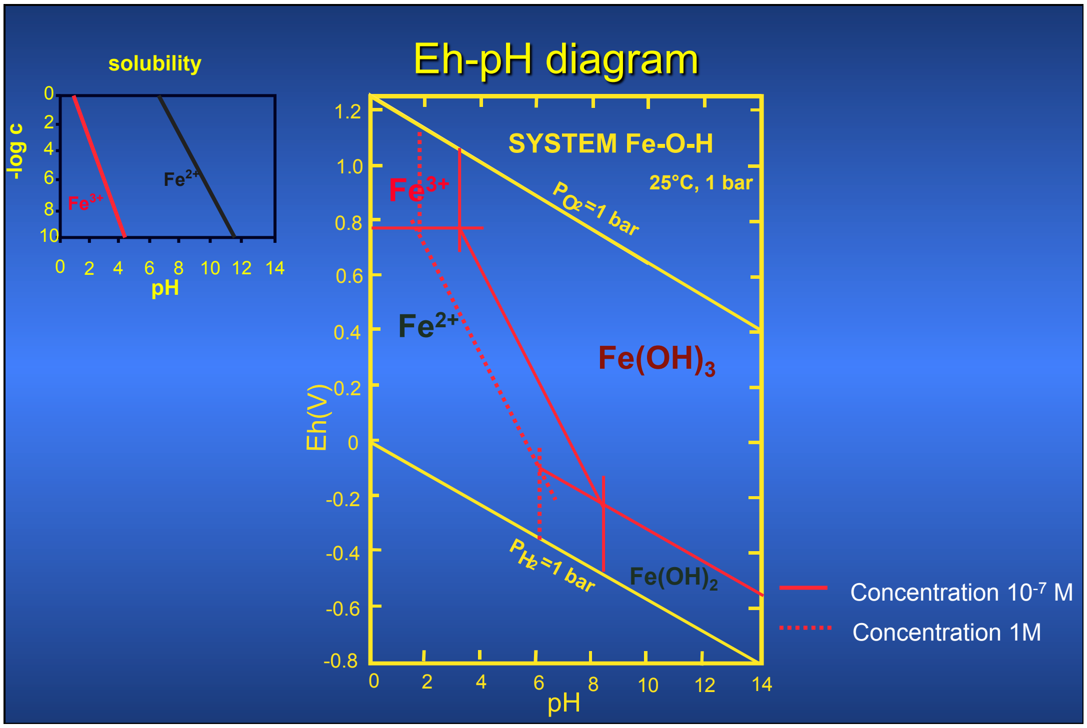


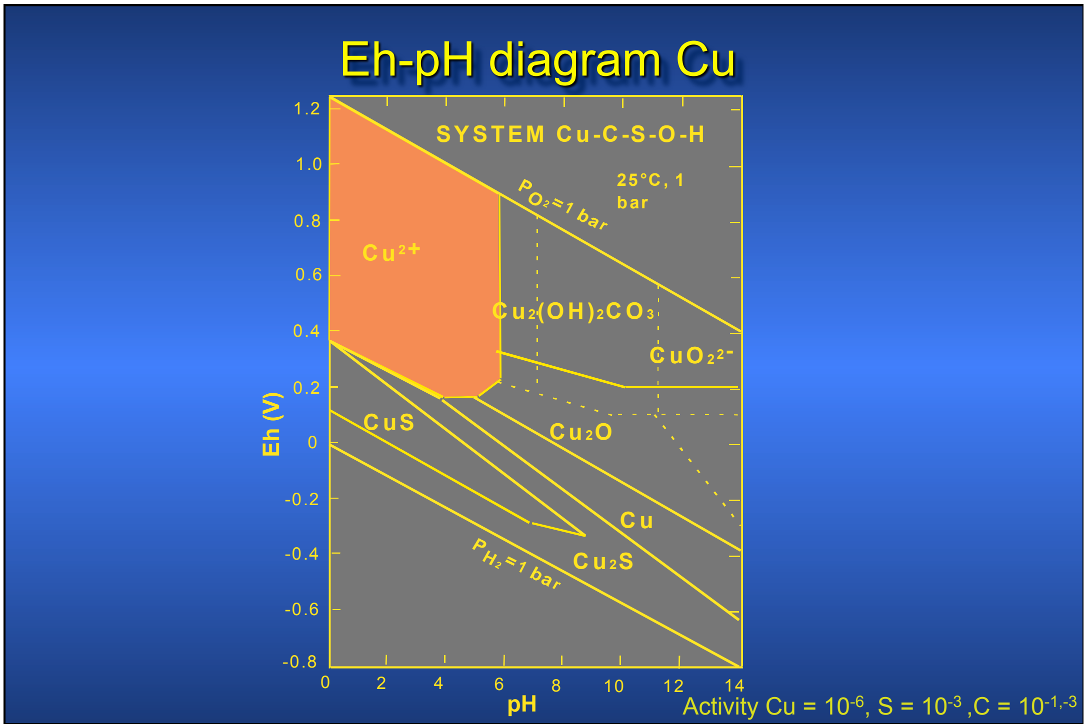
Figure 12.8 Eh-pH diagram at 25°C for aqueous species in the system Fe-O_2-H_2O at concentrations low enough so that polynuclear complexes are not predominant. Circled numbers are the numbers of corresponding reaction equations in Table A12.2.



Eh-pH diagram

Concentration 10^{-7} M

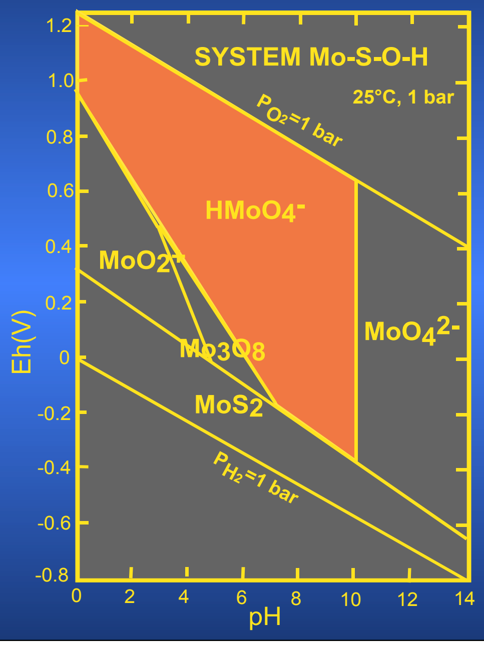
Concentration 1M



Eh-pH diagram Cu

Activity Cu = 10^{-6}, S = 10^{-3} ,C = $10^{-1,-3}$

Eh-pH diagram Mo



Activity Mo = 10^{-8}, S = 10^{-3}

Acid - Base

Acidity

Acidity = capacity of water to donate protons
Acidity is measured by titrating water with a strong base (e.g. NaOH)

A) Strong acids $H^+ + OH^- = H_2O$
$HSO_4^- + OH^- = SO_4^{2-} + H_2O$

B) Weak acids $H_2S_{(aq)} + OH^- = HS^- + H_2O$
$H_2CO_3 + OH^- = HCO_3^- + H_2O$
$HCO_3^- + OH^- = CO_3^{2-} + H_2O$

C) Metal Ions
hydrolysis only: $Al^{3+} + 3OH^- = Al(OH)_3$
oxidation & hydrolysis: $2Fe^{2+} + 4OH^- + H_2O + {}^1/_2O_2 = 2Fe(OH)_3$

e.g. AMD total acidity:
$C_A = H^+ + HSO_4^- + 2Fe^{2+} + 3Fe^{3+} + 2FeOH^{2+} + 3Al^{3+}$

Mineral acidity: **e.g. jarosite, schwertmannite,**
or Fe^{3+} sulfates: $Fe_2(SO_4)_3 \cdot nH_2O$ e.g. lausenite, coquimbite, cornelite etc. => hydrolysis

Acid Producing Processes

- Sulfide oxidation (e.g. pyrite)

$FeS_2 + {}^7/_2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$
$FeS_2 + 14\,Fe^{3+} + 8H_2O \rightarrow 15\,Fe^{2+} + 2SO_4^{2-} + 16H^+ \; (2H^+)$

$Fe^{2+} + {}^1/_4O_2 + H^+ \leftrightarrow Fe^{3+} + {}^1/_2H_2O$ (microbiological catalyzed e.g., *A.ferrooxidans*)

- Hydrolysis

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$
$\Rightarrow FeS_2 + {}^{15}/_4O_2 + {}^7/_2H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+$

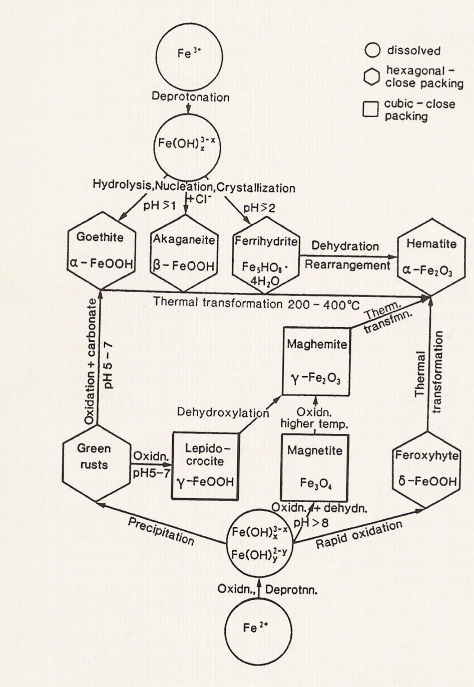
- Transformation (jt & sh => gt)

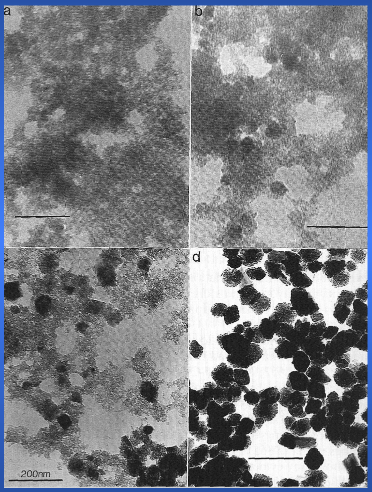
$KFe_3(SO_4)_2(OH)_6 = 3FeO(OH) + K^+ + 2SO_4^{2-} + 3H^+$
$Fe_8O_8(OH)_6SO_4 + 2H_2O = 8FeO(OH) + SO_4^{2-} + 2H^+$

acid production by hydrolysis

Phase	Equation	H^+/mol mineral
$Fe(OH)_{3(s)}$	$Fe^{3+} + 3H_2O = Fe(OH)_{3(s)} + 3H^+$	3
ferrihydrite	$10Fe^{3+} + 60H_2O = 5Fe_2O_3{\cdot}9H_2O + 30H^+$	3
schwertmannite	$8Fe^{3+} + SO_4^{2-} + 14H_2O = Fe_8O_8(OH)_6SO_4 + 22H^+$	2.75
jarosite	$3Fe^{3+} + K + 2SO_4^{2-} + 6H_2O = KFe_3(SO_4)_2(OH)_6 + 6H^+$	2

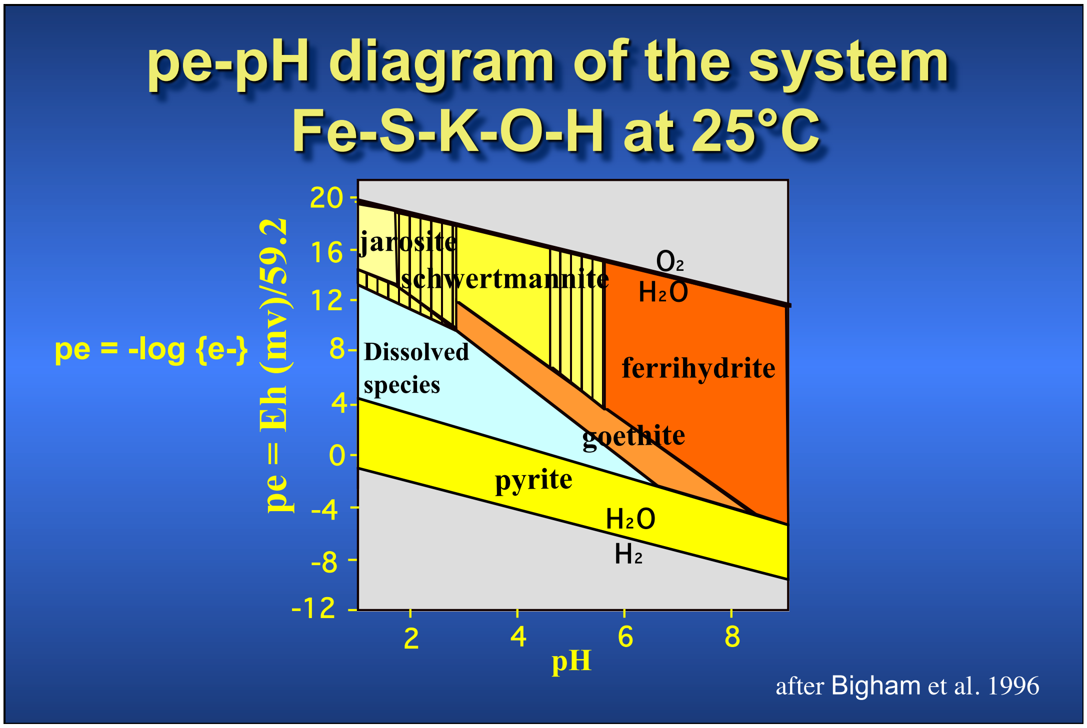
Formation and transformation pathways of iron oxides





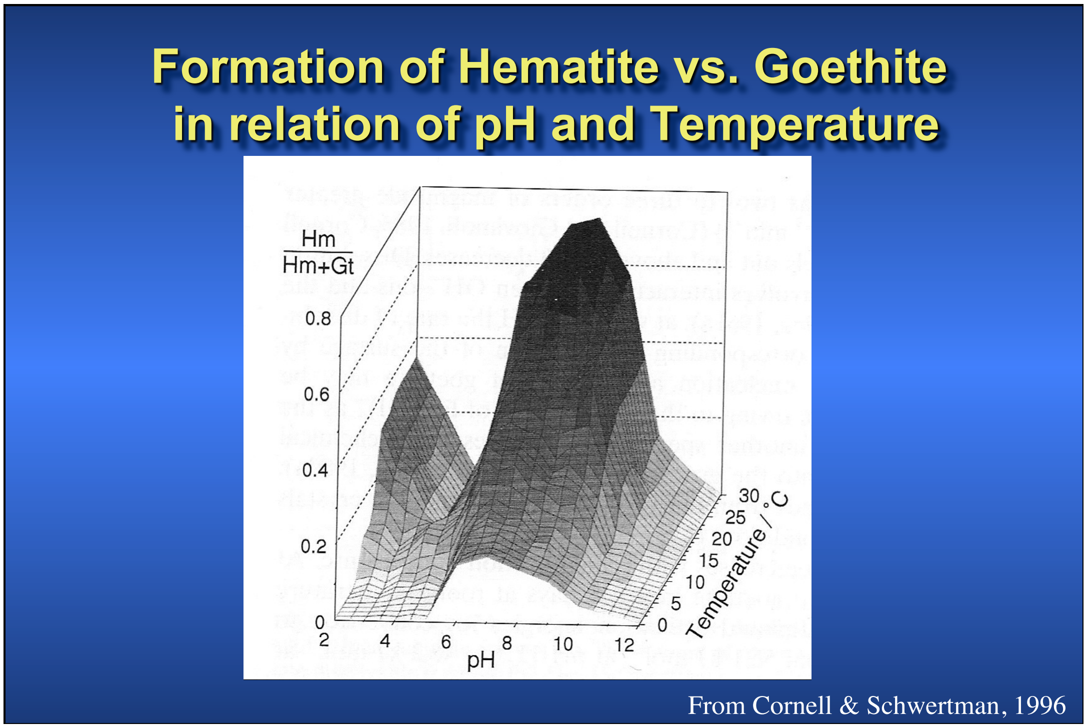
Transformation of ferrihydrite to hematite

From Cornell & Schwertmann, 1996



pe-pH diagram of the system Fe-S-K-O-H at 25°C

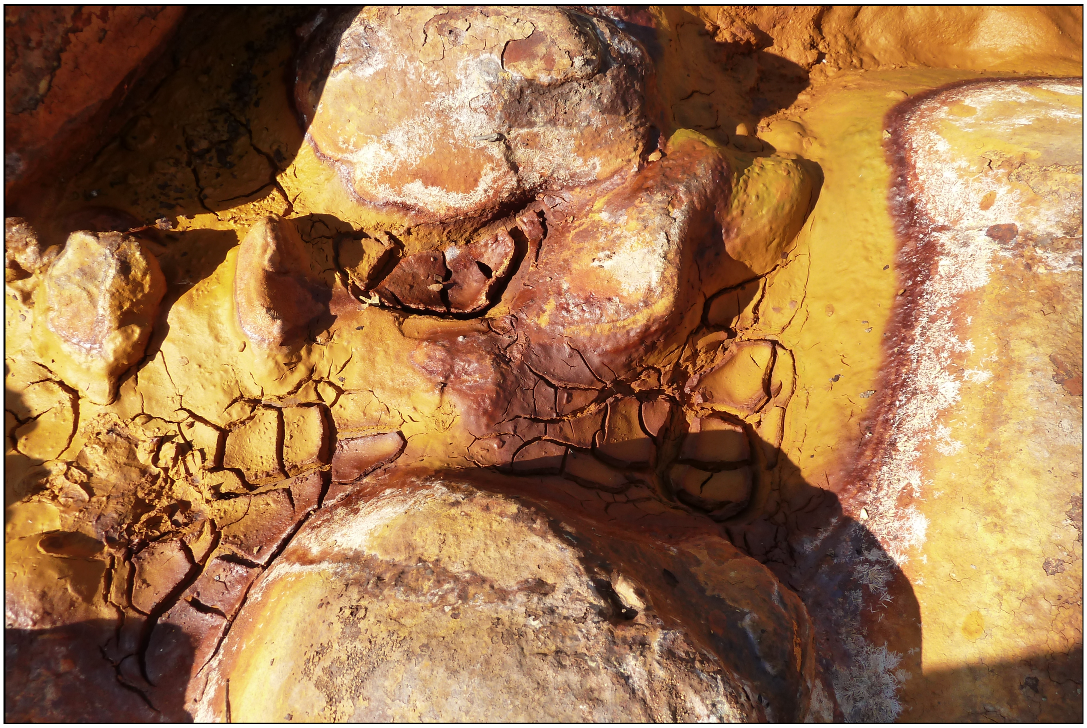
after Bigham et al. 1996



Formation of Hematite vs. Goethite in relation of pH and Temperature

From Cornell & Schwertman, 1996

Formation of Hematite vs. Goethite in relation of Temperature



Other acid producing sulfides

- Pyrrhotite ($Fe_{(1-x)}S$)

$Fe_{(1-x)}S + (2-x/2)O_2 + xH_2O \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+$

x can vary from 0.125 (Fe_7S_8) to 0.0 (FeS, troilite)

if x = 0 and the formula is FeS, no H^+ will be produced in the oxidation reaction

- Chalcopyrite ($CuFeS_2$)

$2CuFeS_2 + 4O_2 \rightarrow 2Cu^{2+} + Fe^{2+} + SO_4^{2-}$

$2CuFeS_2 + 17/2O_2 + 5\,H_2O \rightarrow 2Cu^{2+} + 2Fe(OH)_3 + 4SO_4^{2-} + 4H^+$

- Arsenopyrite (FeAsS)

$4FeAsS + 13O_2 + 6H_2O \rightarrow 4Fe^{2+} + 4SO_4^{2-} + 4H_2AsO_4^- + 4H^+$

$FeAsS + {}^7/_2O_2 + 6H_2O \rightarrow Fe(OH)_3 + SO_4^{2-} + H_2AsO_4^- + 3H^+$

Non acid producing sulfides

- Sphalerite (ZnS) and galena (PbS)

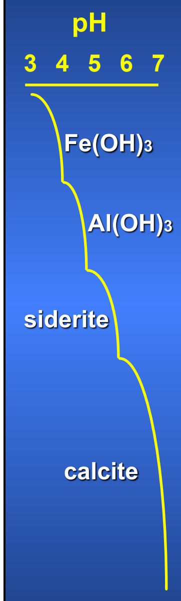
$ZnS + 2O_2 \rightarrow Zn^{2+} + SO_4^{2-}$

$PbS + 2O_2 \rightarrow Pb^{2+} + SO_4^{2-}$

sphalerite may contain environmentally dangerous amounts of Cd and Thallium (Tl). In addition, Fe may significally substitute for Zn, in cases up to 15 mole %, in sphalerite.

- $2MeS + 4Fe^{3+} + 3O_2 + 2H_2O \rightarrow 2Me^{2+} + 4Fe^{2+} + 2SO_4^{2-} + 4H^+$

Neutralization



- Carbonates

$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$	calcite	pH 7
$FeCO_3 + 2H^+ = Fe^{2+} + H_2CO_3^-$	siderite	pH 5

- Hydroxides

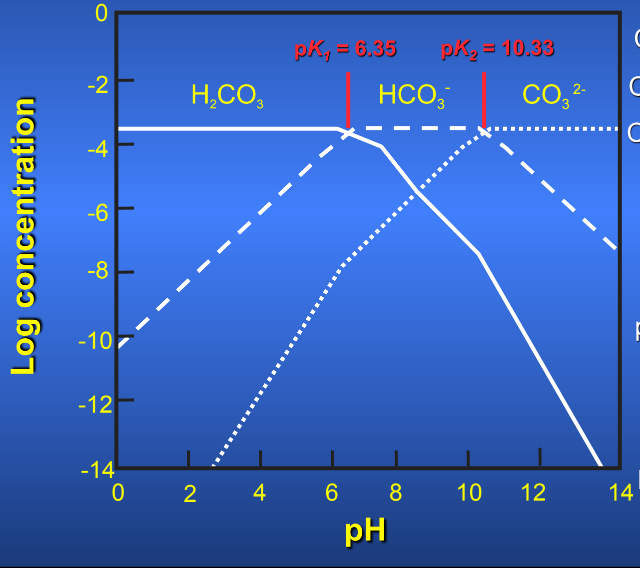
$Al(OH)_3 + 3H^+ = Al^{3+} + 3H_2O$	gibbsite	pH 4.3
$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	ferrihydrite	pH 3.5

- Silicates

$2KAlSiO_3O_8 + 9H_2O + 2H^+ = Al_3Si_2O_5(OH)_4 + 2K^+ + 4H_4SiO_4$

K-feldspar kaolinite

carbonate speciation



$CaCO_3 = Ca^{2+} + CO_3^{2-}$

$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$

$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3^o$

$H_2CO_3^o = HCO_3^- + H^+$

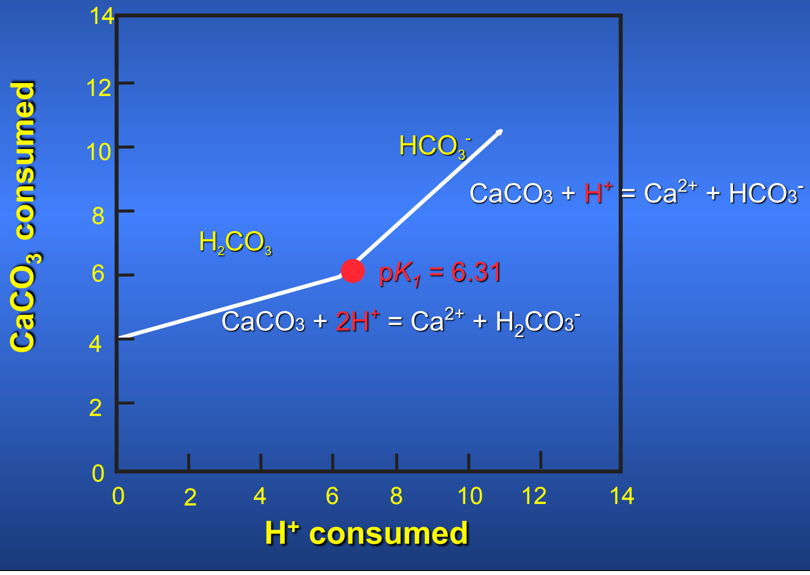
$$pK_1 = K_1 = \frac{[HCO_3^-] + [H^+]}{[\ H_2CO_3^o]} = 10^{-6.35}$$

$HCO_3^- = CO_3^{2-} + H^+$

$$pK_2 = K_2 = \frac{[CO_3^{2-}] + [H^+]}{[HCO_3^-]} = 10^{-10.33}$$

carbonate neutralization

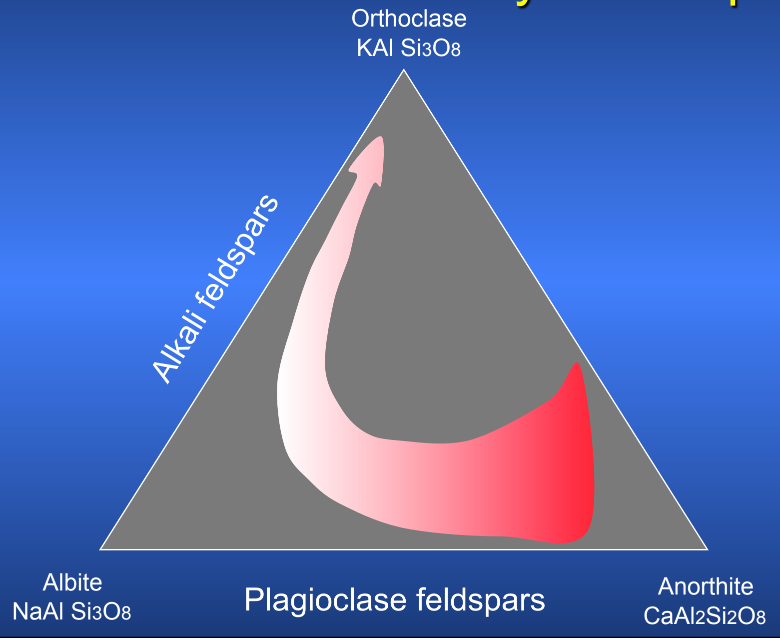
$FeS_2 + {}^{15}/_4O_2 + {}^{7}/_2H_2O \text{ --> } Fe(OH)_3 + 2SO_4^{2-} + 4H^+$



$CaCO_3 + H^+ = Ca^{2+} + HCO_3^-$

$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3^-$

Neutralization reactivity of feldspars



Neutralization Reactivity

Table 4: *Acid-neutralization capacity of minerals (in Jambor and Blowes, 1998, after Sverdrup, 1990).*

Group	**Typical Minerals**	**Relative Reactivity (pH5)**
1. Dissolving	calcite, dolomite, magnesite, aragonite, brucite	1.0
2. Fast weathering	anorthite, olivine, garnet, diopside, wollastonite, jadeite, nepheline, leucite, spodumene	0.6
3.Intermediate weathering	enstatite, augite, hornblende, tremolite, actinolite, biotite, chlorite, serpentine, talc, epidote, zoisite, hedenbergite, glaucophane, anthophyllite	0.4
4. Slow weathering	plagioclase (Ab_{100}-Ab_{30}), kaolinite, vermiculite, montmorillonite, gibbsite	0.02
5. Very slow weathering	K-feldspar, muscovite	0.01
6. Inert	quartz, rutile, zircon	0.004

Titration of Acid - Base

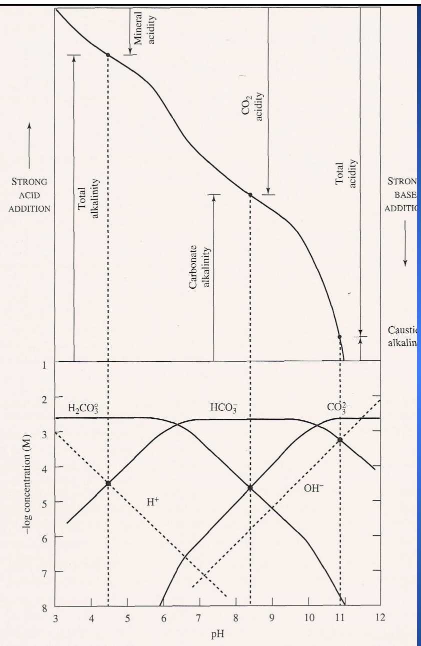


Figure 5.6 The carbonate distribution diagram of a solution with constant $C_T = 2.5 \times 10^{-3}$ M showing **(a)** the strong acid titration curve for the same solution from pH 12 to 3 and strong base titration curve between pH 3 and 12. Dashed straight lines in **(b)** indicate concentrations of H^+ and OH^-, which are independent of C_T. Modified after V. L. Snoeyink and D. Jenkins, *Water Chemistry.* Copyright © 1980 by John Wiley & Sons, Inc. Used by

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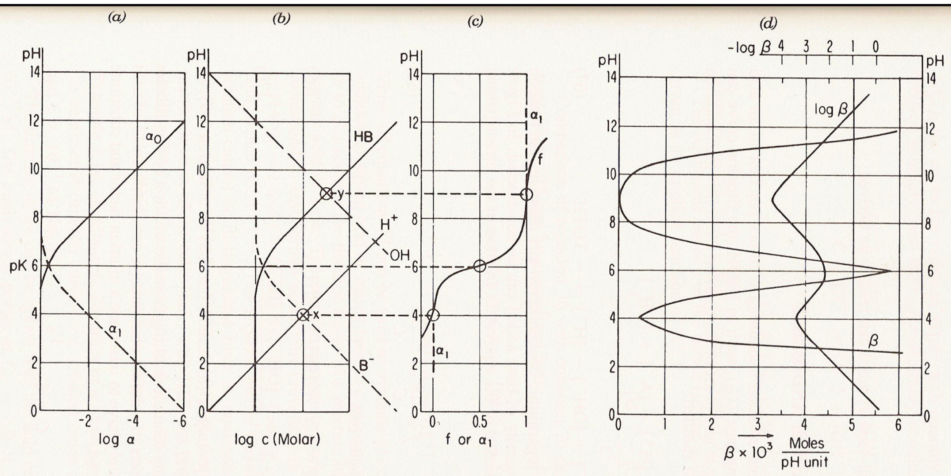

Figure 3.8. The titration curve and the buffer intensity are related to the equilibrium species distribution. For a monoprotic acid–base system (HB–B), (a) gives the logarithmic distribution diagram. α_1 and α_0 are the ionization fractions of B and HB, respectively. (b) The log concentration–pH diagram is the superimposition of the semi-logarithmic distribution diagram (a) and the concentration condition (log C = constant). Points X and Y correspond to the equivalence points on the alkalimetric or acidimetric titration curve. (c) Plot of the titration curve. The equivalence points (X and Y) and the half-titration point pH = pK are as given in (b). The equivalence fraction of the titrant added, f, shows, over a significant portion of the titration curve ($0.1 < f < 0.9$), the same dependence on pH as α_1. (d) The buffer intensity, β, corresponding to the inverse slope of the titration curve (dC_B/d pH), can be computed from a log concentration–pH diagram by multiplying by 2.3 the sum of all concentrations represented by a line of slope + 1 or − 1 at that particular pH in the diagram. (See Section 3.9.)

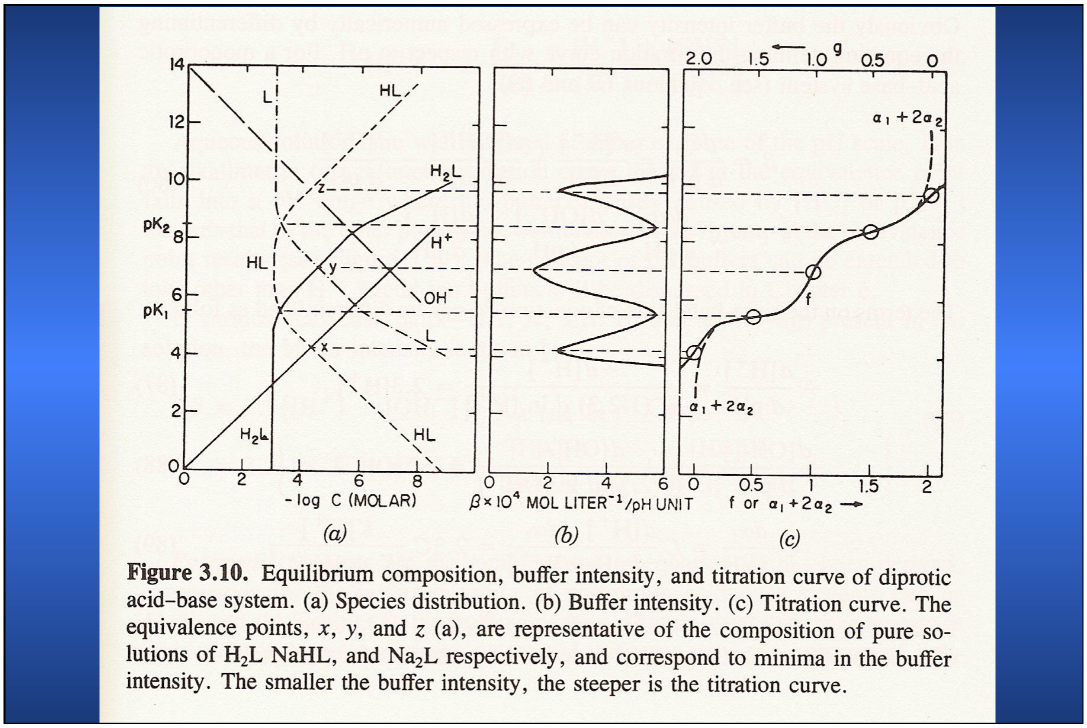

Figure 3.10. Equilibrium composition, buffer intensity, and titration curve of diprotic acid–base system. (a) Species distribution. (b) Buffer intensity. (c) Titration curve. The equivalence points, *x*, *y*, and *z* (a), are representative of the composition of pure solutions of H_2L NaHL, and Na_2L respectively, and correspond to minima in the buffer intensity. The smaller the buffer intensity, the steeper is the titration curve.

Sorpción
Adsorción-Absorpción