

ASR and Water Compatibility

Geochemistry of Aqueous Solutions

Dennis Nelson

Groundwater Coordinator

DHS/Drinking Water
Program

Development of an ASR system

- System design, e.g.,
 - Wellhead assembly,
 - Piping system,
- Hydrogeologic feasibility, e.g.,
 - Aquifer characteristics,
 - Groundwater flow characteristics.
 - Potential impacts
- Health related water quality, e.g.,
 - Drinking water standards
 - Microbiological considerations
- Water Chemical Characteristics
 - Geochemical reactions, **compatibility of source and ambient waters**

Potential Chemical Compatibility Concerns with respect to ASR

- Precipitation of solid phases and resulting clogging of aquifer and/or screens
 - e.g., iron hydroxide, calcite
 - Loss of production
- Mobilization of chemical constituents from existing solid phases within aquifer
 - e.g. arsenic, uranium, iron, manganese
 - Potential health/aesthetic issues

Chemical characteristics of water

- Waters are complex aqueous solutions, e.g., having different dissolved solids and gases
- Controlling factors: Chemical state parameters
 - Temperature
 - pH
 - Redox potential (dissolved oxygen content)
- For a given aquifer or substrate matrix, the chemical state parameters control the chemical composition of the water in equilibrium with surroundings
- Impact of aquifer matrix on groundwater composition

Groundwater Composition (mg/L)

Limestone

Basalt

Calcium	144	6.5
Magnesium	55	1.1
Sodium	~27	~37
Potassium	~2	~3
Bicarbonate	622	77
Sulfate	60	15
Chloride	53	17
Silica	22	103
TDS	670	222
pH	~8.2	6.7

What happens when we introduce the source water to an aquifer?

- Mixing of ambient groundwater and source water:
 $C_{i_{\text{soln}}} = xC_{i_{\text{source}}} + (1-x)C_{i_{\text{gw}}}$, where x is the portion of source water in the mixture
- Source water not in equilibrium with aquifer matrix
 - May lead to chemical reactions to move solution towards equilibrium
 - $C_{i_{\text{soln}}} = xC_{i_{\text{source}}} + (1-x)C_{i_{\text{gw}}} \pm \Delta C_{i_{\text{rxn}}}$, where $\Delta C_{i_{\text{rxn}}}$ refers to changes in the solution composition as a result of constituent i being added or removed by chemical reactions

General observations regarding ambient groundwater and source water

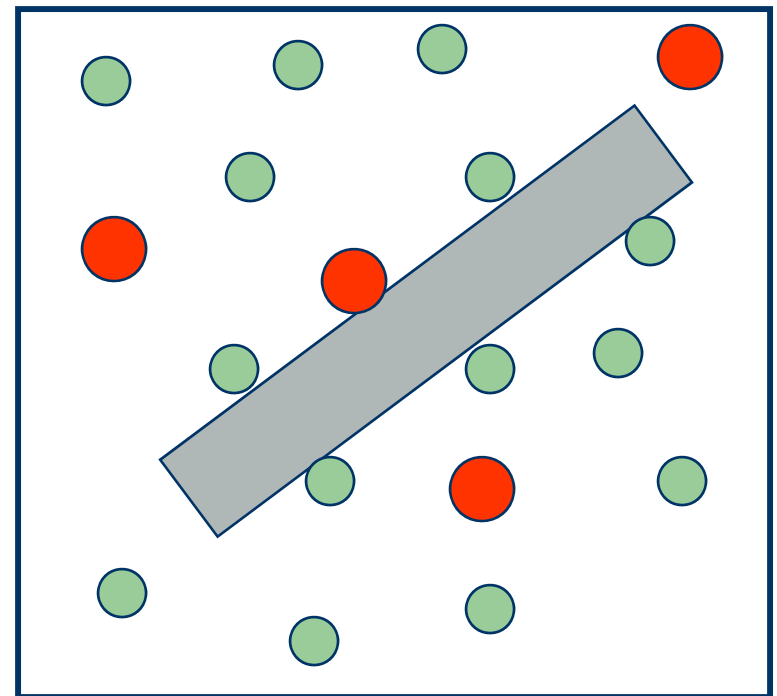
- Source (Surface) water
 - Oxidizing – In contact with atmosphere
 - Lower pH (6 – 7) – Water dominated by precipitation; in Oregon, rainfall pH ~5.7
 - High in DOC (?)
 - Lower TDS – Short residence time with solid phases
- Ambient Groundwater
 - Reducing – Dissolved oxygen consumed by reducing reactions
 - Neutral to slightly alkaline pH (7.5 – 8.5) – Hydrogen ion consumed by water-rock reactions
 - Higher TDS – Longer residence time with solid phases

Source Water and Ambient Groundwater: Processes

- Simple mixing
 - Solution = $x C_{sw} + y C_a$ where $x + y = 1.0$
 - Conservative ions, e.g., Cl^-
- Chemical reaction in the solution
 - Characteristics of dissolved species, e.g., ion activities, complex ions, valencies, etc.
- Reaction with aquifer matrix
 - Ion exchange
 - Dissolution/Precipitation of solid phase

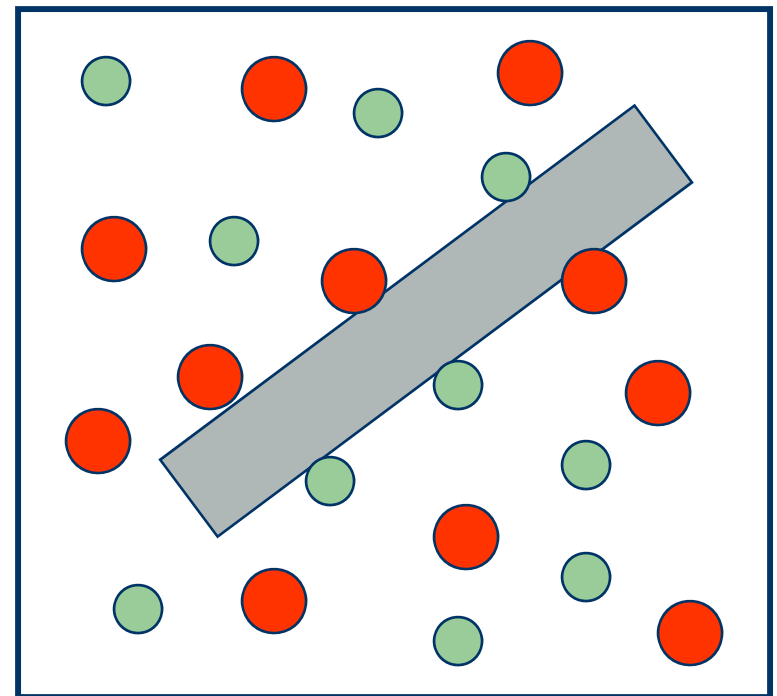
Cation Exchange

- Inorganic and organic constituents “attached” to solid phase surfaces of aquifer
- Distribution of ions on surface and in solution controlled parameters of state and solution composition
- Ratio of ions attached to solid related to ratio in solution



Cation Exchange

- If concentrations within solution change, the distribution of ions between solid phase and solution changes to reflect them
- As a result, some ions may be released (leached) into solution



Potential Leaching Effects

- Displacement of trace constituents by exchange from solids to solution when exposed to differing solution character
 - Clays, hydrous oxides, organic matter
 - Pb, Cu, Cd, Zn, Ni, Co, As
- Release of trace constituents during solid phase breakdown
 - Pyrite (FeS_2), volcanic glass
 - As, U, Fe, and others

Oxidizing versus Reducing Environment: Redox Conditions

- Controls the valence (charge) of ion
- Redox state may have strong influence on the behavior of specific constituents, i.e., whether they occur in **solution**, as a **gas**, or in a **solid** phase
 - Fe^{2+} vs. Fe^{3+}
 - U^{4+} vs. U^{6+}
 - H_2S vs. SO_4^{2-}
 - N_2 vs. NO_3^{2-}
- May lead to precipitation-dissolution or mobilization (leaching to solution) of species
- Complex ion formation => Higher ion concentration

Reducing Conditions

- Generally results from microbial activity
- In oxygenated water decay of organic matter described by $\text{CH}_2\text{O} + \text{O}_2 \Rightarrow \text{CO}_2 + \text{H}_2\text{O}$
- Oxidation of organic matter releases e^- , Need e^- acceptor
- In increasingly oxygen-deficient water, sequence of electron acceptors as reactions continue
 - $\text{NO}_3^- \rightarrow \text{N}_2(\text{aq})$
 - $\text{MnO}_2 \rightarrow \text{Mn}^{2+}$
 - $\text{Fe}(\text{OH})_3 \rightarrow \text{Fe}^{2+}$
 - $\text{SO}_4^{2-} \rightarrow \text{FeS}_2$ or $\text{H}_2\text{S}(\text{aq})$

Mineral Dissolution/Precipitation

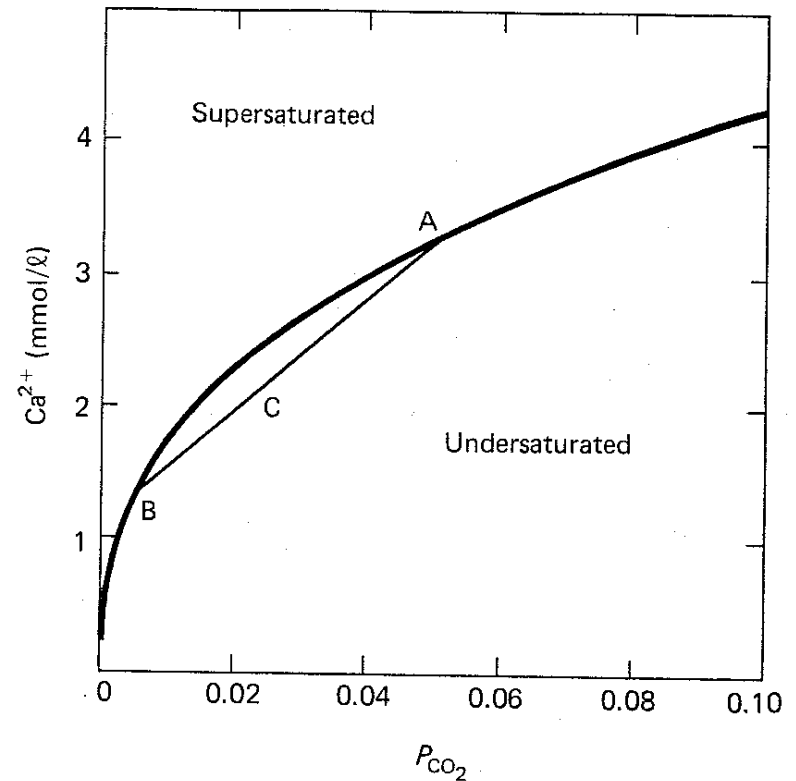
- Solubility, how much mineral will dissolve in a given solution: a function of chemical state and ion concentrations
- Equilibrium concentration defined by K, equilibrium constant
- Consider the mineral Calcite => CaCO_3
 - $K = [\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$
 - K calculated based on thermodynamic data
 - For a given solution, if $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}] =$ the calculated K, then solution is saturated with respect to calcite
- Value of K is function of chemical state, particularly temperature; not influenced by solution composition

Mineral Dissolution/Precipitation

- For a given solution, Degree of mineral saturation a function of actual concentrations:
 - Mineral's Ion Activity Product (IAP)
 - IAP for calcite = $[\text{Ca}^{2+}] \times [\text{CO}_3^{2-}]$
- Groundwater tends to be over-saturated, i.e.,
 - $\text{IAP}/K_T \geq 1$, or $\log \text{IAP}/K_T > 0$: specific phase might precipitate, would not dissolve
- Surface water tends to be undersaturated, i.e.,
 - $\text{IAP}/K_T < 1$, $\log \text{IAP}/K_T < 0$: specific phase might dissolve, would not precipitate.

Predicting Chemical Changes

- Chemical changes tend toward equilibrium
- Therefore predictable as they will follow generally understood processes
- Can be very complicated do not lend themselves to speculation
- For example, Calcite Saturation: Mixing Results (from Drever, 1982)



Predicting Chemical Reactions

- PHREEQC (USGS) provides tool for evaluation
 - Calculates composition at varying mixing proportions of endmembers
 - Distributes ions appropriately
 - Calculates IAP and compares to K for specific minerals
 - Will the mineral, e.g., limonite or calcite, precipitate and potentially clog pore space or screen openings?
 - If $IAP/K_T > 1.0$, mineral will tend to precipitate
- PHREEQC input: T, pH, redox, solution composition

PHREEQC Output: chemical speciation

As a Function of the Chemical State of the Solution

DISTRIBUTION OF SPECIES

Ionic Species	Z	Molality	LOG MOLAL	Activity*	LOG ACT
1 H+	1.0	1.343E-08	-7.872	1.259E-08	-7.900
2 E-	-1.0	1.000E-08	-8.000	1.000E-08	-8.000
3 H2O	.0	9.999E-01	.000	9.999E-01	.000
4 Ca+2	2.0	6.291E-04	-3.201	4.886E-04	-3.311
5 Mg+2	2.0	3.515E-04	-3.454	2.737E-04	-3.563
6 Na+	1.0	6.084E-04	-3.216	5.706E-04	-3.244
7 K+	1.0	8.695E-05	-4.061	8.147E-05	-4.089
14 Cl-	-1.0	1.100E-04	-3.959	1.031E-04	-3.987
15 CO3-2	-2.0	8.093E-06	-5.092	6.288E-06	-5.201
16 SO4-2	-2.0	5.354E-05	-4.271	4.151E-05	-4.382
31 OH-	-1.0	3.451E-07	-6.436	3.451E-07	-6.464
32 O2 AQ	.0	8.111E-27	-26.087	8.111E-27	-26.087
34 HCO3-	-1.0	2.211E-03	-2.640	2.111E-03	-2.667
35 H2CO3	.0	7.111E-07	.111	7.111E-07	.144
77 CaHCO3+	1	9.966E-04	.966	9.966E-04	.960
78 CaSO4	.0	4.437E-04	.437	4.437E-04	.437
87 MgHCO3+	1	1.177E-03	.177	1.177E-03	.177
88 MgSO4	.0	6.696E-04	.696	6.696E-04	.696

“Activity” of a given ion differs from its actual concentration in the solution because of the impact of other nearby ions in the solution

Analytical Concentration “Effective” Concentration

PHREEQC Output: Saturation Indices

Will a Mineral Dissolve or Precipitate?

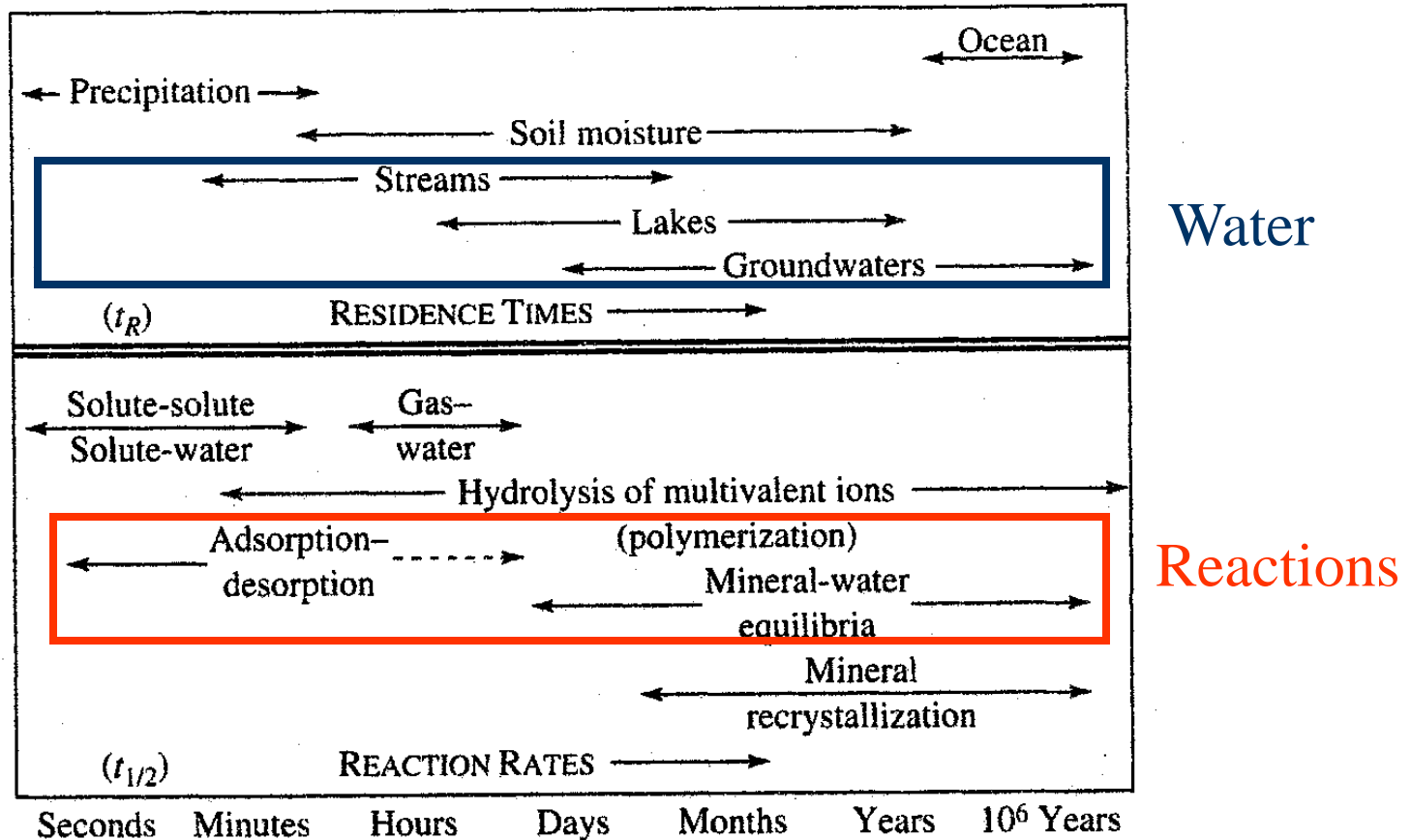
---- LOOK MIN IAP ----

PHASE	LOG IAP	LOG KT	LOG IAP/KT	
<u>Calcite</u>	-8.4280	-8.4280	<u>.0000</u>	← Equilibrium
Aragonit	-8.4280	-8.2764	-.1516	
Dolomite	-16.8375	-16.8375	.0000	
<u>Gypsum</u>	-7.5690	-4.5851	<u>-2.9839</u>	← Tend to Dissolve
Anhydrit	-7.5688	-4.3349	-3.2339	
SiO2 (a)	-2.5054	-2.8013	.2959	
<u>Chalcedy</u>	-2.5054	-3.6777	<u>1.1723</u>	
Quartz	-2.5054	-4.1407	1.6353	← Tend to Precipitate
Talc	-60.8637	-63.4958	2.6321	
Chrysotl	30.3333	33.5483	-3.2151	
Sepiolit	16.0463	16.0463	.0000	
PCO2	-3.3339	-1.3339	-2.0000	
O2 gas	-27.9481	-2.9107	-25.0374	
H2 gas	-33.9723	-3.1029	-30.8693	

Precipitation Examples:

- Consider a mixture of source water and groundwater
 - In aquifer with porosity of 0.20, i.e., 20% voids
 - Ambient groundwater contains 10 mg/L Fe and 50 mg/L Ca
 - IAP/K_T of mixture > 1.0 w/respect to CaCO_3 and $\text{Fe}(\text{OH})_3$
 - Assume all Fe and 25 mg/L Ca removed from solution by precipitation of solid phases
- Approximately 5 cm³ of pore space/m³ of aquifer could be filled under static conditions (per cycle?)
- Approximately 0.025 cm³/liter of solids passing through screen (not likely, given velocity)

Residence Time and Reaction Rates (Langmuir and Mahoney, 1985)



Reaction Rates

- Half-Times vs. Length of ASR Cycle
 - Redox and desorption/adsorption reactions $<$ cycle duration
 - Dissolving Precipitation phases $>$ cycle duration
- Implications of “Age” of the ASR Project
 - Decreasing solution concentrations of desorbed ions with increasing cycles?
 - Increasing accumulations (precipitation) of solid phases with increasing cycles?

Summary

- Source water and ambient groundwater have differing chemical characteristics: pH, redox, TDS – Not in equilibrium
- Blended water: mixing, water-rock reactions
- Redox reaction, ion exchange, dissolution-precipitation
- Redox reaction and ion exchange short term; dissolution-precipitation longer term
- Concentration of desorbed ions decrease with age of ASR system: health-related constituents, e.g., As
- Precipitation of phases, e.g., $\text{Fe}(\text{OH})_3$, accumulate with age: clogging of system

Acquiring PHREEQC

- Public domain software sites
- USGS Geochemical Software Site
 - <http://water.usgs.gov/software/lists/geochemical>
 - User manual
 - Other programs
- Extended Windows Version (Vincent Post)
 - www.xs4all.nl/~appt
 - Download documentation
 - Examples

Reference Text

- Appelo and Postma, 2005, Balkema Publishers:
ISBN 04 1536 421 3 HB
ISBN 04 1536 428 0 PB
- Incorporates PHREEQC into a number of situations, e.g., mineral equil, ion Ex, forward and inverse models, mixing, and transport
- Provides PHREEQC “Get going Sheets”

