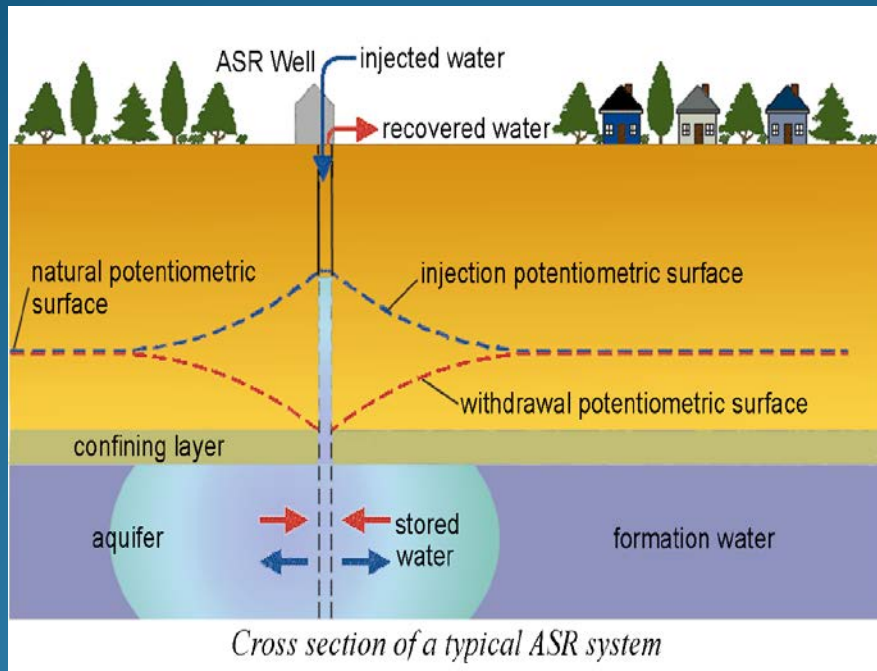


Managing Metals During ASR Cycle Tests

John Jansen, Ph.D., P.G., Pg.P., Collier Consulting



Goals of ASR



- Receive large volumes of water through well bore
- Store the water in a permeable zone with minimal mixing or changes in water quality
- Recover the water at a useful rate with minimal treatment
- No additional cost other than electricity and disinfection
- O&M is one of the greatest cost components of ASR!

Tools to Implement ASR

- Basic hydrogeologic and physical principles
- Geochemical Modeling (PHREEQC)
- Solute transport (Dispersivity) modeling
- Design for Storage - not the same as typical production wells

Potential Problems of ASR

- **Plugging or formation** of well face
 - Usually silt plugging around well bore
 - Occasionally precipitation of material from water quality incompatibility or air entrainment in formation
- **Chemical Reactions** between injected water and formation or formation fluids mobilizing metals
- **Mixing** of injected and native water



Status of ASR in the US

- Reliable numbers for ASR problems are hard to find
- USEPA estimates that of 307 active ASR sites (542 wells) in 2009, 14 non-operational, 65 plugged and abandoned (15% failure rate)
- Several wells abandoned due to plugging and new wells have made modifications to make cleaning more effective
- Existing data suggest clogging and water quality changes are the biggest problems
- Water quality changes, primarily mobilization of arsenic and other metals have been a serious problem in FL, WI and other states
- New interpretation of institutional control has probably reduced number of ASR systems with ceased operations

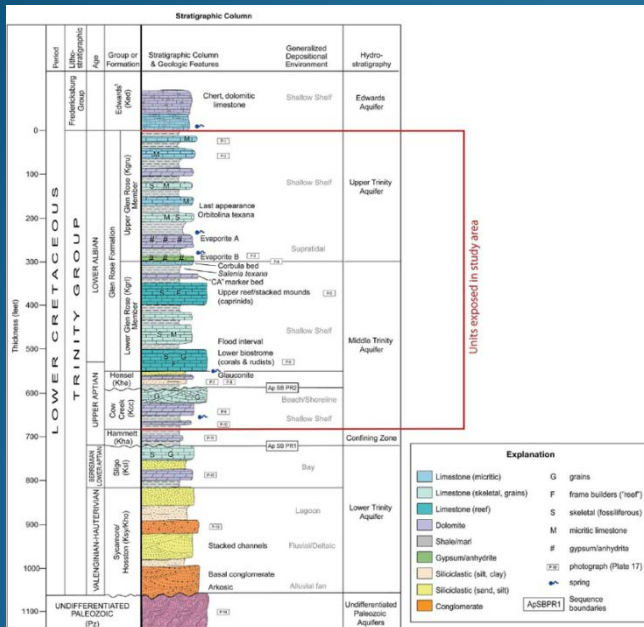
Typical Sources of ASR Storage Water



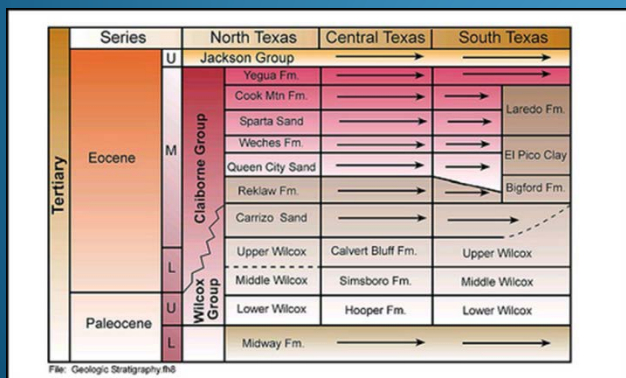
- Surface water
- Treated waste water
- Treated drinking water
- Water from shallower aquifers
- Common theme is all are oxic
 - 2 to 10 ppm dissolved oxygen,
 - 1 to 2 ppm with free chlorine,
 - often several ppm organic carbon



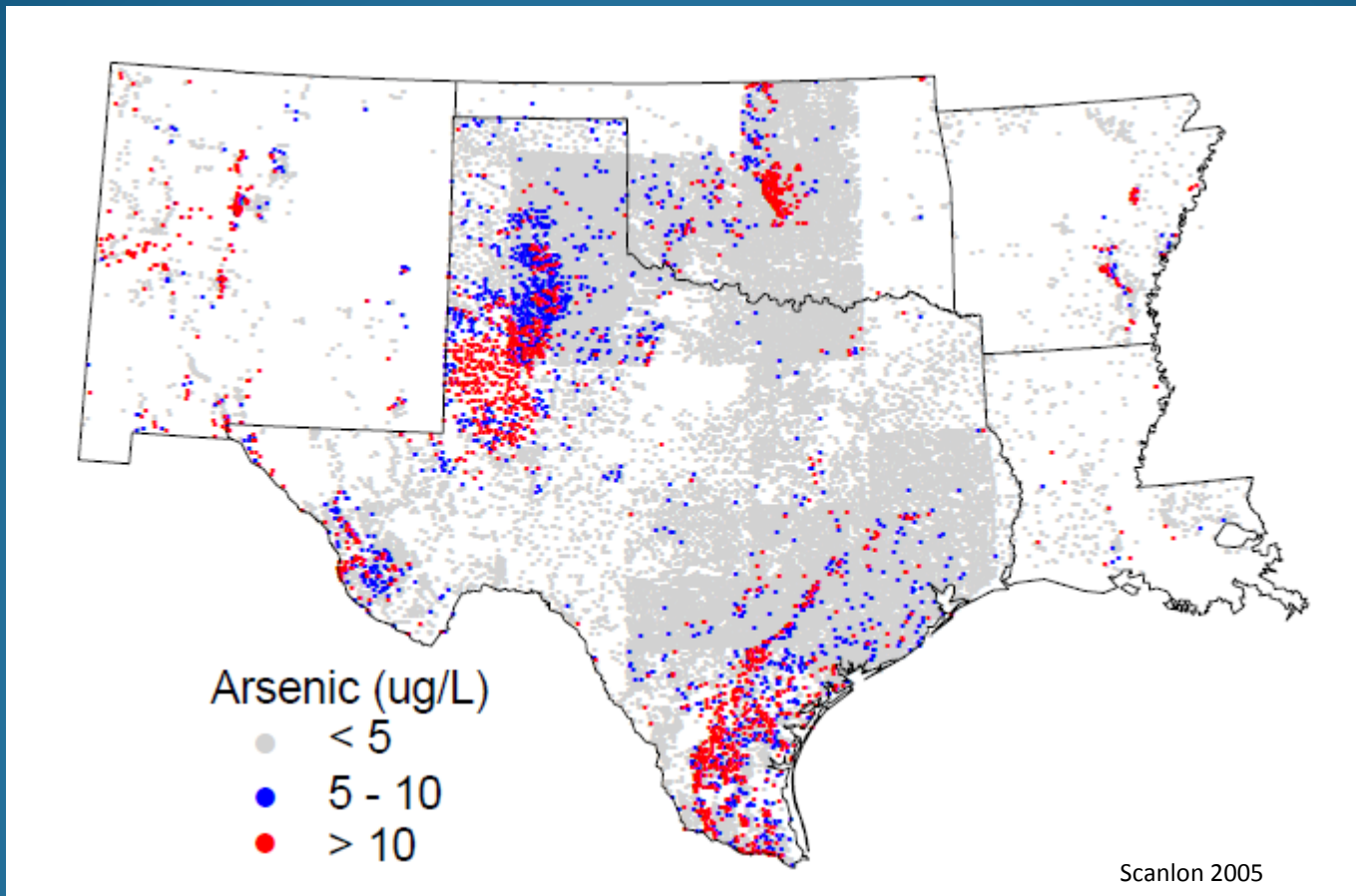
Most ASR Recharge Zones are Confined Aquifers



- Virtually no dissolved oxygen ASR Recharge water may be the first exposure of aquifer to oxygen in millions of years
- Reduced geochemical conditions
- Little to no arsenic mobilization under typical production well operation
- Initiates chemical reactions of limited duration but significant impact
- Geochemical modeling in Upper Suwanee aquifer in FL indicates that 6ppm DO in recharge water could create 80ppb As (MCL=10ppb) in recovered water

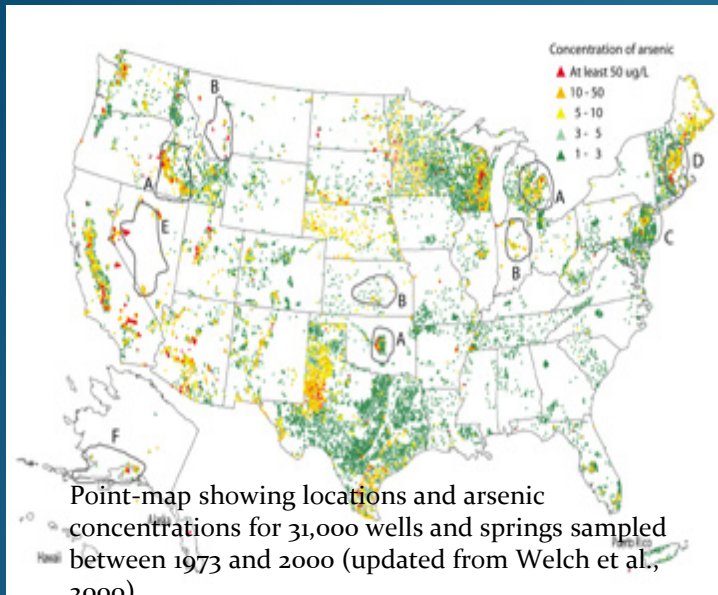


Arsenic in Groundwater In TX and Surrounding States



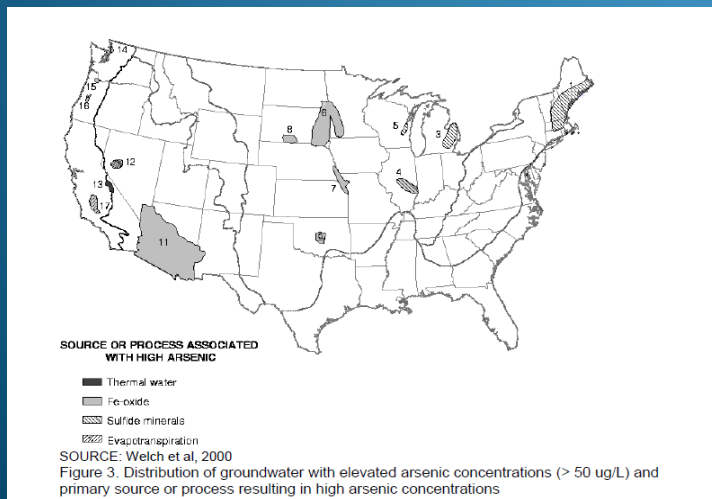
Does not have to be a problem for ASR if mixing is controlled

Mechanisms for Mobilizing Arsenic and Metals in ASR Cycles



- Oxidation of pyrite when introducing oxygenated water into aquifer under reducing conditions
- Reduction of Iron hydroxides when driving aquifer to more reducing conditions
- Desorption of metals from aquifer matrix
- Mixing with native water

Any of these mechanisms can mobilize metals in ASR wells



Pyrite Oxidation



http://www.windows.ucar.edu/earth/geology/images/pyrite_sm.jpg

Pyrite



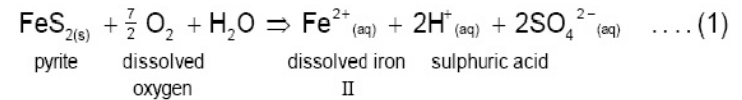
<http://www.dlimages.com/discover/previews/965/75014124.JPG>

Limonite

<https://image.slidesharecdn.com/weatheringmine-110213212016-phpapp01/95/weathering-mine-20-728.jpg?cb=1297632106>

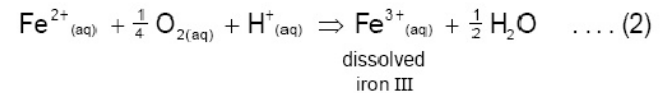
What are the chemical reactions, involved?

Step 1



Oxidation of pyrite by oxygen is slow

Step 2



Generation of Fe³⁺ is mediated by iron-oxidising bacteria, particularly *Thiobacillus ferrooxidans*.

<https://image.slidesharecdn.com/acidsoilandimpactsinsrilanka-120414072105-phpapp01/95/acid-soil-and-impacts-in-sri-lanka-10-728.jpg?cb=1334390480>

Trace metals associated with pyrite oxidation:

As: MCL= 10 ppb

Mn: No MCL

Ni: MCL= 100 ppb*

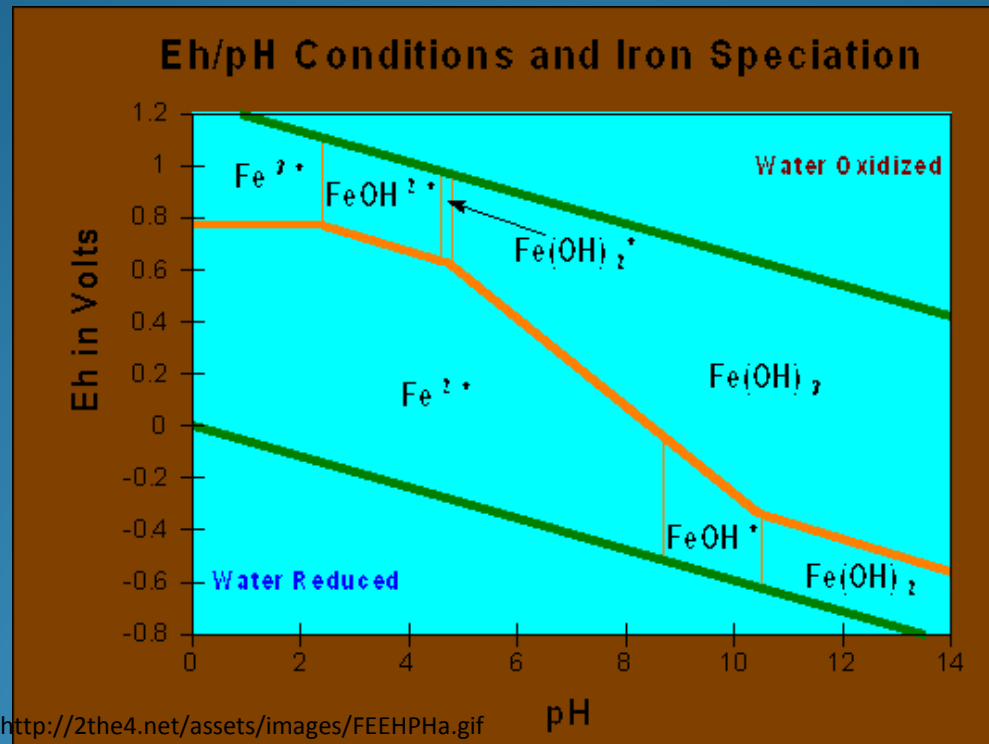
Co: No MCL

Cu: MCLG= 1.3 ppm

Pb: Action Level =15 ppb

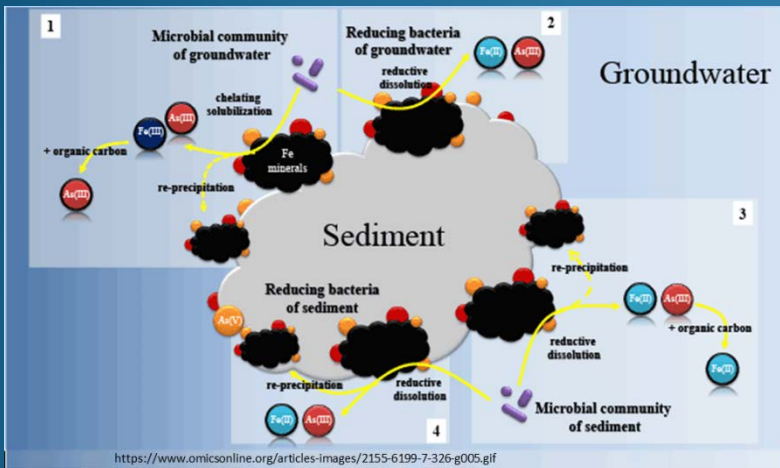
*(remanded in 1995)

Reduction of Iron Oxides in Storage Zone



- Reduction of oxides liberate metals
- Uncommon in most aquifer/well systems
- Requires drop in redox potential in storage or mixing zones

Sorption/Desorption of Metals

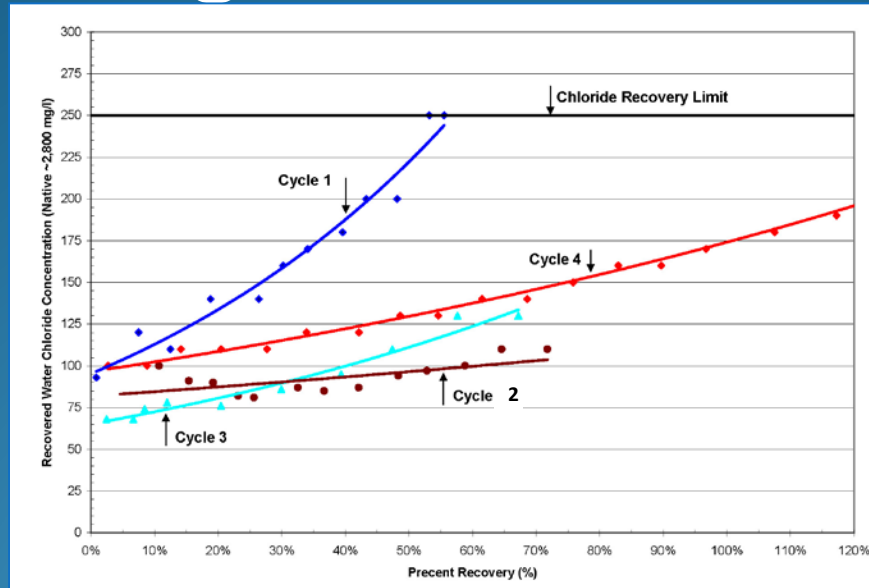


- Iron Oxides are common in neutral to oxidized aquifers
- Iron Oxides sorb metals like softener resin (As, Mn, Mg, Ni, Co, etc)
- Shift to reducing conditions or change in solubility index can liberate metals

Short Term and Long Term Changes of Water Quality in ASR Cycles

- Short term flushing of storage and mixing zone (oxidizing pyrite near well, flushing iron oxide in storage zone)
- Problem usually declines after several storage cycles
- Long term persistent changes in quality are bigger problems (long term oxidation of pyrite in mixing zone, mixing with native water)
- Problem may not get better without some form of pretreatment or modification of ASR cycles

Cycle Testing Results with Decreasing Concentration



- Recovery efficiencies increase with subsequent cycles
- Cycle 1 about 50% recovery
- By cycle 4 recovery over 100% (recovering water left over from previous cycles)
- Recovery efficiency improves on each cycle
- Indicates minimal mixing and no adverse reactions
- The goal for a successful ASR system

Cycle Testing With Concentrations Increasing with ASR Cycles

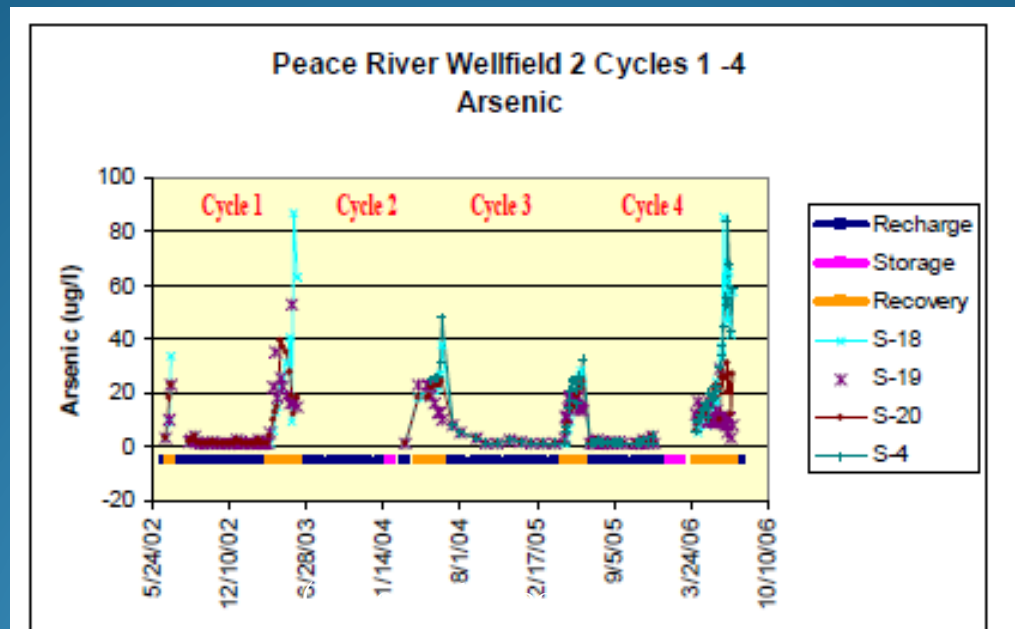


Figure 46 Peace River Wellfield 2 Cycles 1 to 4 Arsenic

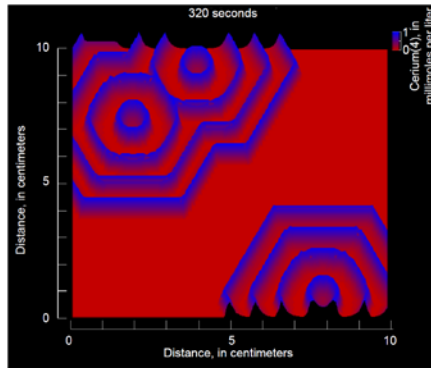
- adverse reaction (Arsenic Mobilization)
- excessive mixing
- A major problem with design or water compatibility
- Must be corrected before ASR system placed in service

Geochemical Modeling Can Quantify Physical Processes and Geochemical Reactions



Description of Input and Examples for PHREEQC Version 3—A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport, and Inverse Geochemical Calculations

Chapter 43 of
Section A, Groundwater
Book 6, Modeling Techniques



Techniques and Methods 6–A43

U.S. Department of the Interior
U.S. Geological Survey

- USGS Geochemical Modeling Codes
 - PHREEQC
 - NETPATH
- Calculates mineral saturation indices, ion exchange, mixing
- What precipitates? What dissolves?
- Will reactions clog the screen or aquifer?

Data Needs for Geochemical Modeling at the Feasibility Stage

- Requires complete water quality analysis – major inorganic constituents plus pH, total alkalinity
- Aquifer mineralogy (clays, silicates, carbonate) can be determined by literature review
- Check USGS NWIS database, TWDB database
- All data serve as input to Geochemical Modeling effort

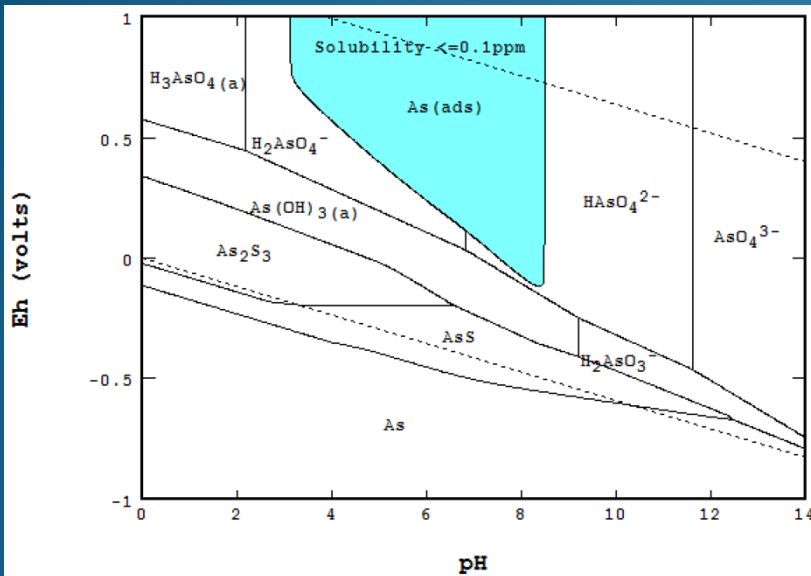
Data required for Geochemical Modeling at the Design Stage



https://iodp.tamu.edu/curation/gcr/geol106lab/core_images/group1_122-760B-22R-2.jpg

- Source of arsenic (and other metals) and chemistry of source mineral.
- Arsenic concentration in bulk rock and host mineral.
- Arsenic concentration and Eh of injected, recovered, and native water.
- Relative fraction of native water in recovered water.
- DO levels of injected and recovered water.
- Sulfide levels in recovered water.
- Arsenic speciation, Fe concentration, Fe oxidation state.

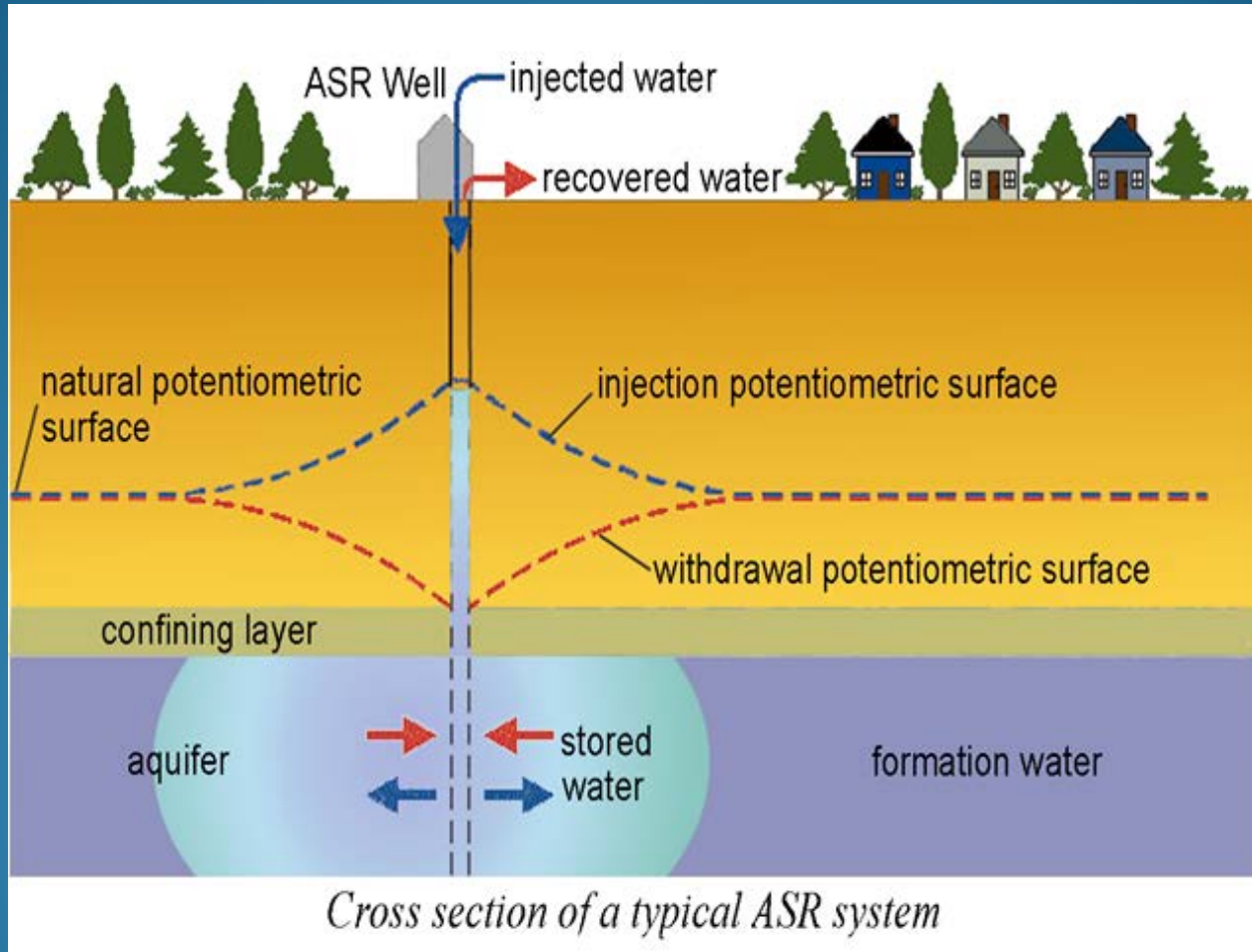
Geochemical Modeling Output



http://www.mdpi.com/metals/metals-06-00023/article_deploy/html/images/metals-06-00023-g008.png

- Speciation of all major elements
- Mineral Saturation Indices (precipitation or dissolution)
- Inverse models calculate mixing proportions (or end-member mixing proportions can be specified)
- Quantify changing redox conditions in the aquifer

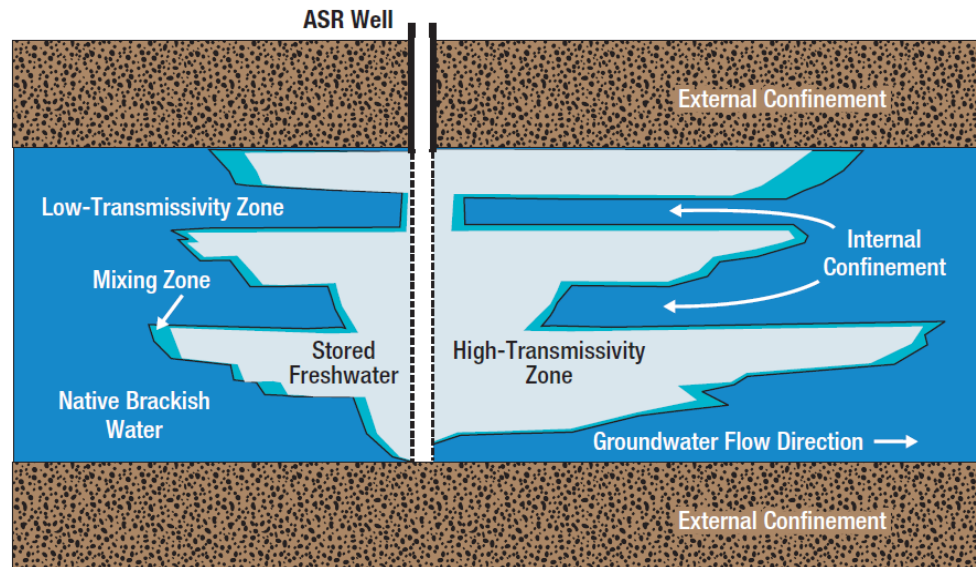
Mixing with Native Formation Water



Idealized ASR Storage Bubble

More Realistic Storage Zone

Figure 4. A heterogeneous ASR storage zone



Freshwater will preferentially enter high-transmissivity flow zones. Relatively low transmissivity strata will receive relatively little freshwater and act as internal confining units to the flow zones. Water in the flow zones will migrate at a more rapid rate under prevailing ambient hydraulic gradients.

Maliva and Missmer, 2010

- Higher the heterogeneity in aquifer, the more complex the storage zone
- Buoyancy in brackish zones creates “upside down Christmas Tree” shape
- Significantly increases mixing and reduces recovery efficiency

Dispersivity Controls Mixing

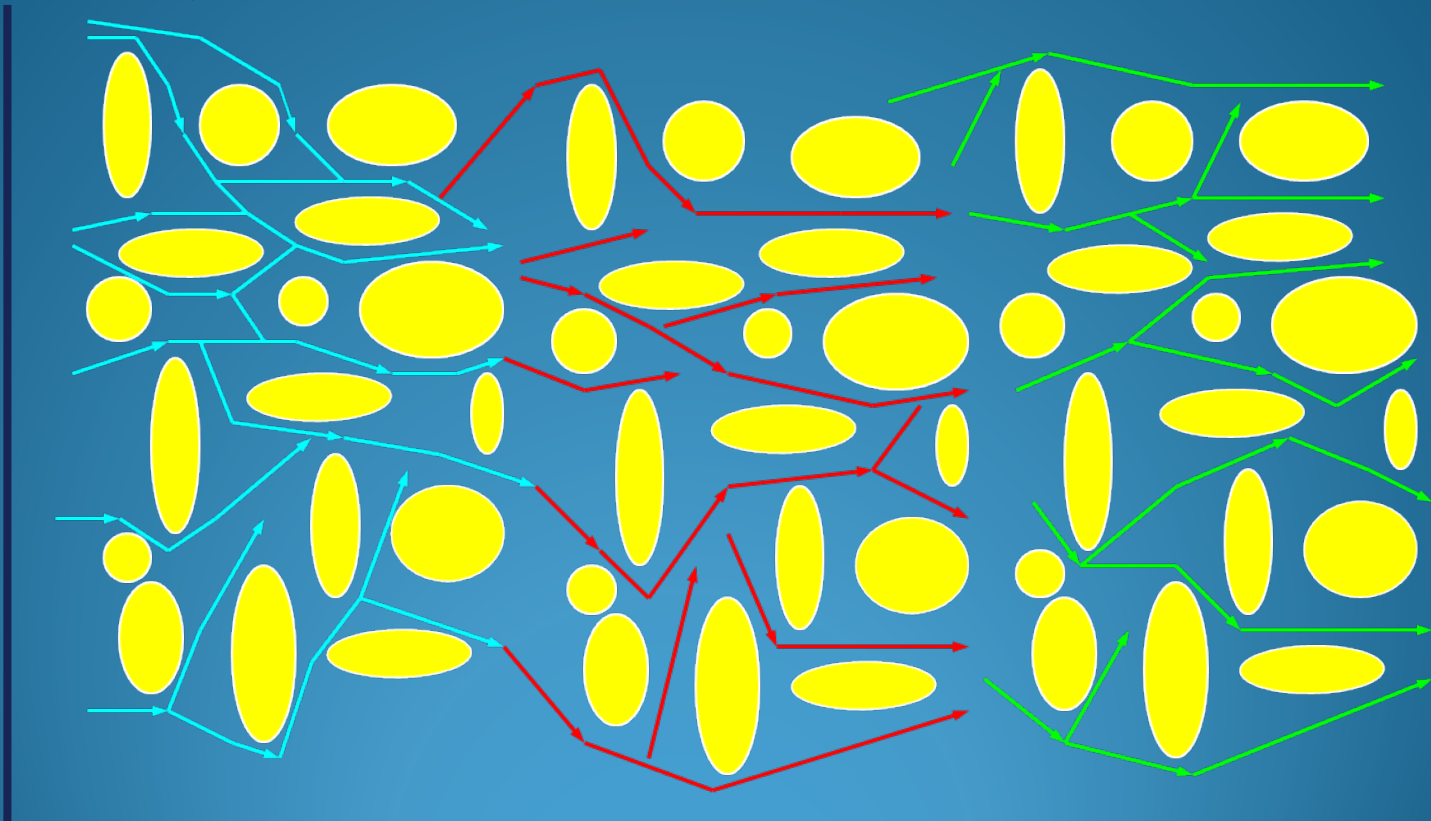
High Quality
Injectate

Mixing Zone

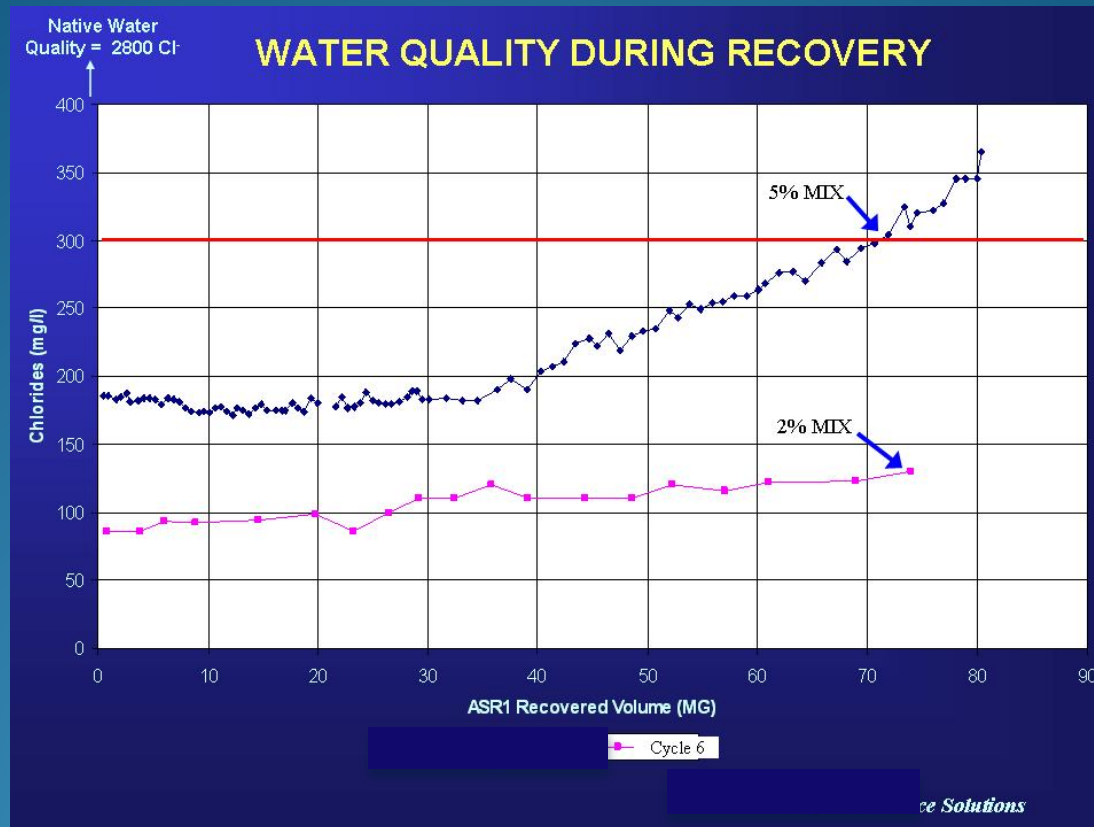
Native Water

W
E
L
L

B
O
R
E

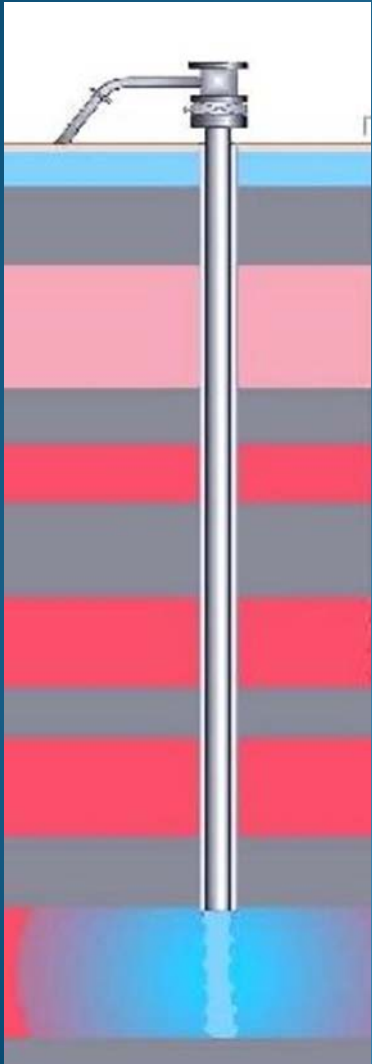


Mixing Ratio Controls Recovery Efficiency



- Simulated recovery efficiency after 6 recharge cycles
- Water can be recovered until chloride levels get too high
- 5% mixing allows 70% recovery of injected water
- 2% mixing allows all of the injected water to be recovered (in theory)

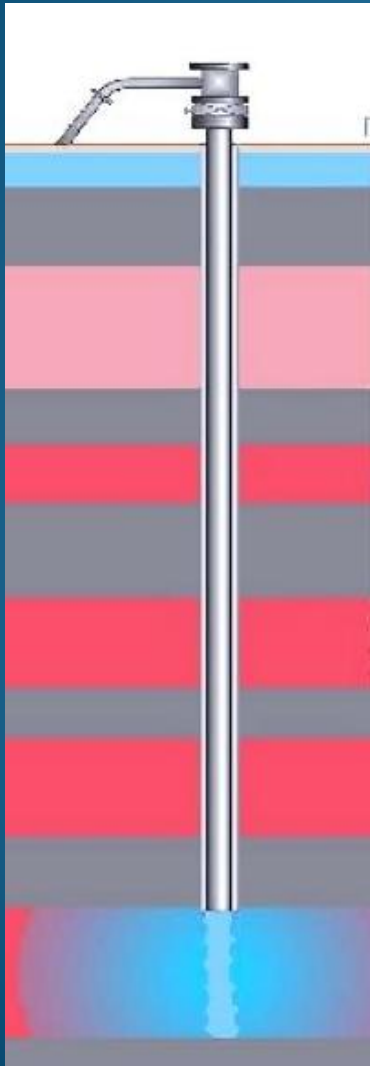
Hydrogeologic Factors of an Ideal ASR Zone (Minimal Mixing)



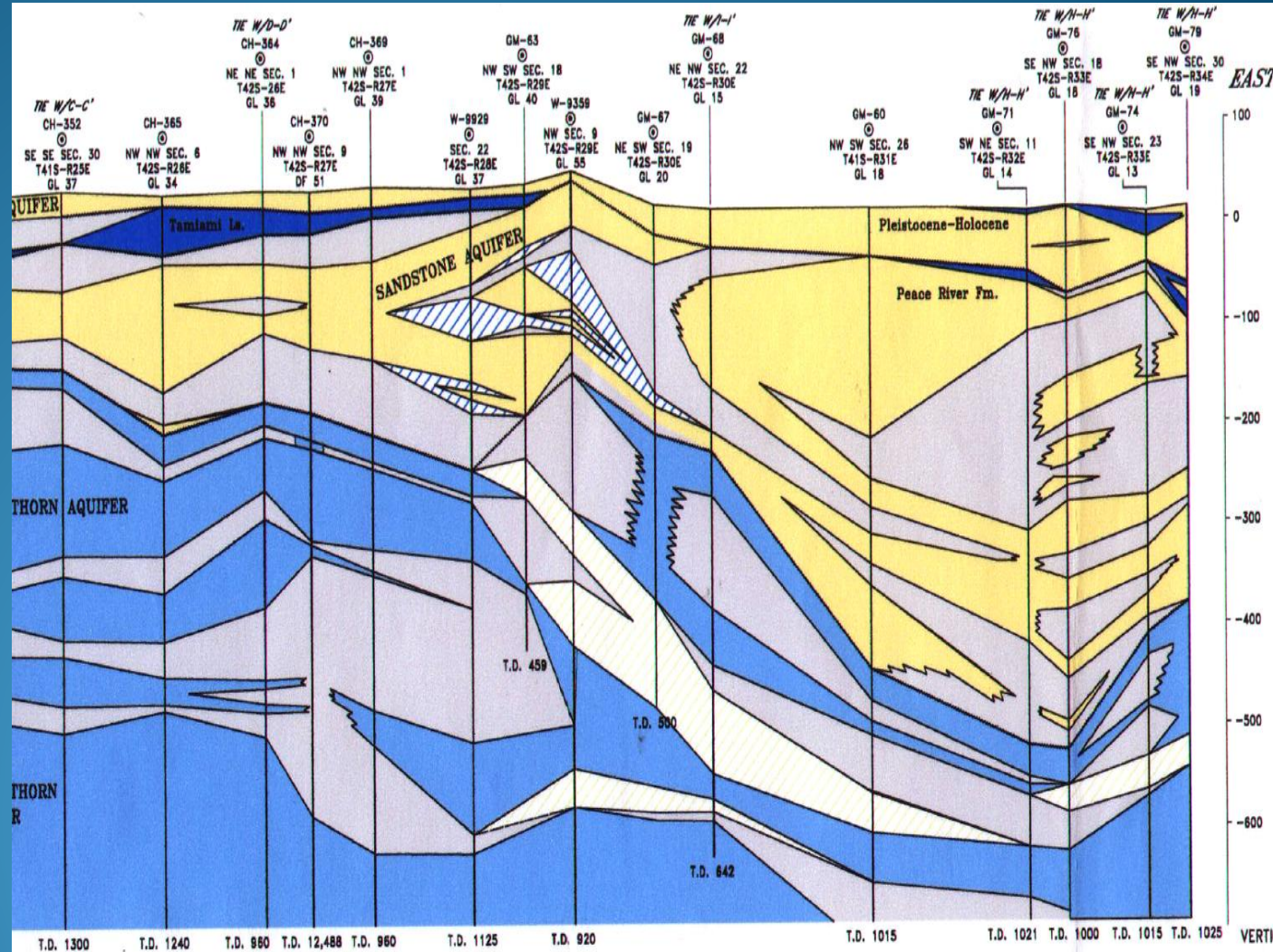
- Often a trade off between flow rate and mixing
- Better native water quality (lower TDS, lower dissolved metals)
- Storage zone that is not too thick (thinner is better)
- Good confinement above and below
- Uniform porosity
- No fractures or voids
- Intermediate transmissivity
- Minimal regional gradient
- Formation and native water chemically stable with injected water

The Biggest Problem is Theory vs Reality

Concept



Reality



Pretreatment of ASR Source Water

- Simpler, cheaper and easier
- Mechanical and chemical to remove oxidants (free oxygen or chlorine)
 - Membranes
 - Degasification Processes
 - Catalytic Oxygen Removal
- Chemical reducing agents used to scavenge oxidizers from injected water:



Class V Wells for Injection of Non-Hazardous Fluids into or Above Underground Sources of Drinking Water

- EPA's regulations define Class V wells as injection wells not included in other well classes.
- Class V well category includes deep complex wells used at commercial and industrial facilities.
- Complex Class V well types may include:
 - Aquifer storage and recovery wells
 - Geothermal electric power wells
 - Experimental wells used for pilot geologic sequestration

“no owner or operator shall construct, operate, maintain, convert, plug, abandon, or conduct any other injection activity in a manner that allows the movement of fluid containing any contaminant into underground sources of drinking water, if the presence of that contaminant may cause a violation of any primary drinking water regulation under 40 CFR part 142 or may otherwise adversely affect the health of persons.” (40 CFR 144.12L)



- Early interpretation required land ownership of bubble
- Paralyzed ASR in FL, IL and WI for years
- Just forming contaminants in aquifer was a violation regardless of human exposure

As of 2007, nine states require water used for AR and ASR injection be potable or treated to national or state standards

Some primacy states allow additional types of water to be used in AR and ASR, including:

- **Treated effluent**
- **Untreated surface and ground water**
- **Reclaimed water**

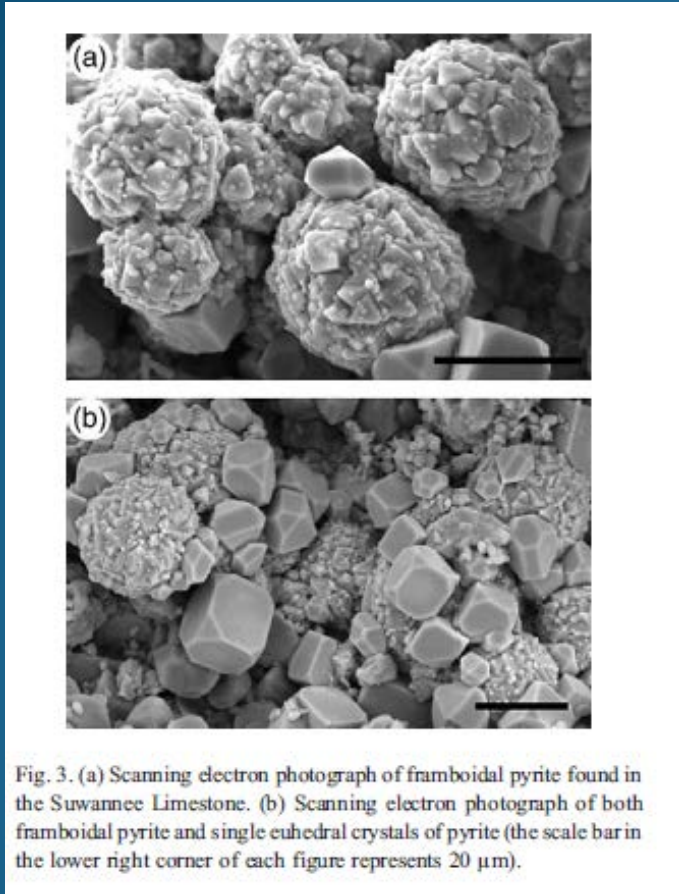
Institutional Control for ASR

- Since 2014 Florida has been using institutional controls as a means to prevent human exposure and permit ASR systems
- Use tools such as pretreatment, consistent operation and full recovery as necessary
- Establishes a Zone of Discharge where primary and secondary standards do not apply
- Access to water within zone of Discharge can be prevented by Institutional Controls
- Acceptable Institutional Controls
 - Local well drilling ordinances / permit restrictions
 - Local land use amendments
 - Watershed management plans
 - Inter-local agreements
 - Private party agreements
 - Other controls like well prohibitions and setbacks

Summary

- ASR cycles can cause geochemical shock in storage zone
- Can oxidize sulfide minerals in reduced aquifers
- Can potentially mobilize metals by reducing iron hydroxides or desorbing metals
- Some metals are regulated based on health impacts (As)
- Other metals nuisance issues (Fe and Mn)
- Some Metals not regulated but could be health risks (Co, Ni, Mo, etc.)
- Many reactions decline over repeated injection cycles and can be controlled with institutional controls
- Some reactions persist and may require pretreatment
- Biggest risk from metals in TX seems to be mixing with native water from poorly chosen storage zones
- Well plugging also a concern worth of design modifications

Trace Pyrite Present in Many Confined Aquifers



(Price and Pichler, 2006)

- Occurs as trace mineral in Florida, Upper Midwest, and other locations
- Consists of Iron Sulfide with trace amounts of arsenic, nickel and other metals
- Readily oxidizes when oxygenated water injected into the aquifer
- Liberates iron, arsenic, and other metals into recovered water
- Problem created by introducing oxidized water into aquifer during ASR storage cycle
- Reaction limited by oxidants in source water and sulfide content of storage zone
- Not a problem in Texas...so far!!

High Mixing Storage Zone

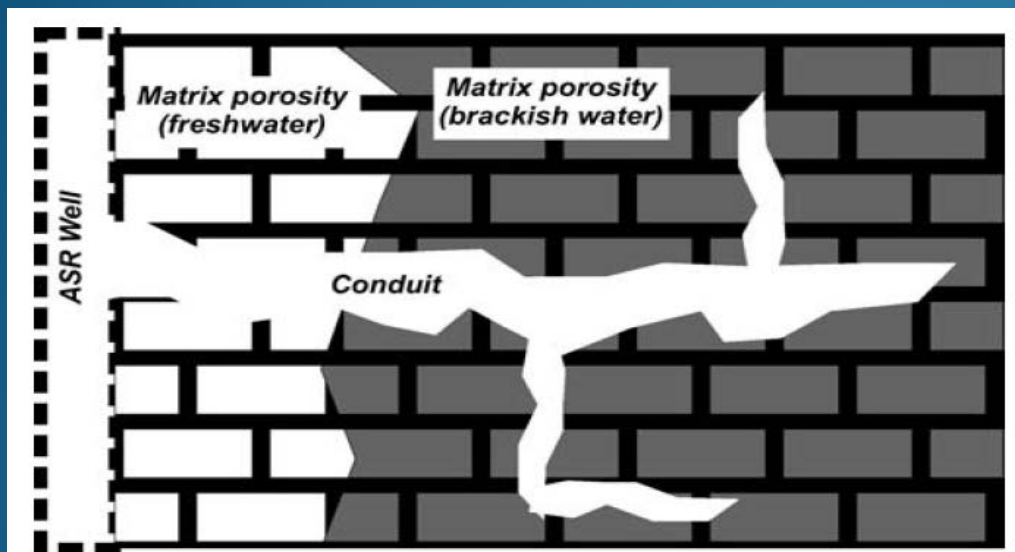
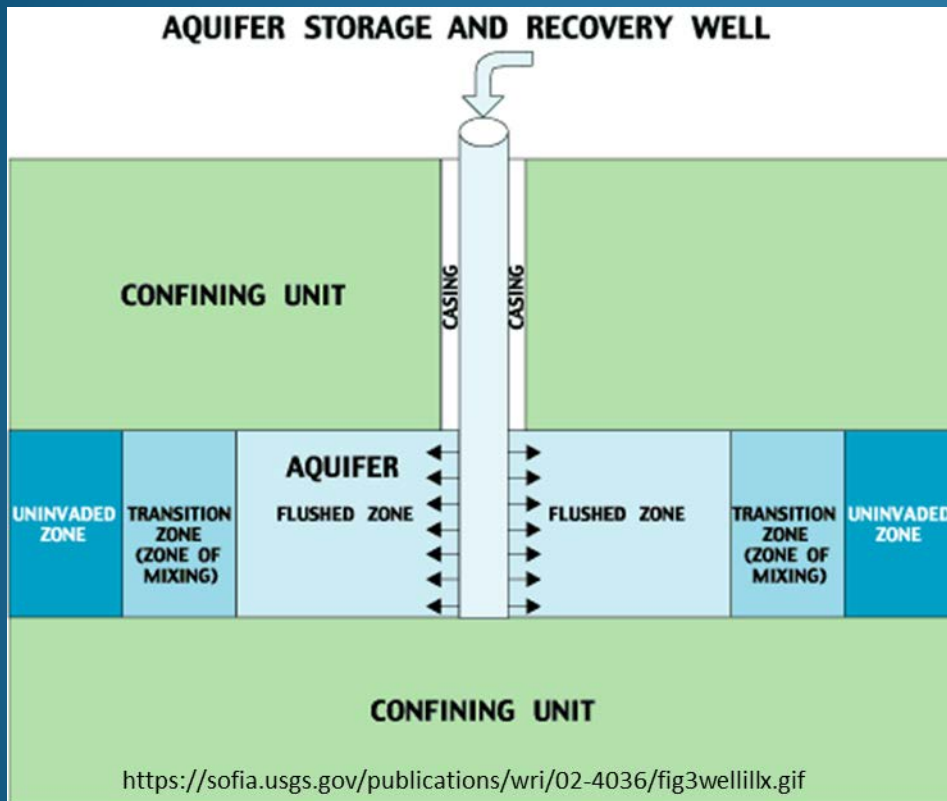


Figure 5—Schematic diagram of a dual-porosity system. Conduits containing freshwater are in contact with matrix containing brackish water, which will result in a deterioration of water quality.

Maliva, Gau and Missmer, 2006

- Voids and fractures
- High dispersion
- Strong contrast between injected water and native water
- Promotes mixing with native water
- Not a problem if water is similar
- Big problem for brackish storage zone or high metals

Mixing With Native Formation Water



- Laminar slug flow
- Low dispersion
- No Mixing
- Ideal, but not realistic

Confusing an ideal thing for a real thing is an act that seldom goes unpunished

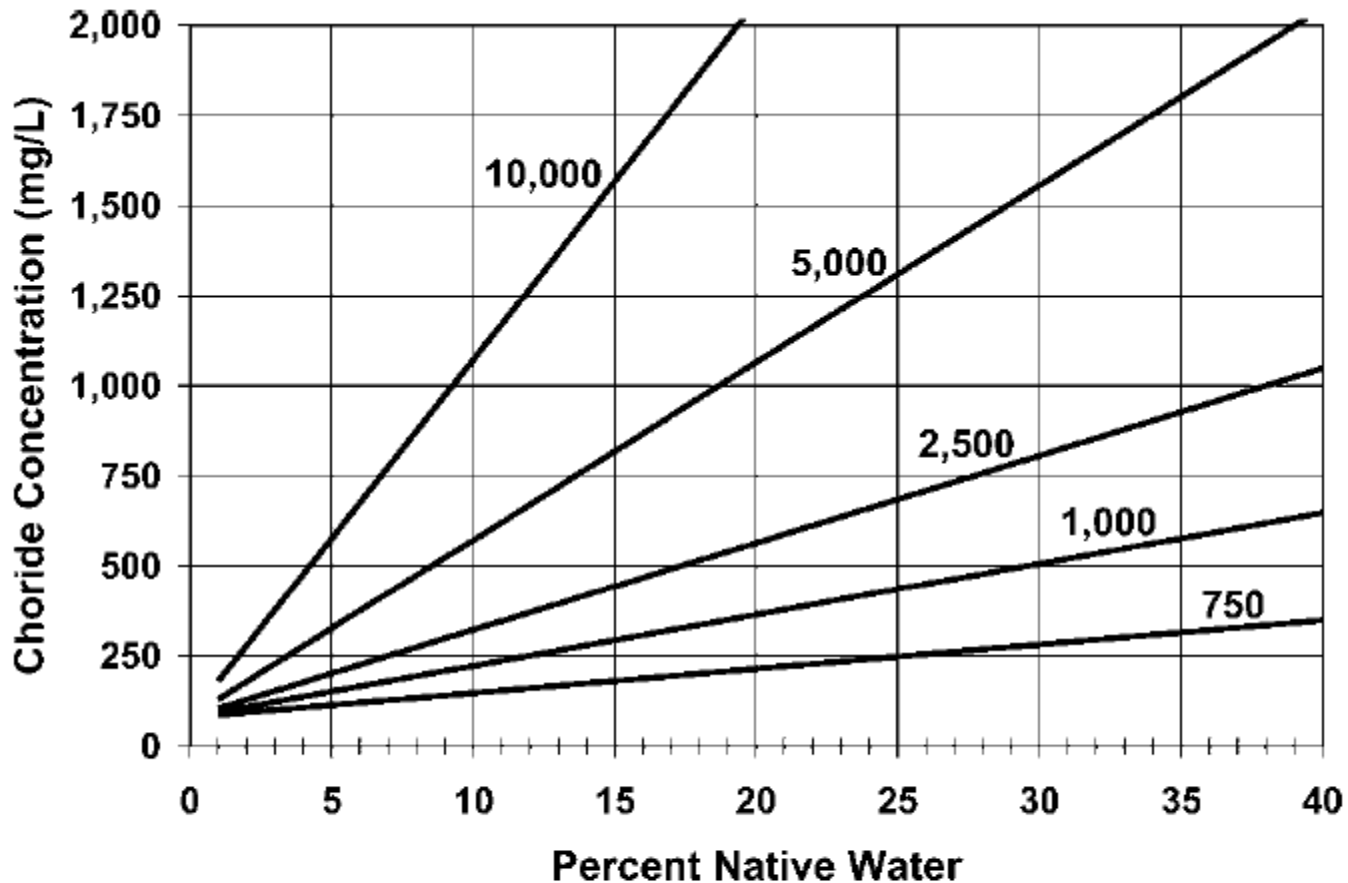


Figure 2—Mixing curves for injected freshwater with a chloride concentration of 50 mg/L and native waters with chloride concentrations of 750, 1000, 2500, 5000, and 10 000 mg/L.

TCEQ New ASR Rules Effective May 19, 2016

- TCEQ notifies groundwater conservation/other special purpose districts with authority to regulate groundwater withdrawal
- Rules no longer require a 2-stage authorization process (i.e., pilot project no longer required)
- Specified injected water must meet requirements of federal SDWA Section 1421 (d)(2)
- Requires all wells for a single ASR project to be located within a contiguous boundary of one parcel of land or two/more adjacent parcels under common ownership, lease, agreement or contract