Solubility (Speciation) Models and Their Limitations

Michael Schock

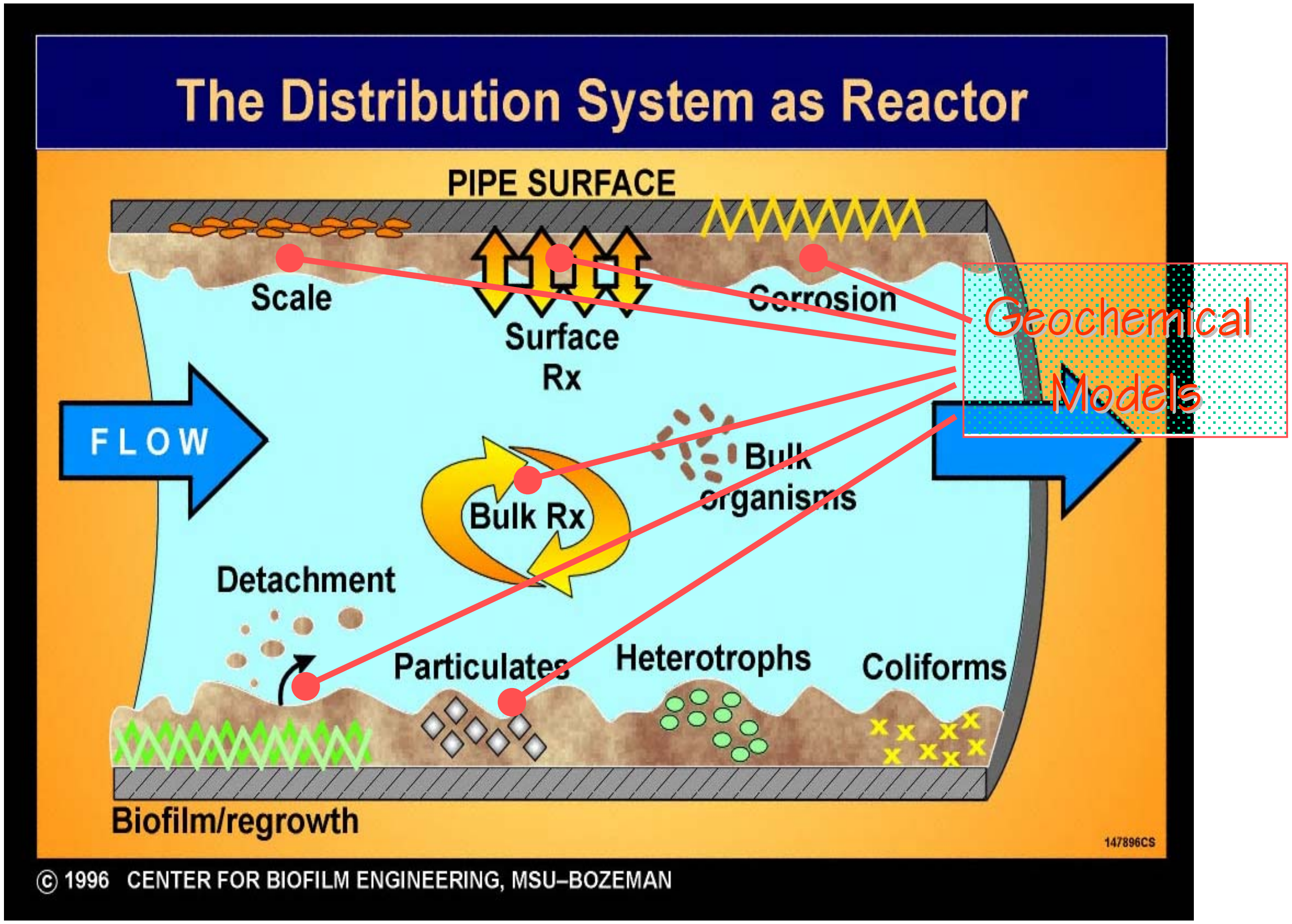
WSWRD, ORD, U. S. Environmental Protection Agency

Cincinnati, OH

Water Quality in DS Affected by:

- Complex physical, chemical, biological interactions between the bulk water and the pipe scale
- Chemical reactions include:
  - hydrolysis
  - complexation
  - precipitation-dissolution
  - oxidation-reduction
  - sorption and partitioning

Heterogeneous and Homogeneous Chemical Reactions



Why Geochemical/Solubility Models?

- Based on fundamental chemistry reactions
- Can take into account complex matrices and interrelationships without needing site/system specific "calibration"
- Can allow prediction to NEW unknown/uncalibrated situations
  - Quantitative impacts of changes to WQPs
  - Mass transfer & metal release (dissolution, precipitation)
  - Secondary impacts of treatment changes on metals

What They Do

- Geochemical models can be used to describe these reactions mathematically through
  - Computation of the activities of different forms or species of a chemical entity as a function of
    - Temperature
    - Background constituents and concentrations
    - ORP
  - Maintaining mass balance in the calculations
  - Mass transfer

What Is the Real Fundamental Solution Parameter?

Thermodyanmic "Activity"

Example: Calcium sulfate ion pair

$Ca^{2+} + SO_4^{2-} = CaSO_4^{\circ}$

log k is 2.3 at 25°C

$10^{2.3} = \alpha_{CaSO4}/\{\alpha_{Ca}\alpha_{SO4}\}$

$\alpha_i=\gamma_i m_i$ or $\alpha_i=\gamma_i M_i$

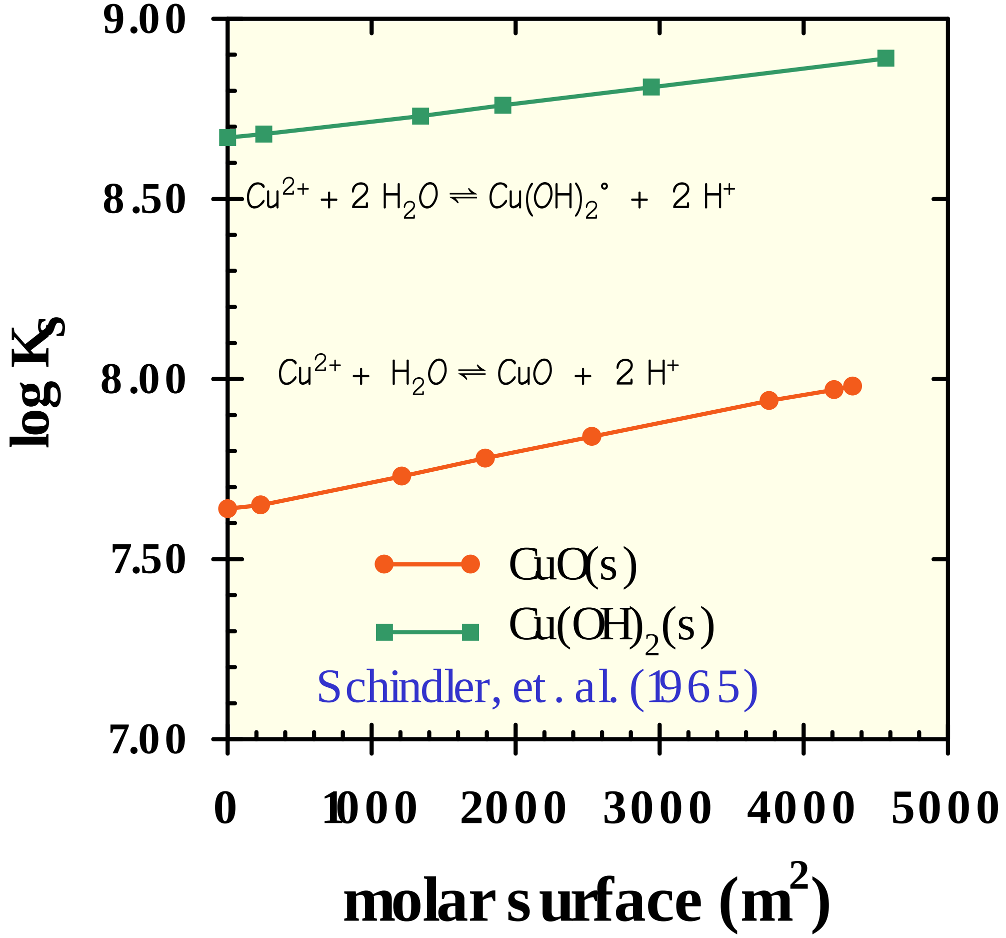
α_i=activity

γ_i = activity coefficient;
m=molality or M = molarity

Limitations……

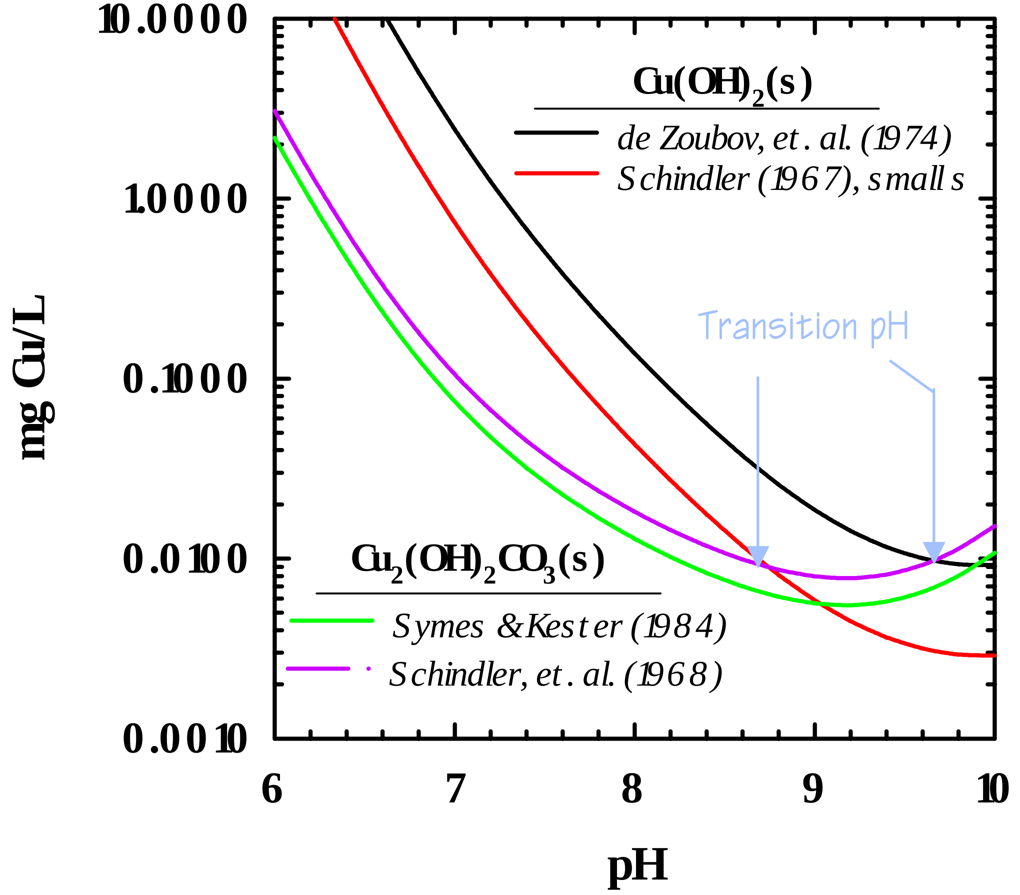
- System must be at equilibrium or quasi-equilibrium over timeframe of interest
  - Aqueous reactions may equilibrate much faster
  - All solids don't equilibrate at same rate
- Complications of metastable solids--the effect of time/scale age, and the direction of reaction, ie. dissolution vs. precipitation

Effect of Molar Surface on Solubility Constants

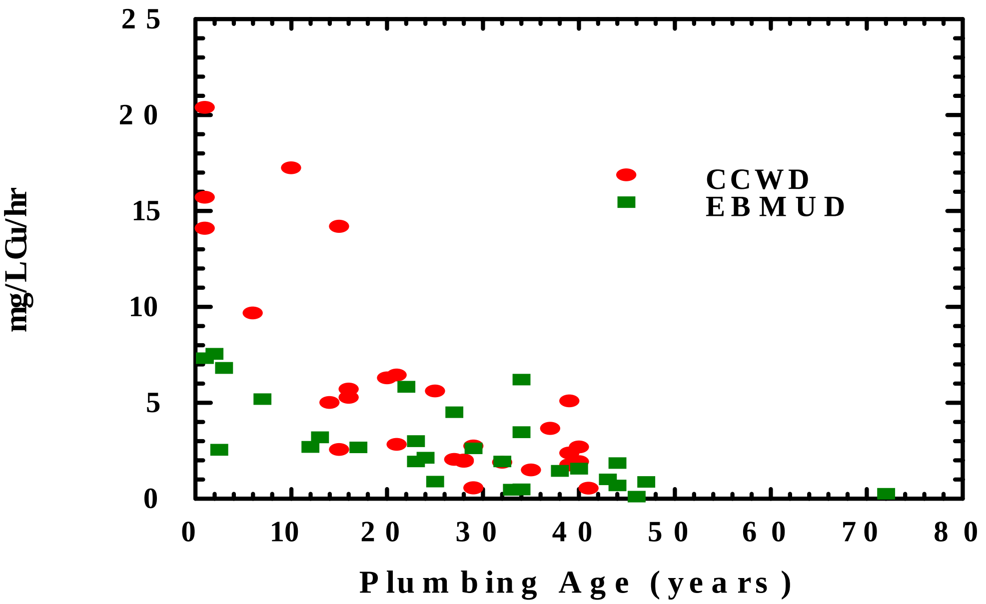


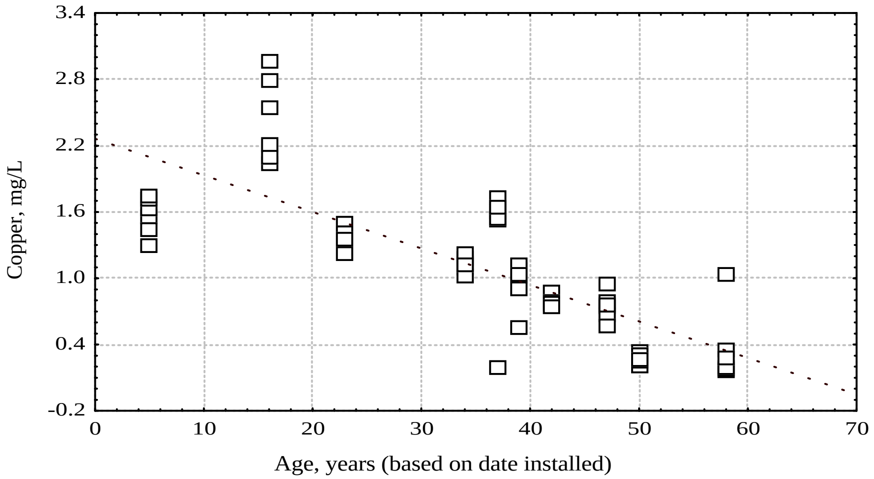
Predicted Copper(II) Solubility by Different Sets of Solubility Constants

DIC = 4.8 mg C/L, I = 0.005, 25°C



Copper Leaching Rate versus Age for California Study





Some Cautions…

- Need critically-evaluated thermodynamic data constants
  - Cannot use random selection from different speciation models
    - Constants may depend on the presumption of what species were present during the data fit
  - Temperature functions may be incomplete or missing for some or all systems & species of interest
  - Need assurance constants represent realistic conditions
    - Analytical verification
    - Careful selection of analogous systems

More Limitations & Cautions

- Some redox couples rarely in equilibrium or are microbially-mediated
- Field data gaps (common to other types as well)
  - Hydraulic effects on particle release/stability in films
  - Physical permeability and electron conductor properties

Some Example Chemical "Models"

- Equilibria, mass-transfer, saturation states, surface reactions
  - PHREEQE (USGS), several forms
  - MINTEQA3 (USEPA, Athens)
  - MINEQL+ (Environmental Research Software)
  - Geochemists' Workbench (Rockware)
  - EQ3/EQ6 (LLL)
  - SOLMINEQ (USGS, high P & T included)

More Examples

- Data reduction from analytical input
  - WATEQ4F and related (USGS)
  - WATEQX (van Gaans)--generalized WATEQF series
  - PHREEQE
  - MINEQL+
  - Many others

Special -Purpose

- Many codes written by individual researchers or groups, eg. for solubility calculations
  - LEADSOL, CU2SOL, ZINCSOL (EPA)
  - SISAS (WRc)
- Sophisticated diagrams, eg. Eh-pH
  - Geochemists Workbench
  - Chess/Jchess
  - Various others, may need post-processing w/ graphics package

Typical Program Data

- Inputs:
  - analytical data
    - Total concentrations
    - Sometimes Individual redox couples
    - Solution parameters eg. pH, temperature, Eh
  - thermodynamic data
    - usually in a separate database
    - Equilibrium constants, reactions, temperature functions, IX selectivity constants
- Outputs:
  - elements, species, redox couples, activities, molality, saturation indices

Example Initial Solution-PHREEQE

```
Initial solution 1.     SEAWATER FROM NORDSTROM ET AL. (1979)

-----------------------------Solution composition------------------------------

        Elements           Molality       Moles

        Alkalinity        2.406e-03   2.406e-03
        Ca                1.066e-02   1.066e-02
        Cl                5.657e-01   5.657e-01
        Fe                3.711e-08   3.711e-08
        K                 1.058e-02   1.058e-02
        Mg                5.507e-02   5.507e-02
```

Etc….

```
----------------------------Description of solution----------------------------

                                       pH  =   8.220
                                       pe  =   8.451
                        Activity of water  =   0.981
                           Ionic strength  =   6.748e-01
                       Mass of water (kg)  =   1.000e+00
                    Total carbon (mol/kg)  =   2.180e-03
                       Total CO2 (mol/kg)  =   2.180e-03
                      Temperature (deg C)  =  25.000
                  Electrical balance (eq)  =   7.936e-04
 Percent error, 100*(Cat-|An|)/(Cat+|An|)  =   0.07
                               Iterations  =   7
                                  Total H  = 1.110147e+02
                                  Total O  = 5.563047e+01
```

Some Example Output-PHREEQE

```
--------------------------------Redox couples-------------------------------

        Redox couple             pe   Eh (volts)

        N(-3)/N(5)           4.6750      0.2766
        O(-2)/O(0)          12.3893      0.7329

---------------------------Distribution of species---------------------------

                                                   Log       Log          Log
        Species              Molality    Activity  Molality  Activity     Gamma

        OH-                2.674e-06   1.629e-06    -5.573    -5.788    -0.215
        H+                 7.981e-09   6.026e-09    -8.098    -8.220    -0.122
        H2O                5.551e+01   9.806e-01    -0.009    -0.009     0.000
         MgHCO3+            2.195e-04   1.640e-04    -3.658    -3.785    -0.127
        NaHCO3             1.667e-04   1.948e-04    -3.778    -3.710     0.067
        MgCO3              8.913e-05   1.041e-04    -4.050    -3.982     0.067
        NaCO3-             6.718e-05   5.020e-05    -4.173    -4.299    -0.127
        CaHCO3+            4.597e-05   3.106e-05    -4.337    -4.508    -0.170
Etc….

-----------------------------Saturation indices-----------------------------

        Phase                SI  log IAP  log KT

        Anhydrite          -0.84   -5.20   -4.36  CaSO4
        Aragonite           0.61   -7.72   -8.34  CaCO3
        Calcite             0.76   -7.72   -8.48  CaCO3
        Chalcedony         -0.51   -4.06   -3.55  SiO2
        Chrysotile          3.36   35.56   32.20  Mg3Si2O5(OH)4
```

Some Frequent Applications….

- Estimating solubility and mobilization of metals
    - Dissoluton/precipitation
    - Surface sorption of metal and ligands
- Computing sorption/IX process performance
- Understand speciation and impact of treatment, blending, or other chemistry changes upon it
- Deducing “control” mechanisms
- Testing “control” hypotheses
- Extracting thermodyamic data, eg. K_{sp}

Solubility Diagram Example: Cu(II)

Copper(II) Hydrolysis Species Frequently Reported

Cu^{2+}

$CuOH^{+}$

$Cu(OH)_2^{\circ}$

$Cu(OH)_3^{-}$

$Cu(OH)_4^{2-}$

$Cu_2(OH)_2^{2+}$

$Cu_3(OH)_4^{2+}$

Reported Copper(II) Carbonate and Hydroxycarbonate Complexes

$CuHCO_3^+$

$CuCO_3^{\circ}$

$Cu(CO_3)_2^{2-}$

$Cu(OH)CO_3^-$

$Cu(OH)_2CO_3^{2-}$

Reported Copper(II) Orthophsphate and Sulfate Complexes

$CuSO_4^{\circ}$

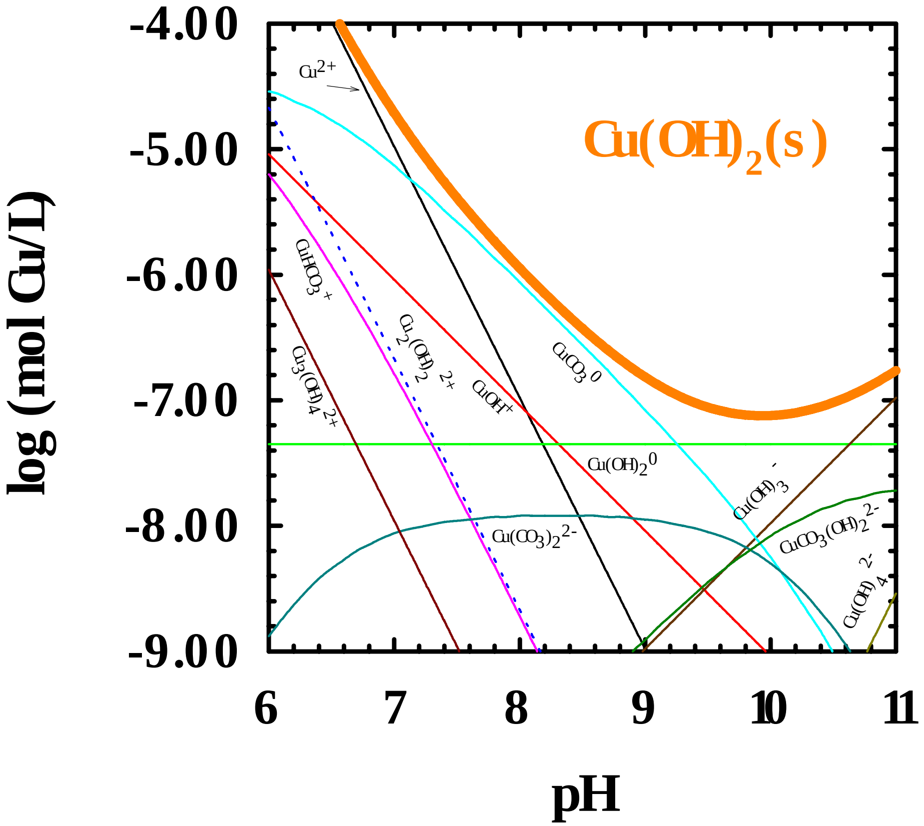
$Cu(SO_4)_2^{2-}$

$CuH_2PO_4^{+}$

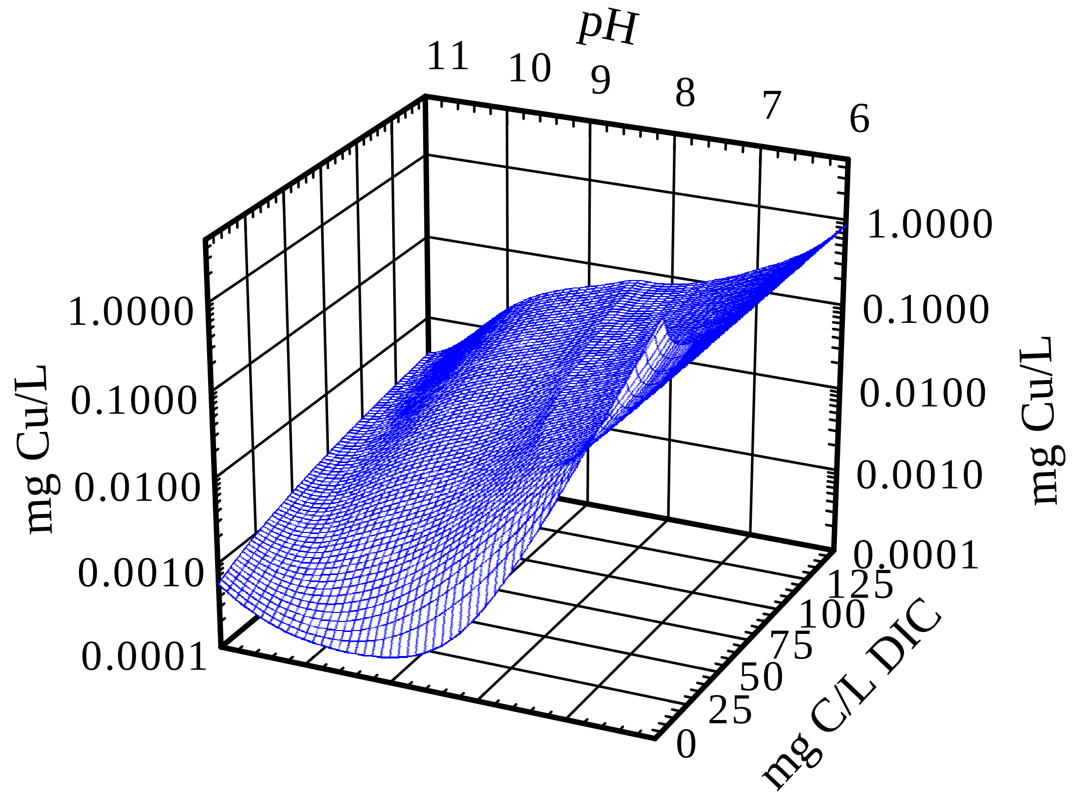
$CuHPO_4^{\circ}$

Copper(II) Speciation in Equilibrium with Cupric Hydroxide

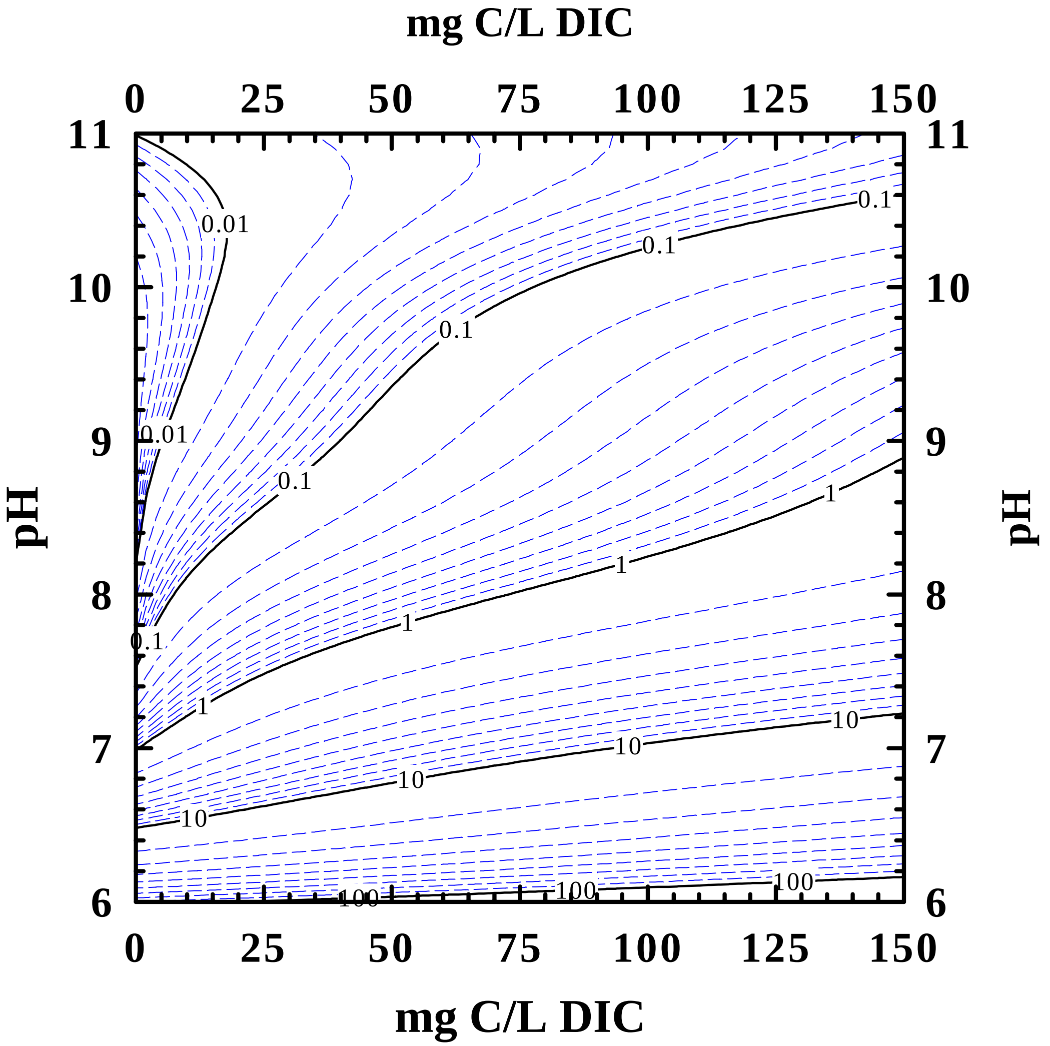
DIC = 4.8 mg C/L, I = 0.005, 25°C



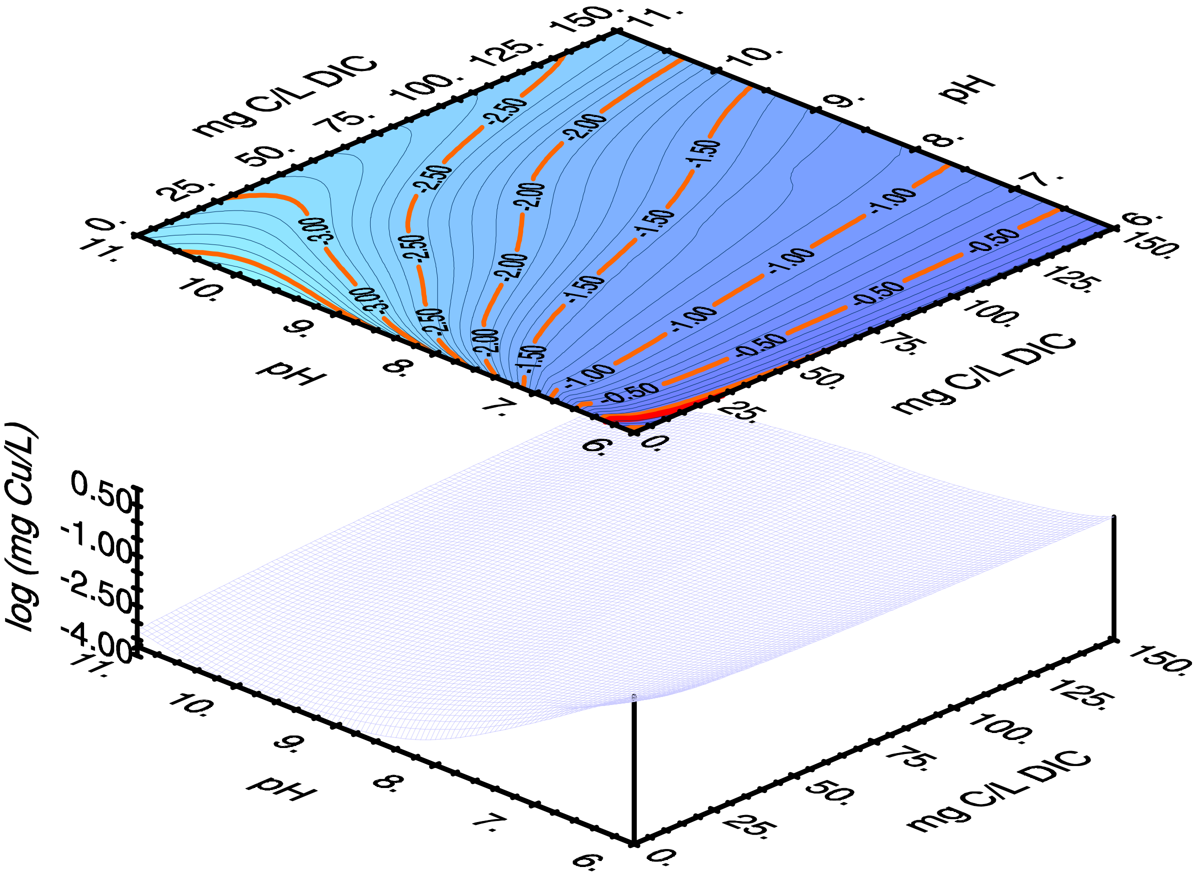
3-D Solubility "Surface" for Cu(II)



“Contour Diagram” Representation for Cu(II)



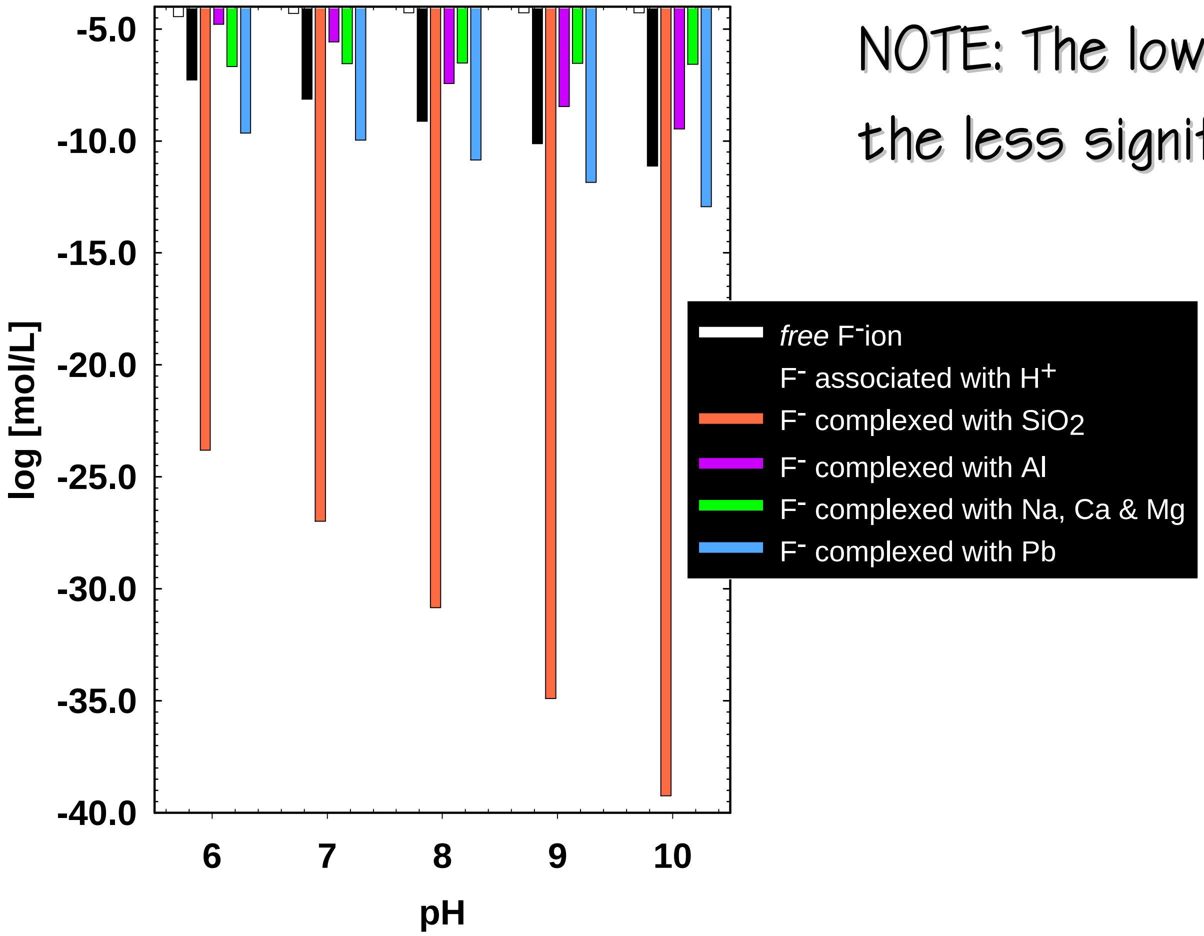
Example Relationship of Contour Diagram to 3-D Surface



Pb-F Interaction Example-MINEQL+

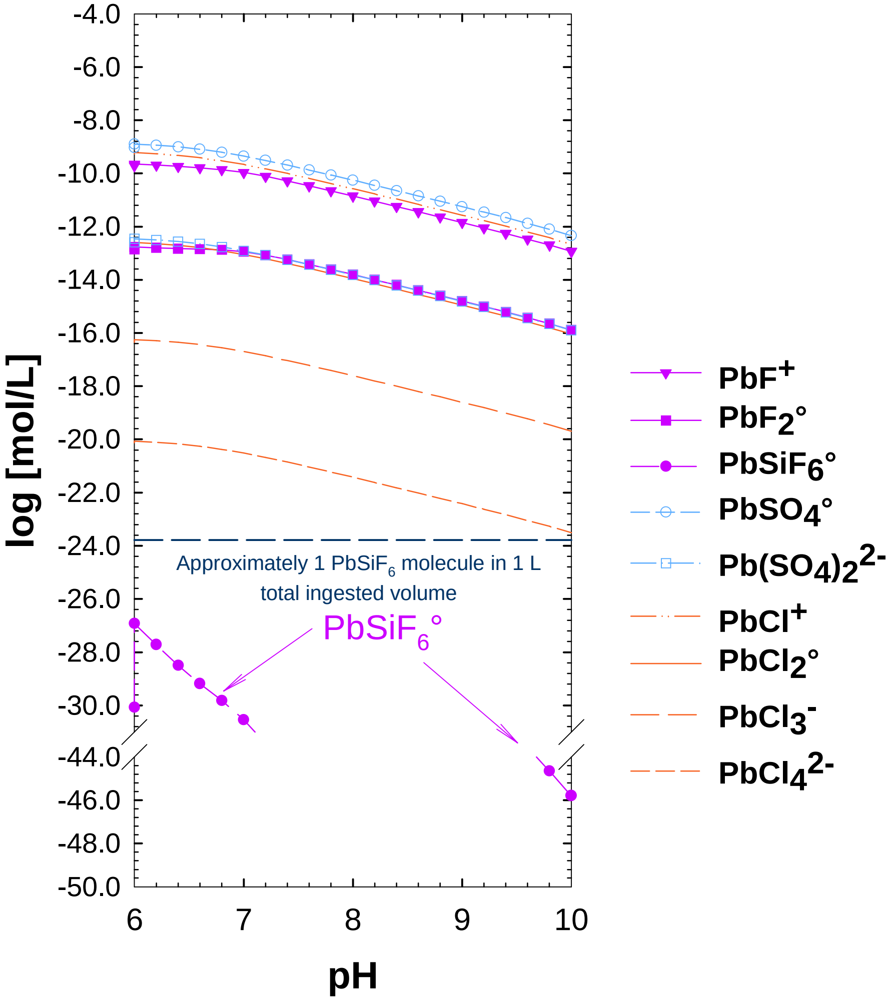
Species	Concentration, mg L^{-1}	Concentration, mol L^{-1}
$[SiO_2]_T$	5.0	8.3×10^{-5}
$[Pb^{2+}]_T$	0.015	7.2×10^{-8}
$[F^{-}]_T$	1.0	5.3×10^{-5}
DIC as C	5.0	4.2×10^{-4}
Ca^{2+}	5.0	1.2×10^{-4}
Mg^{2+}	2.0	8.2×10^{-5}
Na^{+}	10.0	4.4×10^{-4}
Al^{3+}	0.20	7.4×10^{-6}
Cl^{-}	10.0	2.8×10^{-4}
SO_4^{2-}	5.0	5.2×10^{-5}

MINEQL+ Example: Major F^- Associations

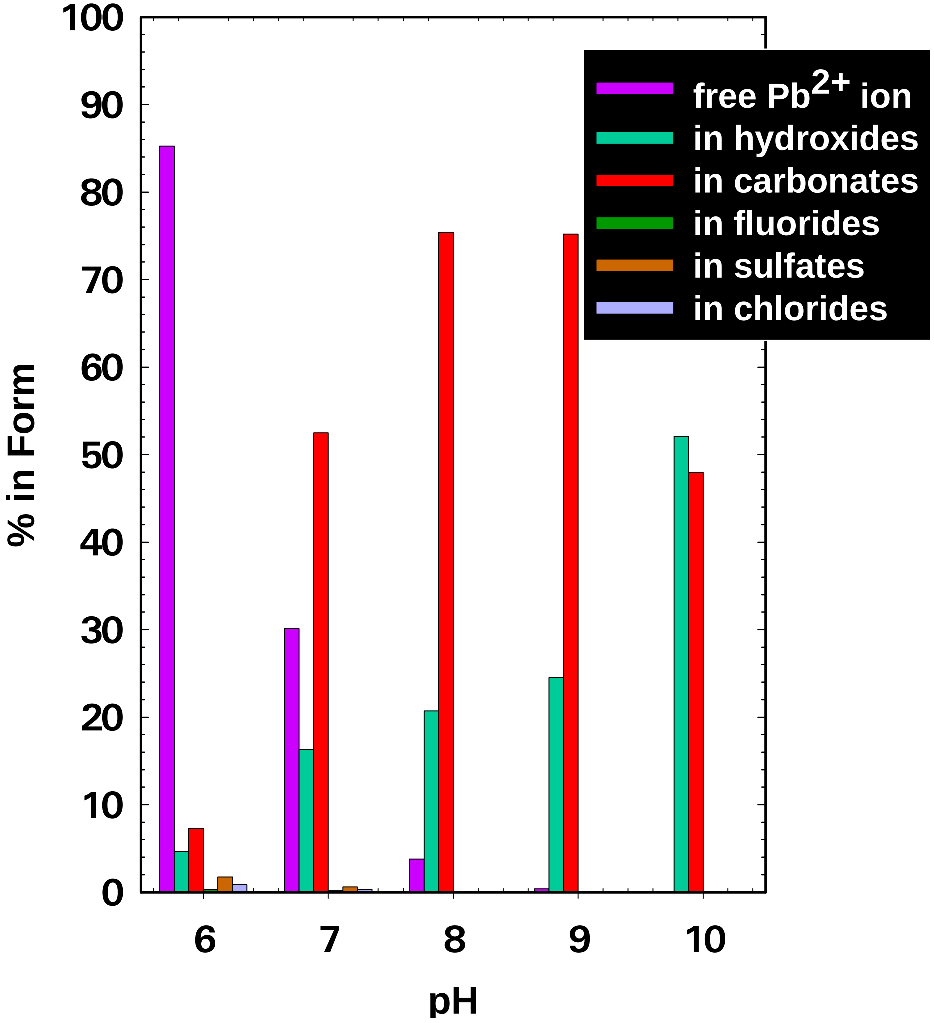


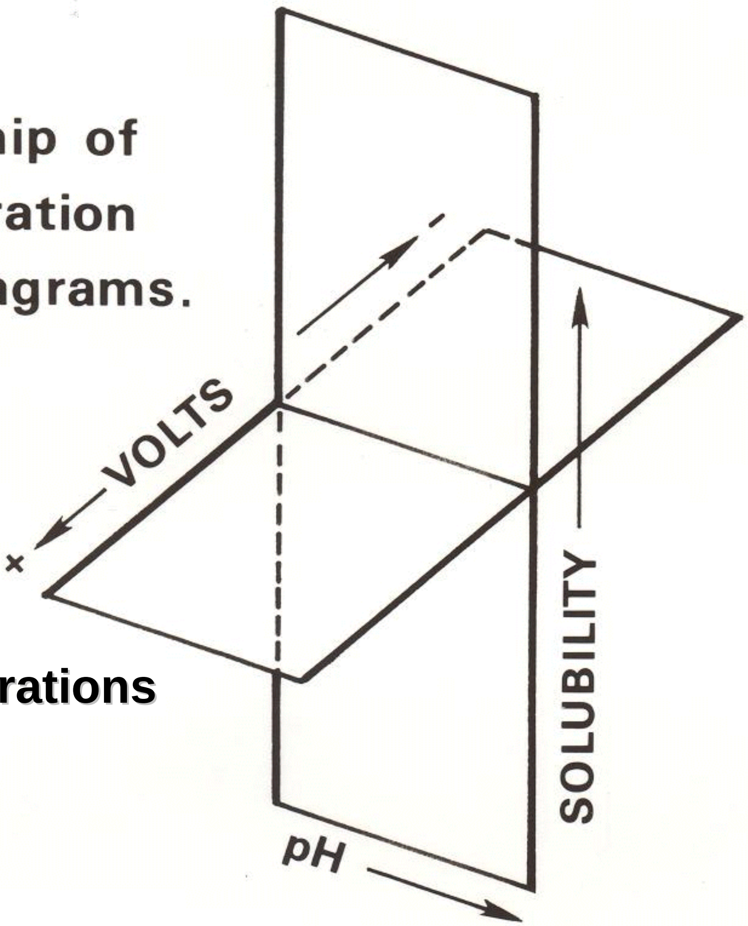
NOTE: The lower the bar, the less significant!

MINEQL+ Example: Major Pb Associations



MINEQL+ Example: Major Pb Associations





The relationship of E-pH to concentration -pH solubility diagrams.

Concentration-pH Diagram:

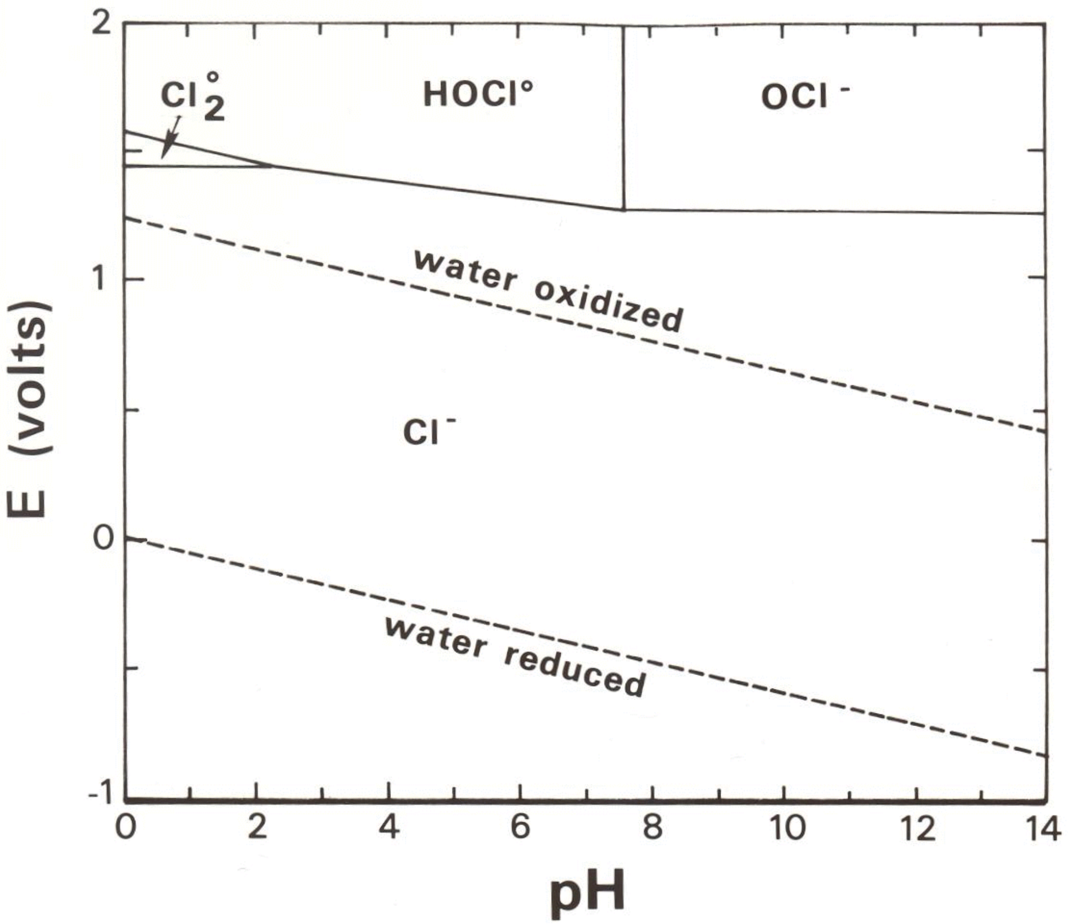
Fixed Eh(pE), Fixed non-metal Concentrations
Variable: pH, metal concentration

Eh-pH Diagram:

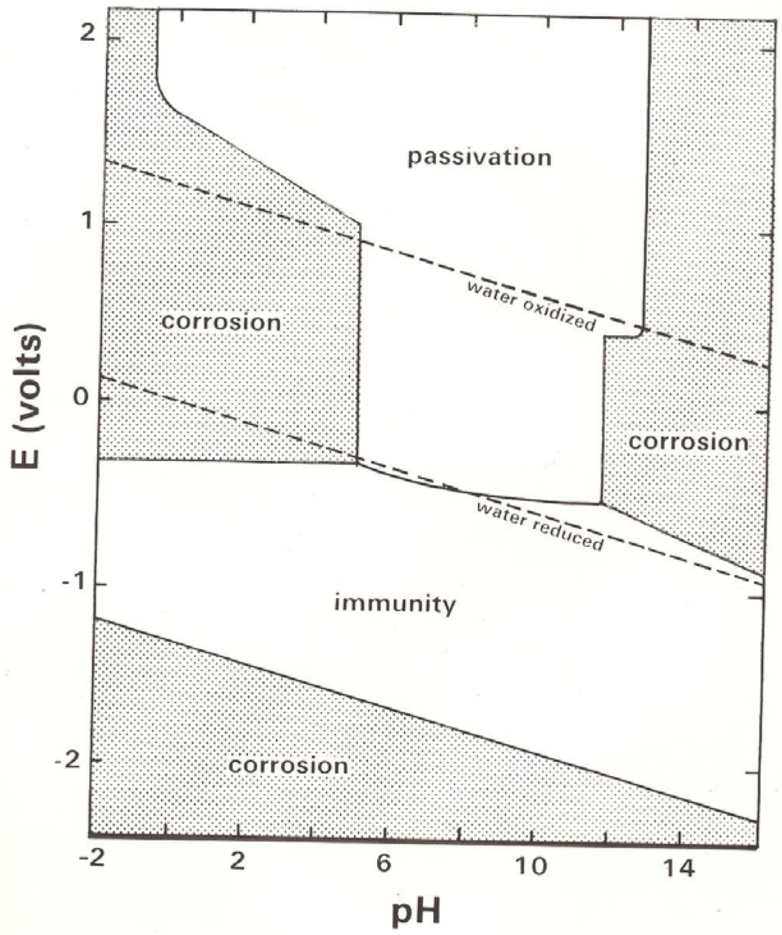
Fixed metal and ligand concentrations
Variable: pH, Eh

Metastable Hypochlorite Species

1 mg/L as Cl_2



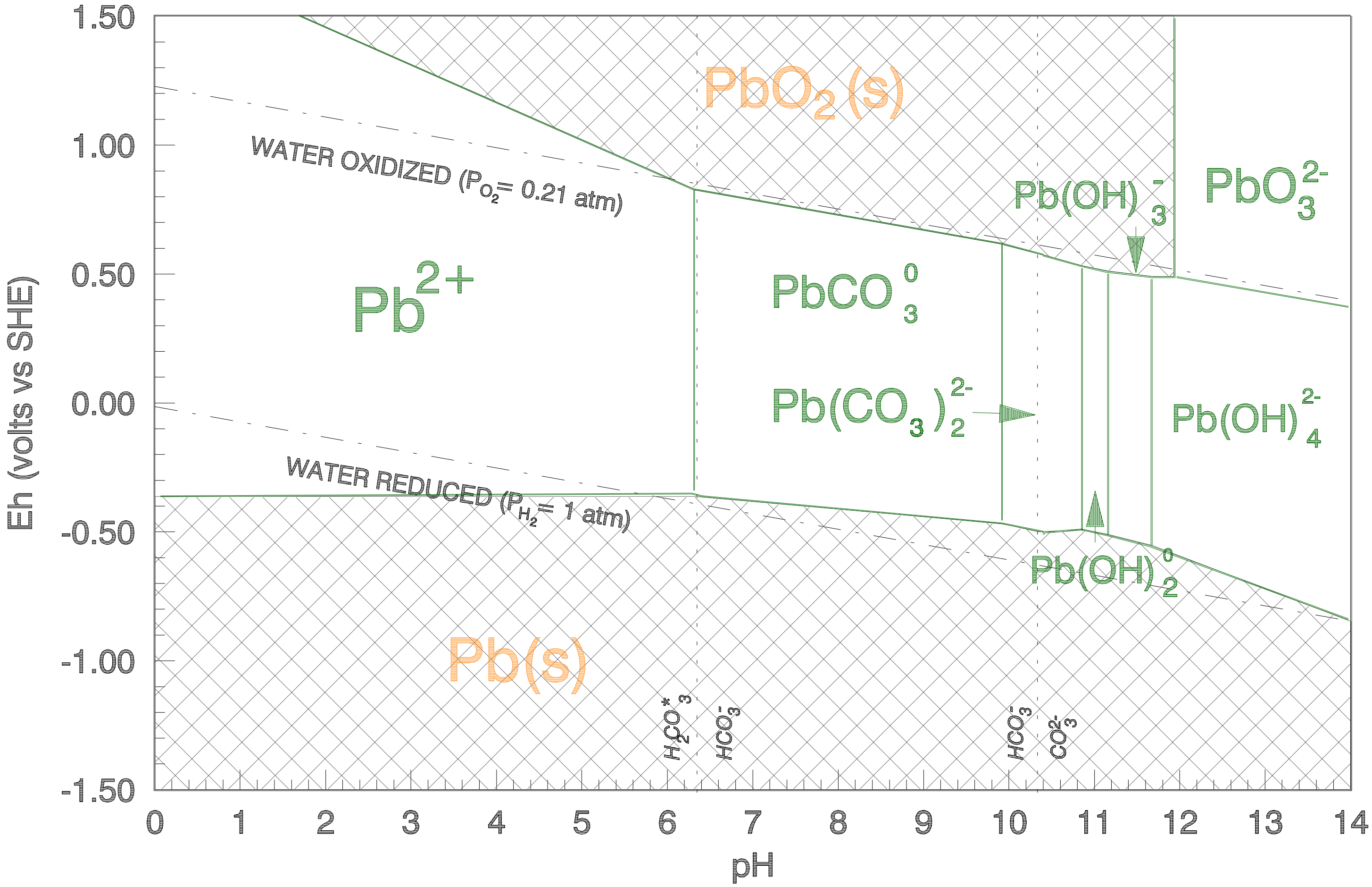
Classic Corrosivity Interpretation



EMF-pH Diagram for Pb - H_2O - CO_2 System

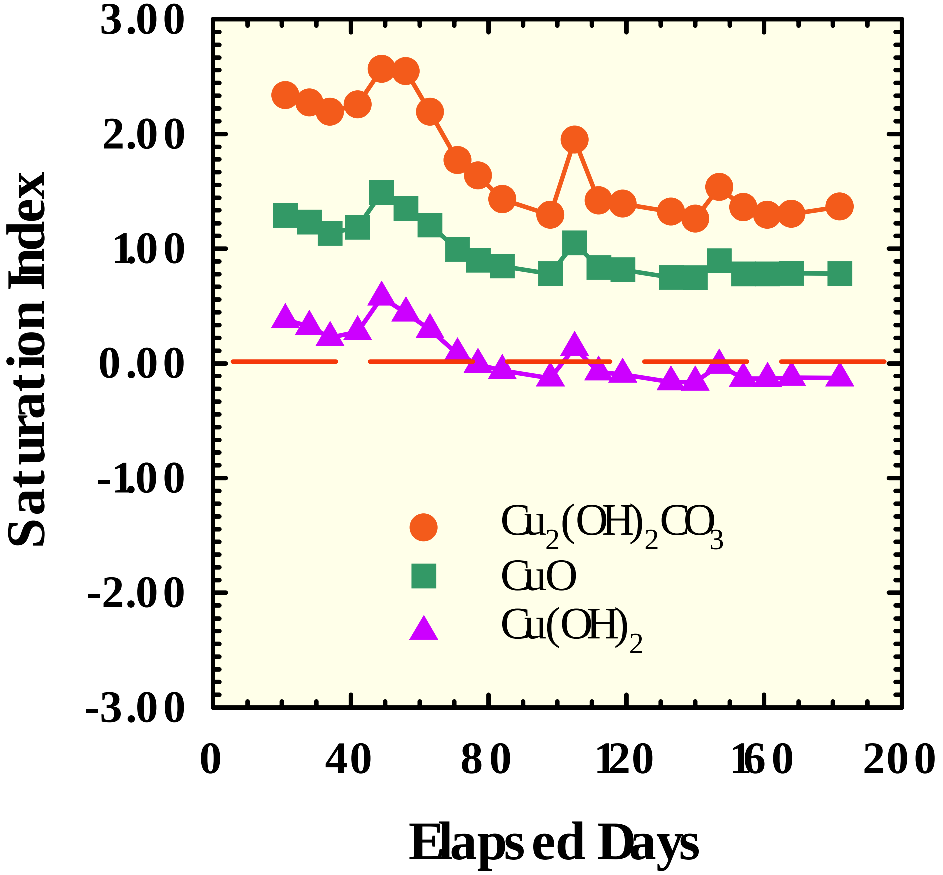
Pb species = 0.015 mg/L; DIC = 18 mg C/L

I=0; 25°C



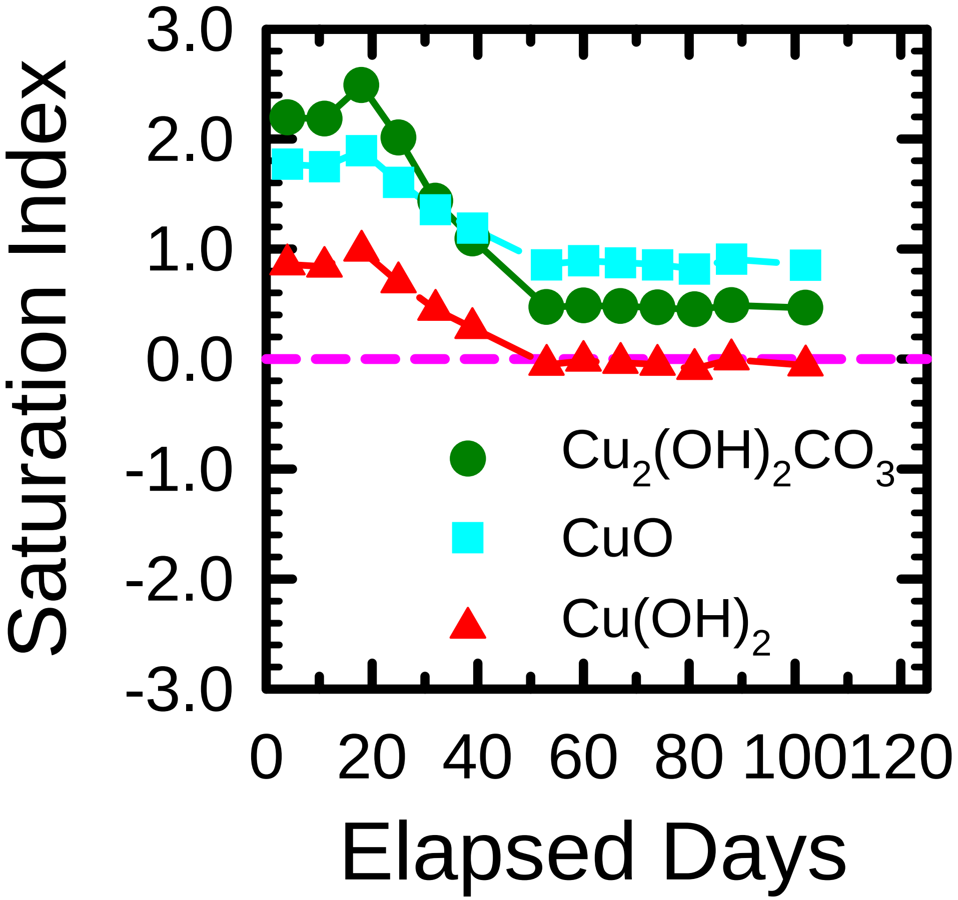
Saturation Indices to Deduce Solubility Controls

pH = 8.0, DIC = 5.2 mg C/L, I = 0.0025, 25°C

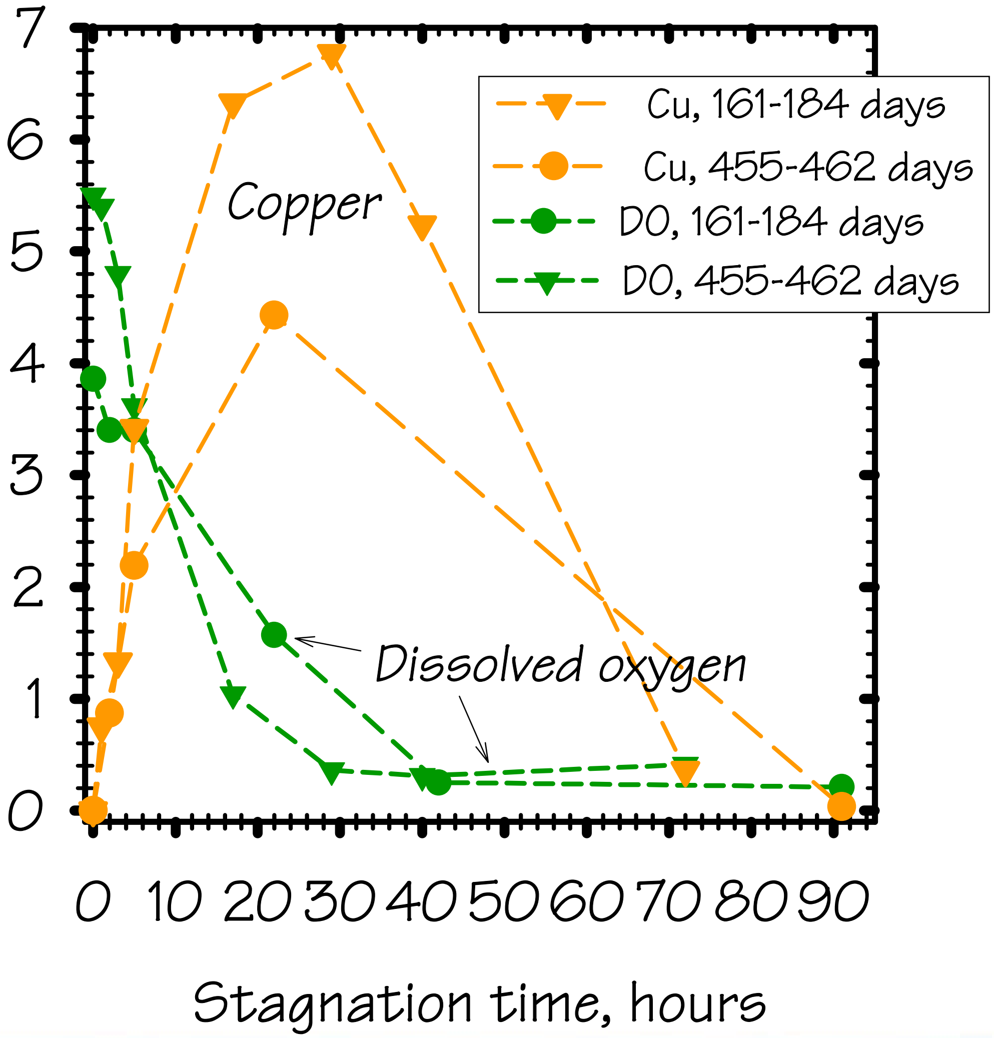


Saturation Index to Test Control Model

pH 9.0, DIC = 5 mg C/L, I= = 0.003, 25° C



Is System at Equilibrium: Stagnation Effects



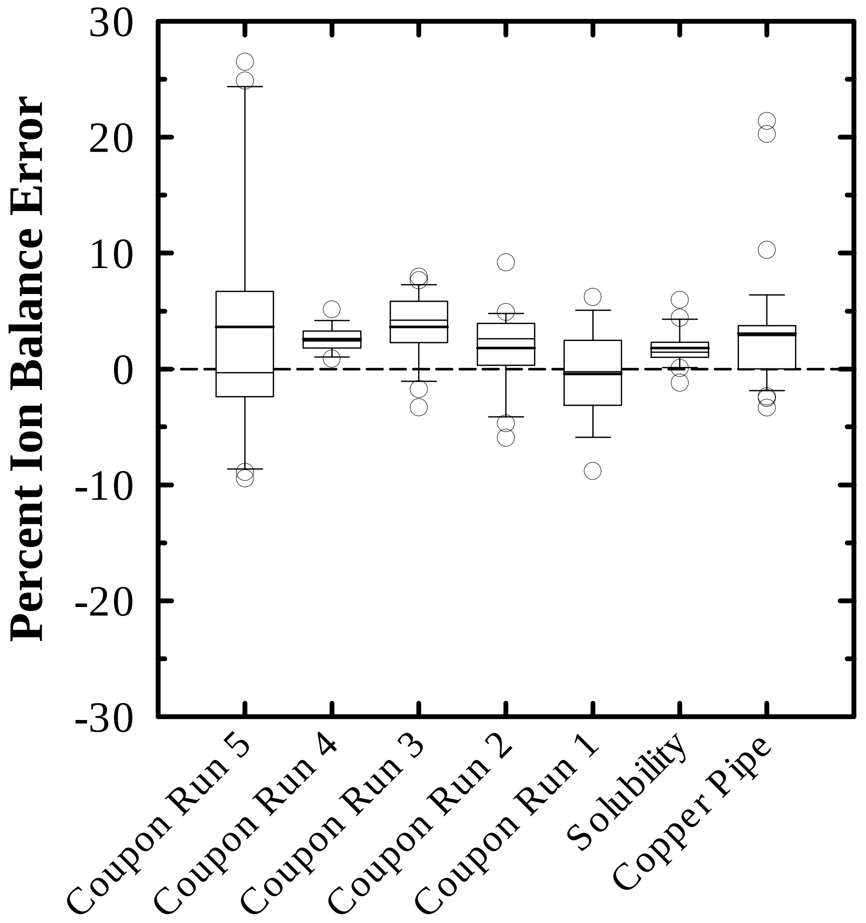
Dealing with Uncertainty

- Results are no better than the quality of the input data (analytical and thermodynamic)
- Check internal consistency
  - Charge balance for completeness
  - DIC from Alk + pH should match analytical
  - Computed DIC must make sense
- Does the field data collection scheme match model assumptions?

Some Typical QA Applications

- Internal consistency of DIC, Alkalinity & pH
- Check for redox equilibrium amongst species
  - Sulfur (sulfide, sulfate, bisulfite, sulfite, sulfur)
  - Nitrogen (nitrate, nitrite, ammonia)
  - Various metals
- Charge/ion balance errors

QC Applications: Ion Balance Error



Wise Analytical Considerations

- The more complete the analyses, the less uncertainty and guesswork
- Gross estimation of uncertainty/error based on input data, and choosing analyses wisely to minimize it
- Background chemistry important!!!
  - Ionic strength corrections
  - Side-reactions with important ligands or metals when present in excess (eg. Ca^{2+}, Cl^{-}, PO_4, Al^{3+})

Conclusions…..

- Broadly applicable and underused
- Many fundamental constants remain unmeasured
  - Temperature effects on solubility and speciation
  - ID and log K's for metastable solids
  - Kinetic equations for disequilibrium systems
    - Mass transfer
    - Reaction rates

Some Shortcomings That Need Attention

- Absence of disinfectant species in most computer programs
- Thermodynamic databases are often not "calibrated" for drinking water applications (metastable solids)
- Problem with handling polyphosphates and NOM
  - Characterizing speciation
  - Quantifying appropriately
- Kinetic complications to modeling--dearth of data, how to incorporate?
  - Reaction rates
  - How to handle crystal growth poisoning (scaling issue)