Electrocoagulation and Water Sustainability: Silica and Hardness Control

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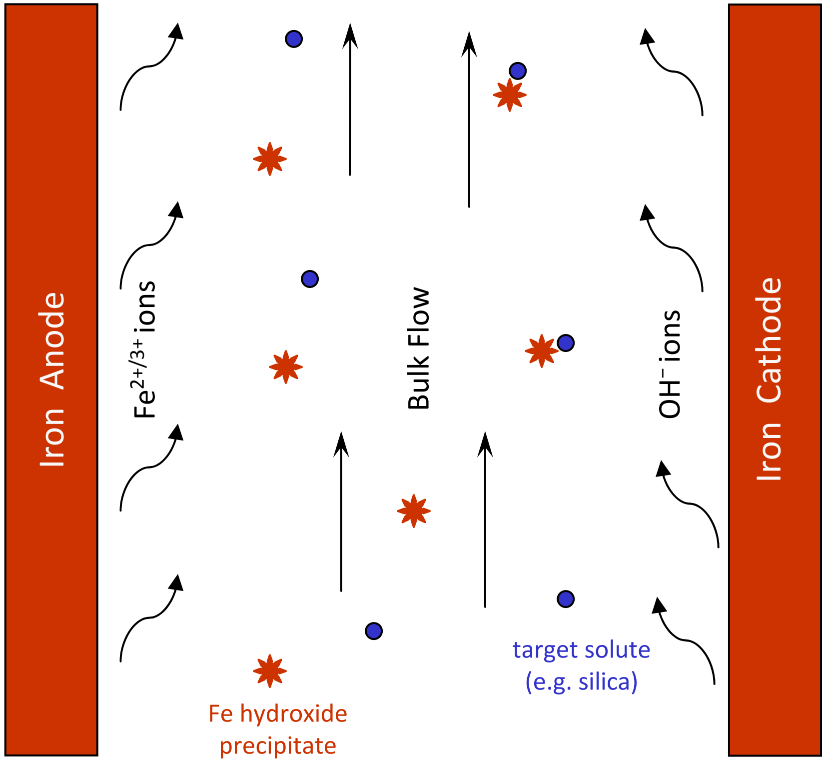
Teleseminar
SRC/SEMATECH Engineering Research Center for Environmentally Benign Semiconductor Manufacturing
26 June 2008

Outline

- Brief description of EC
- Motivation (work is jointly funded by Intel Corporation and U Arizona WSP)
  - Intel's perspective
  - Arizona/Desert SW perspective
- Contaminant Removal Mechanisms
- Operating Parameters: Dose
- Dose response and scale-up:
  - bench & pilot studies on RO reject and cooling tower blowdown
  - results for removal of silica and hardness cations (Ca, Mg)
- Costs to deliver dose
- Summary

Electrocoagulation (EC): The Idea



Metal anode dissolution is coupled to a complementary cathodic reaction that generates OH^{-}; metal hydroxides form and adsorb dissolved contaminants

EC is thus a salt-free**,** ~pH-neutral process that avoids the added counterions of standard coagulating agents, such as $Fe(Cl)_3$ and $Al_2(SO_4)_3$

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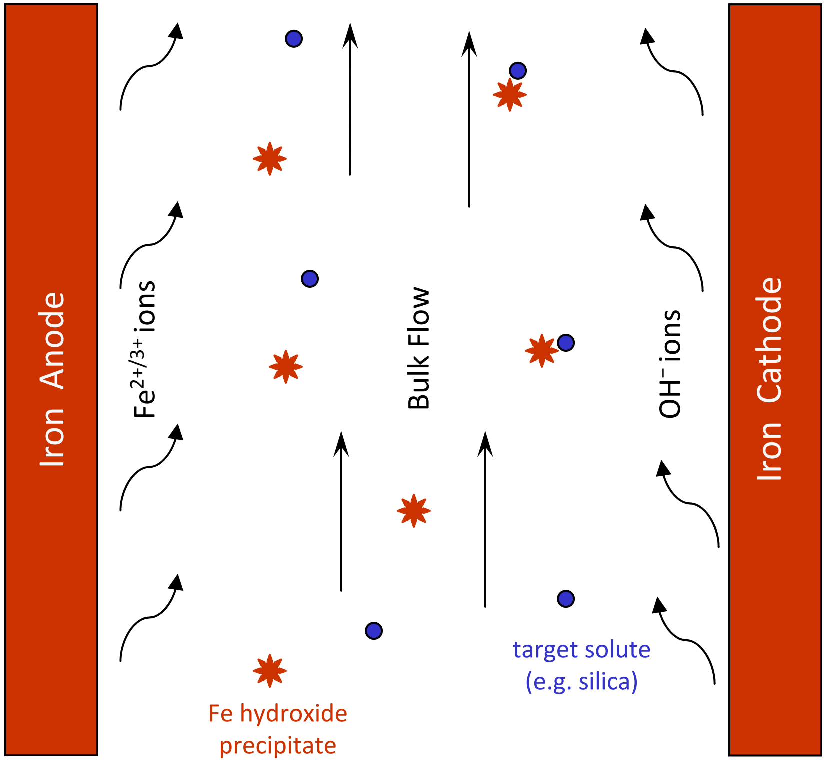

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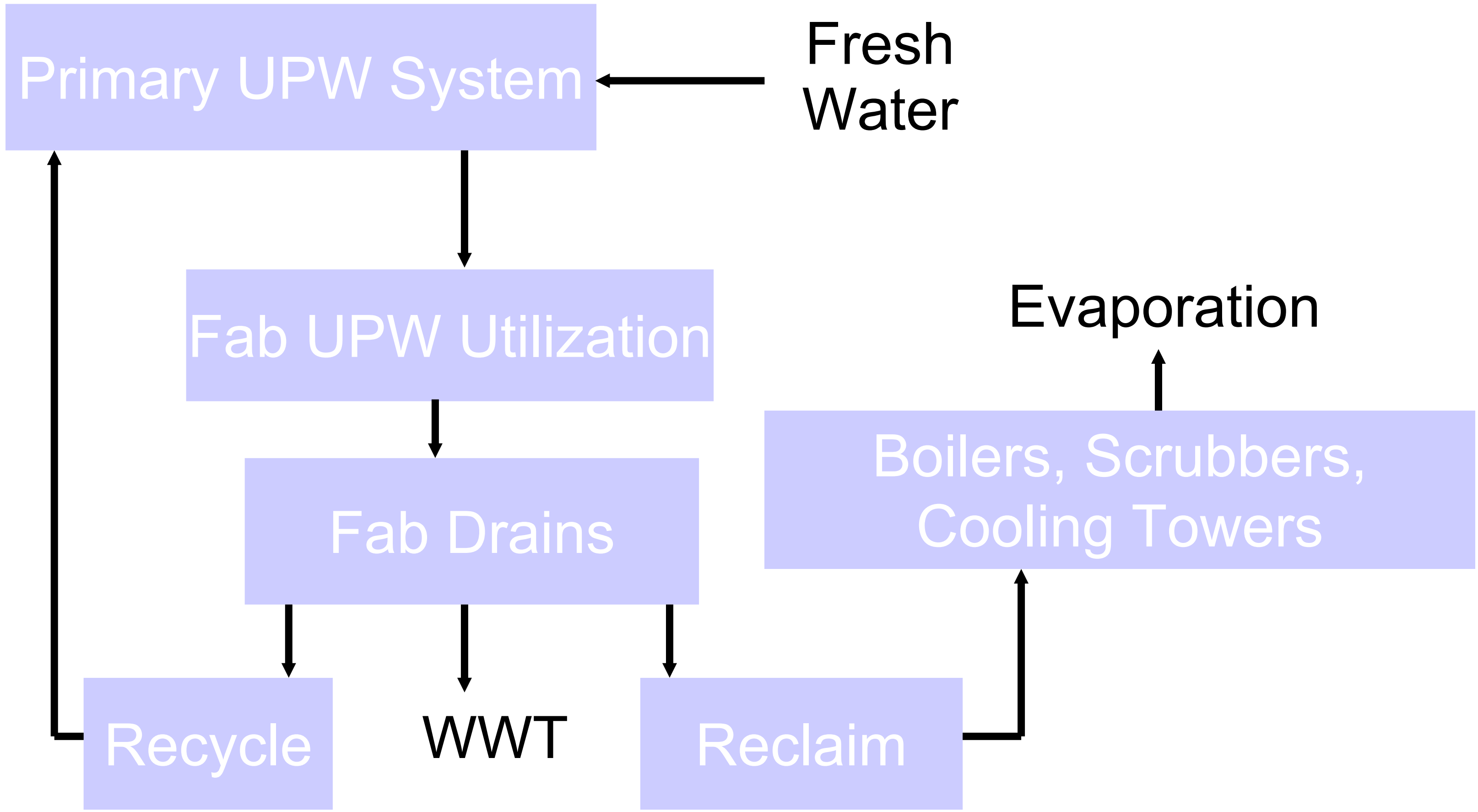
Some Virtues of EC

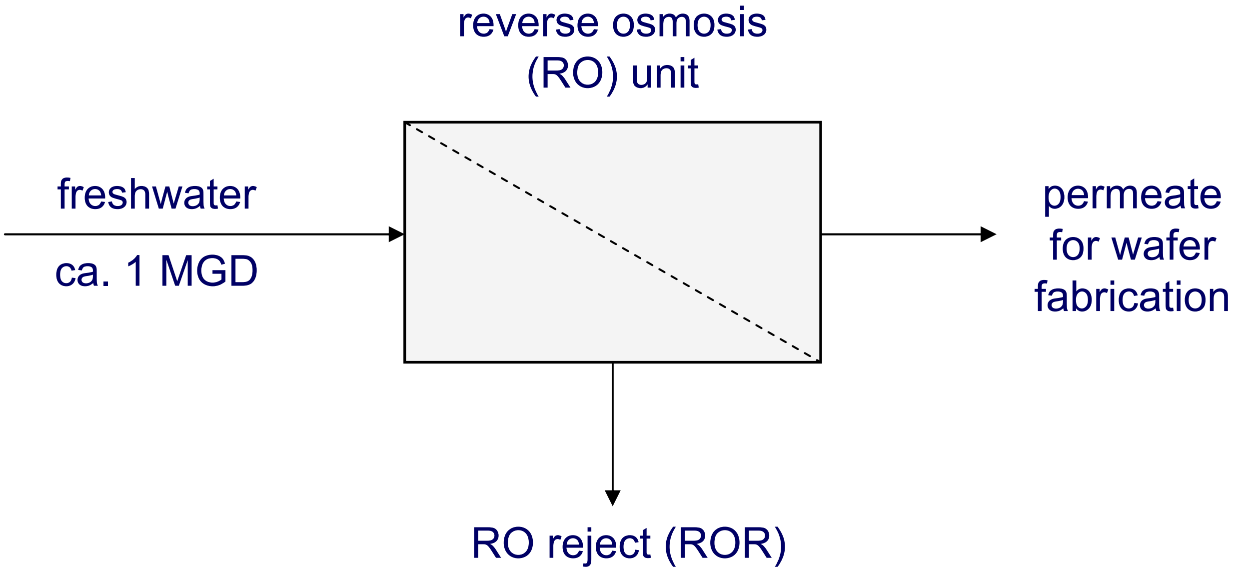
- EC can remove a wide range of inorganic, organic and particulate contaminants.
- Coagulation has a long history of effectiveness as the standard treatment method for removing natural organic matter, dissolved solids, particulates and microorganisms from drinking water
- Low operating costs compared to membrane separations
- Metal hydroxide precipitates have large specific surface area (~500m^2/g); contaminants are physically or chemically adsorbed

Motivation: The Intel Perspective, Water Reclaim in Semiconductor Manufacturing



Kurt Eckert
“Reducing Water Usage in Semiconductor Manufacturing”
NM Water Conservation Alliance Roundtable
23 March 2000
Rio Rancho,NM

Reverse Osmosis Reject (ROR)


reverse osmosis (RO) unit

freshwater

ca. 1 MGD

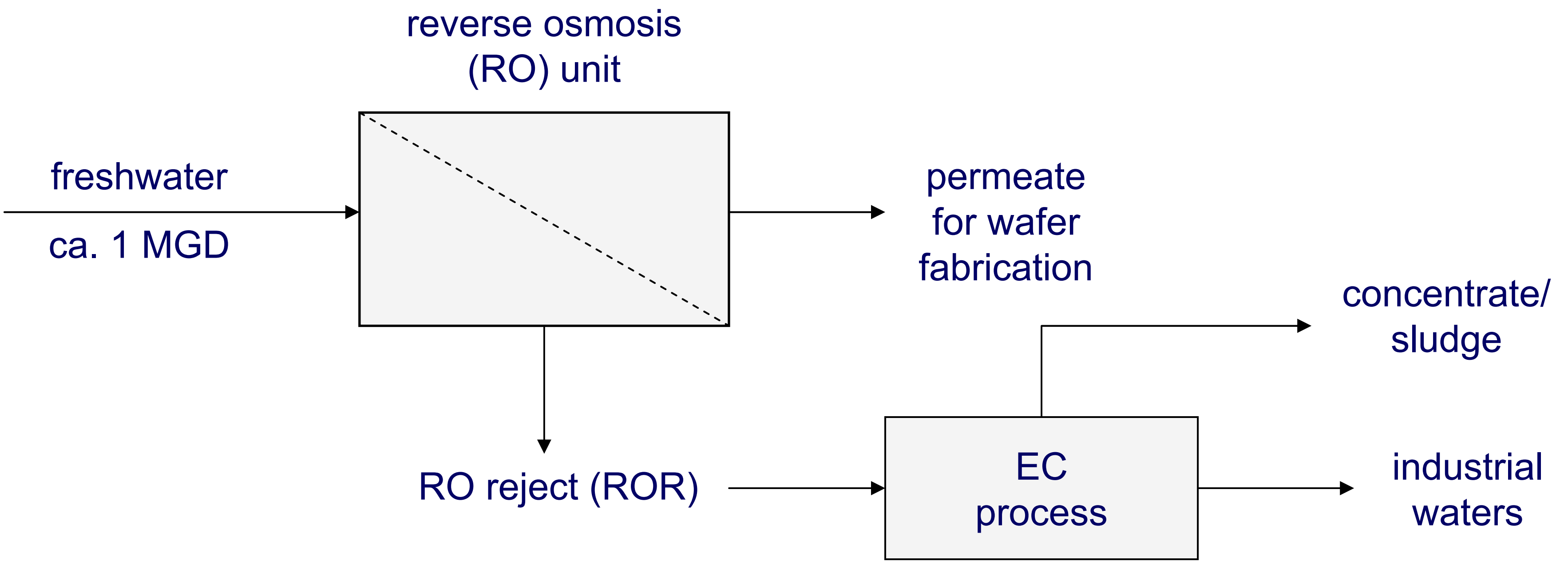
permeate for wafer fabrication

RO reject (ROR)

- too much ROR for evaporation ponds, e.g. 0.3-0.4 MGD in these studies
- silica, 65-75 mg/L (100-140 mg/L max)
- Ca, 30-35 mg/L
- Mg, 8-12 mg/L
- TDS, 275-450 mg/L

→ currently goes to waste;
would prefer to use in “industrial” waters

Reverse Osmosis Reject (ROR)



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RO reject (ROR)

EC process

concentrate/ sludge

industrial waters

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currently goes to waste;
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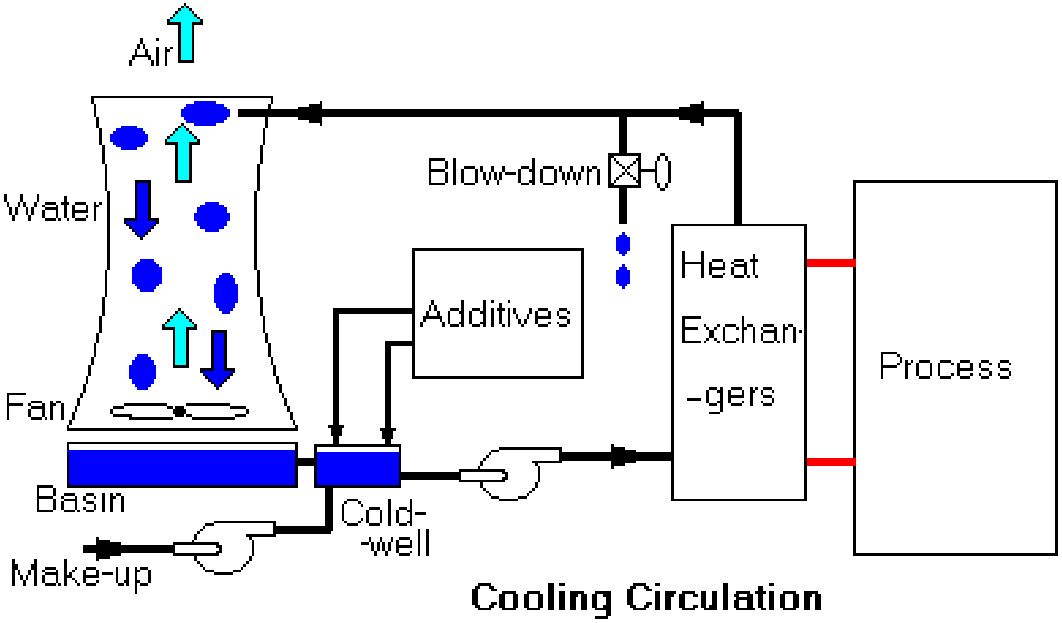
cost of freshwater: ca. $2.5/1000gallons

Cooling Tower Blowdown (CTB)



COC to Water Use	
COC:Cycles of Concentration	Gallons per Day per Ton of Cooling
1.5	10,200 gpd
2.0	7,000 gpd
4.0	4600 gpd
6.0	4200 gpd

CTB solutes of interest:

- silica, 40-50 mg/L (100-140 mg/L max)
- Ca, 17-23 mg/L
- Mg, 4-6 mg/L
- phosphate, 15-20 mg/L
- TDS, 620-815 mg/L

TNT Technology Company (2003)
1st CASS Report, Appendix M

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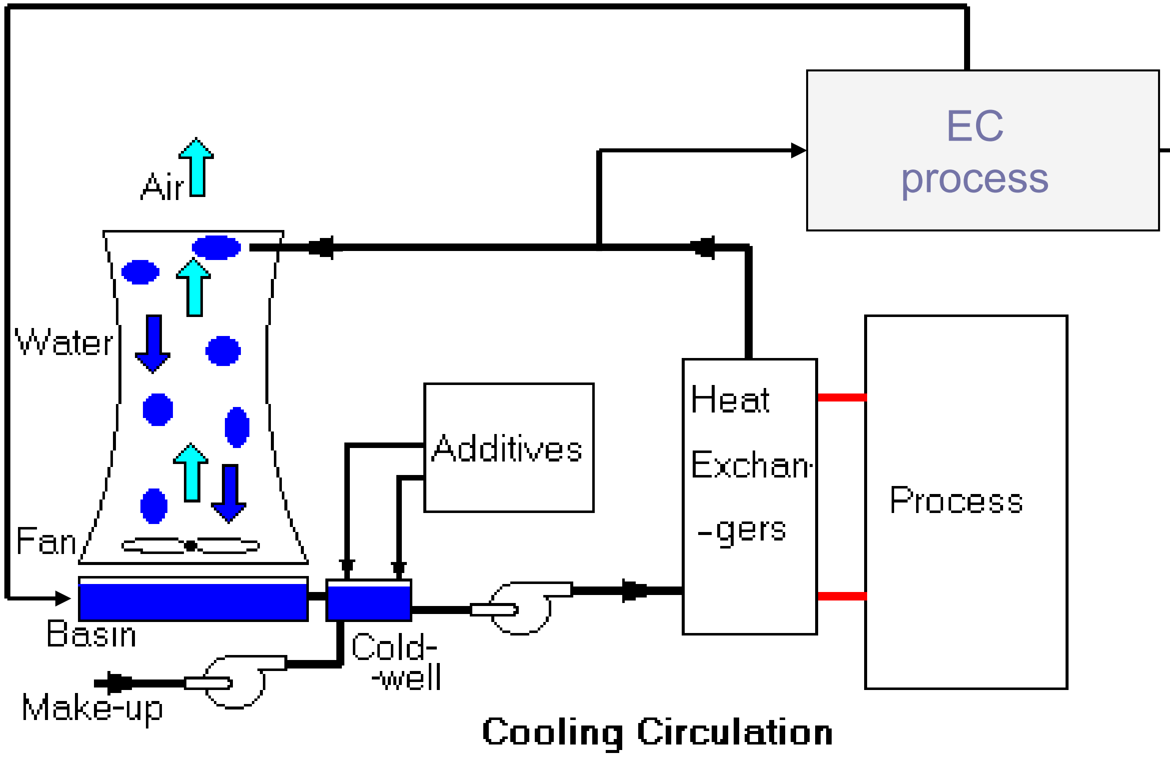

EC
process

concentrate/
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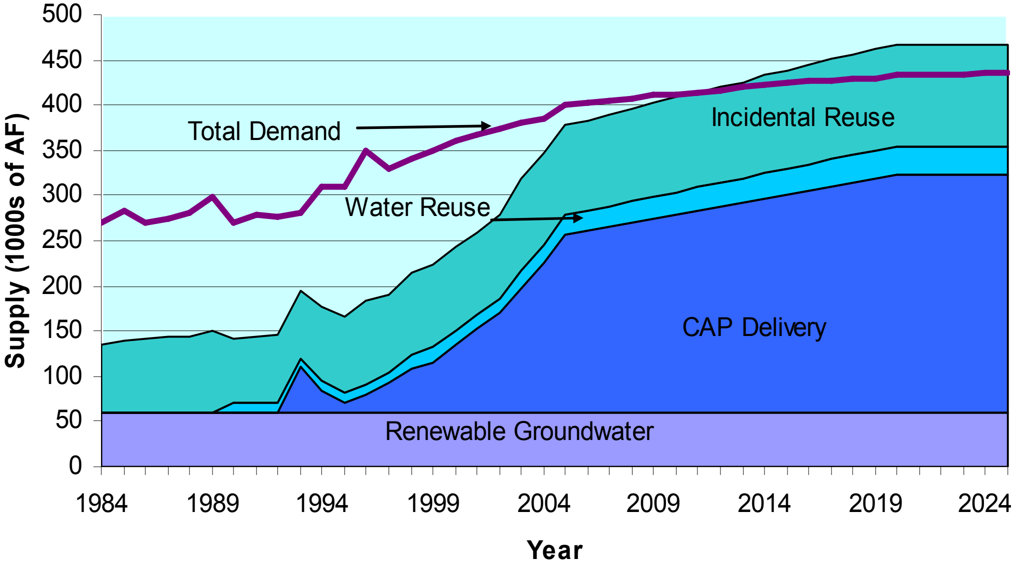
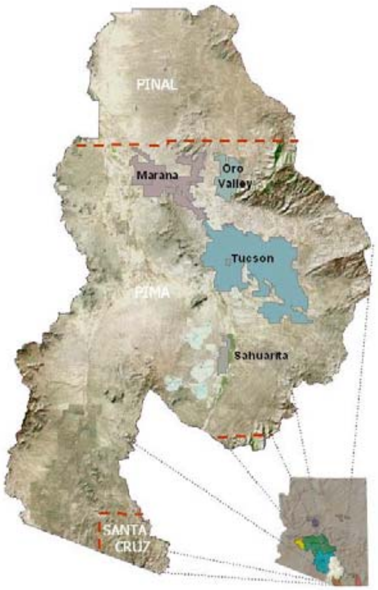
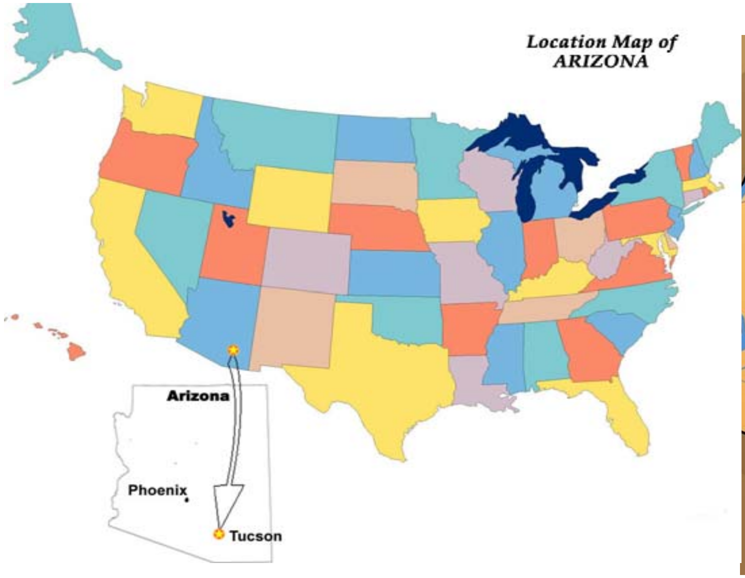
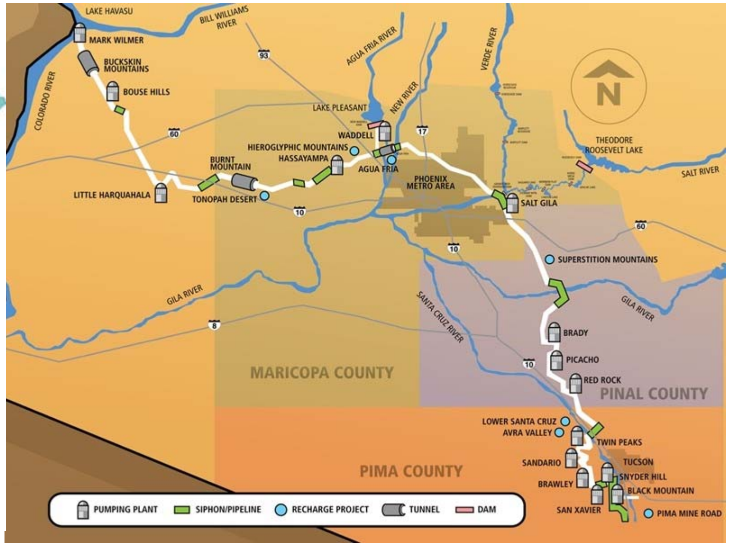
Motivation: The Tucson/AZ Perspective

Water Demand/Supply in the TAMA

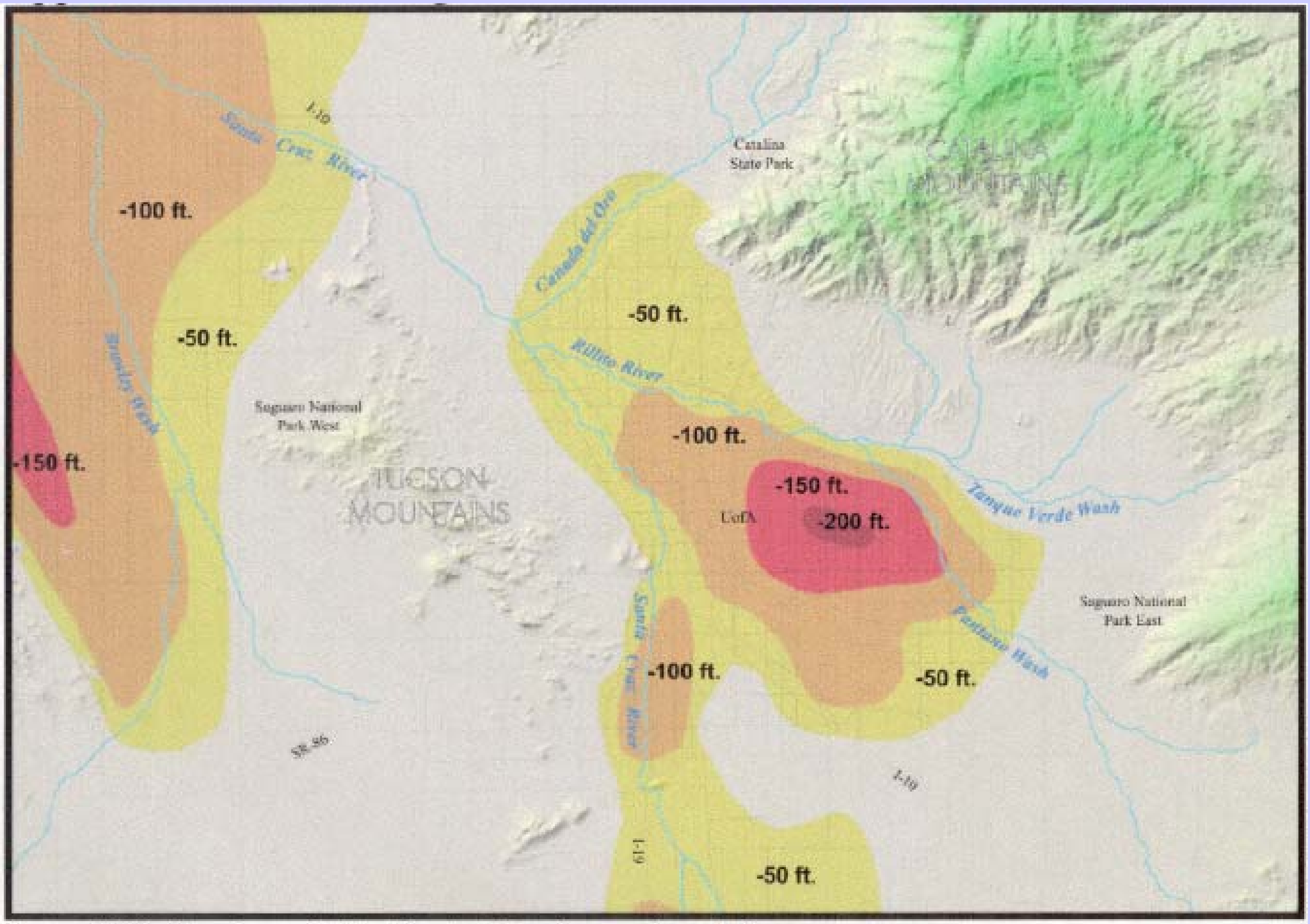








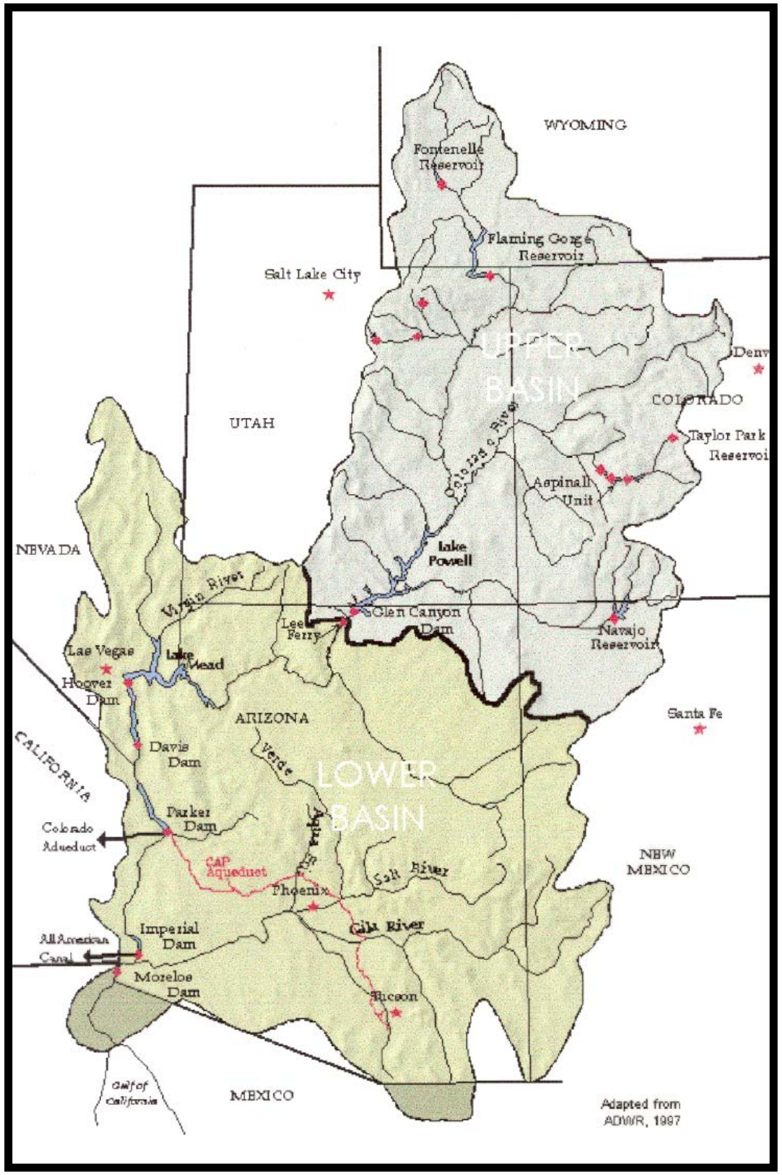
Approximate Decline in Groundwater Levels 1940-1995



Source: ADWR, Pima County Technical Services, Water Resources Research Center

Water Resources Research Center, College of Agriculture, The University of Arizona

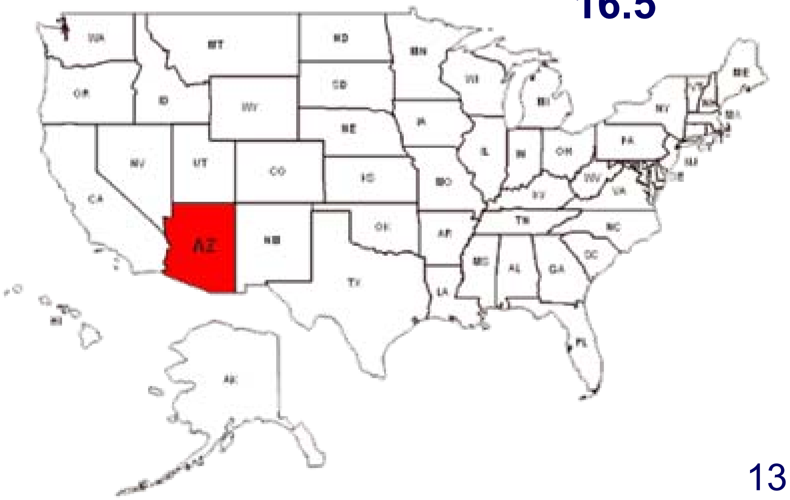
Colorado River Basin and River Allocations



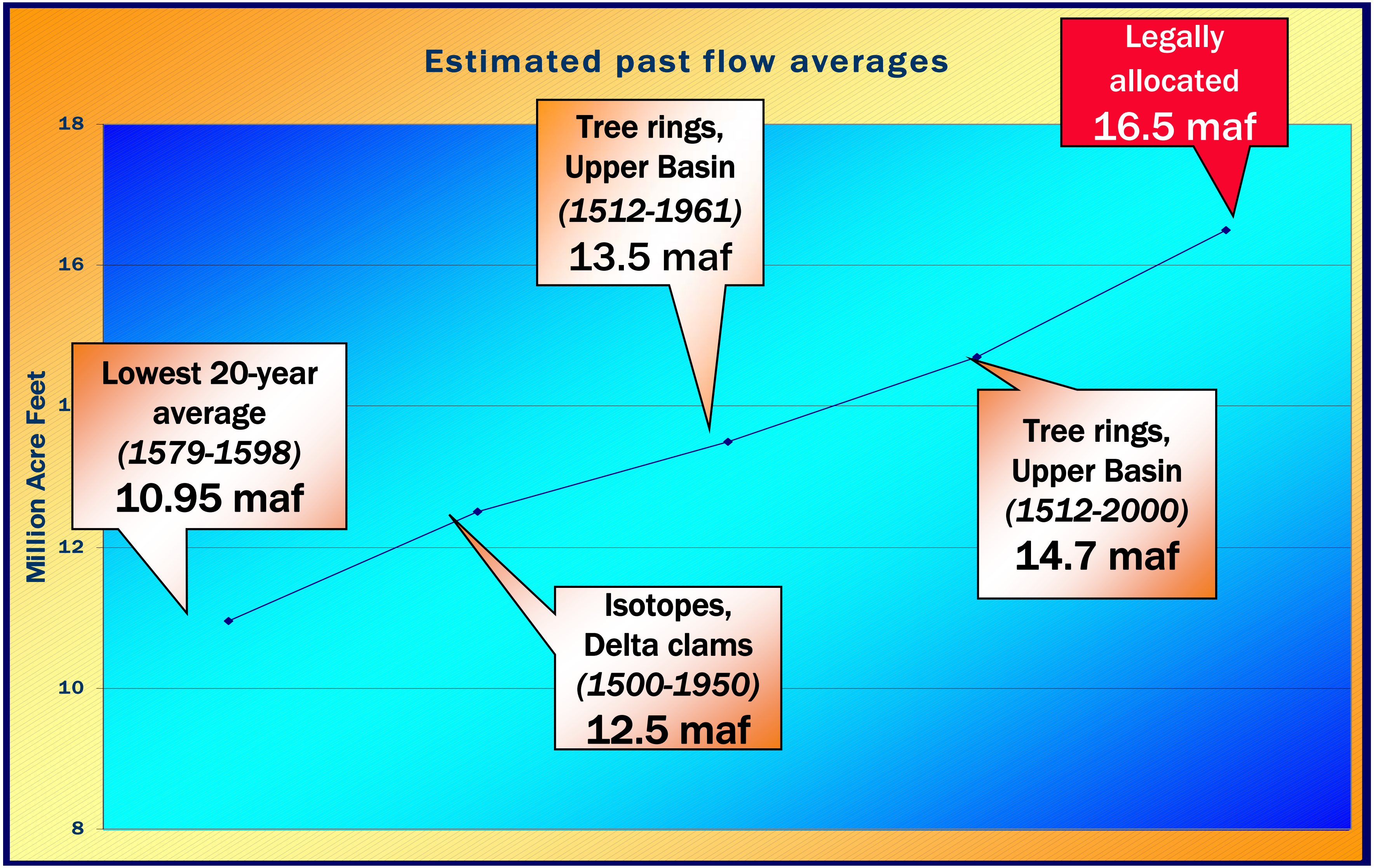
Adapted from ADWR, 1997

Allocation of Colorado River (MAF per year):

Upper Basin States		**7.5**
Lower Basin States		
	California	**4.4**
	Arizona	**2.8**
	Nevada	**0.3**
	Lower Basin Total	**7.5**
Mexico		**1.5**
TOTAL		**16.5**



Colorado River Flows



Estimated past flow averages

Legally allocated
16.5 maf

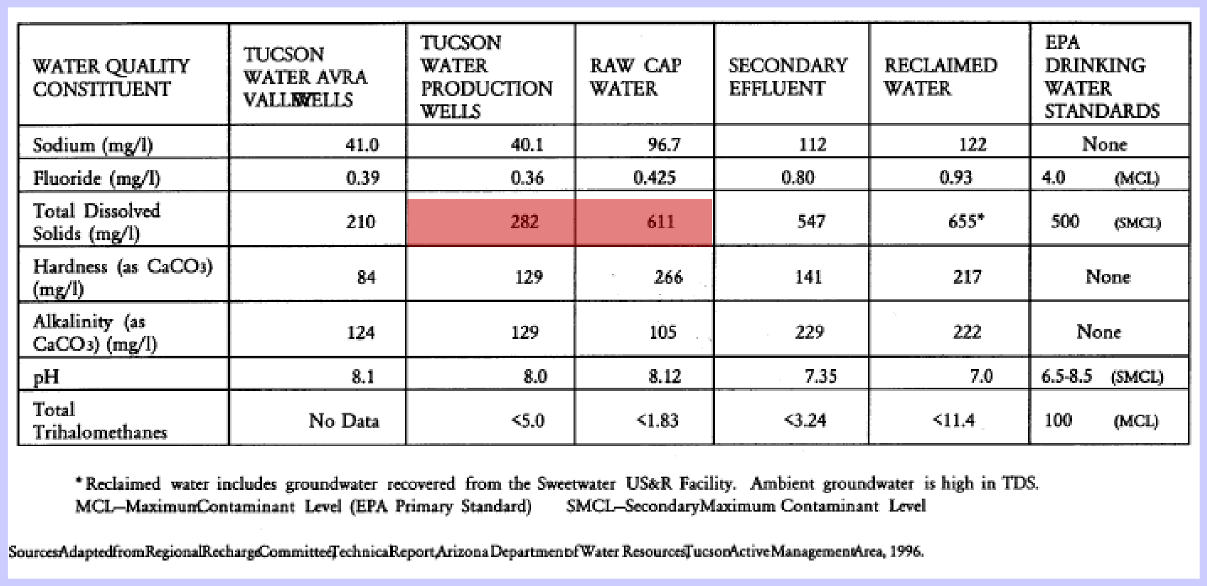
Tree rings,
Upper Basin
(1512-1961)
13.5 maf

Lowest 20-year average
(1579-1598)
10.95 maf

Tree rings,
Upper Basin
(1512-2000)
14.7 maf

Isotopes,
Delta clams
(1500-1950)
12.5 maf

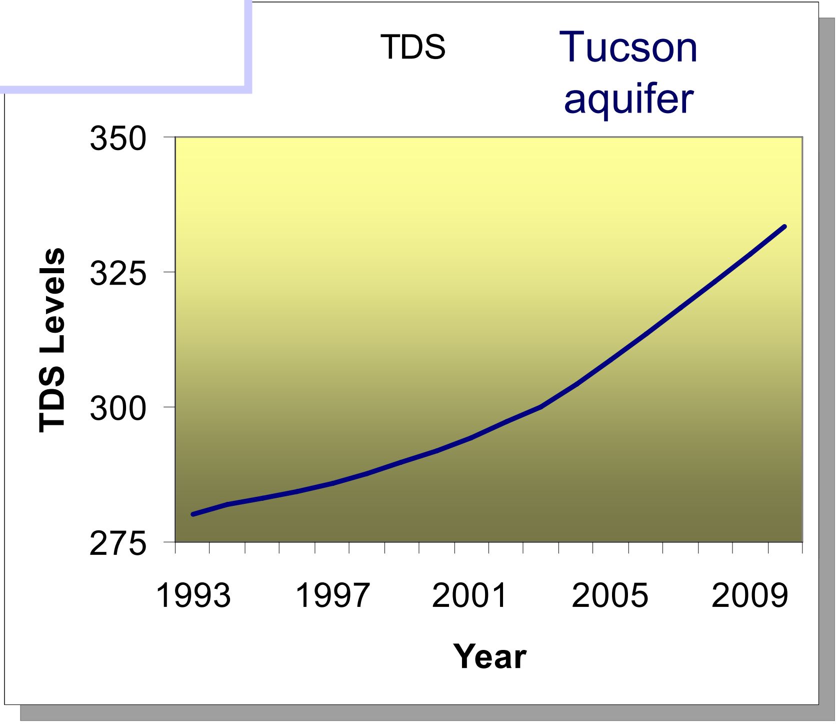
Water Quality and the Colorado River



WATER QUALITY CONSTITUENT	TUCSON WATER AVRA VALLEY WELLS	TUCSON WATER PRODUCTION WELLS	RAW CAP WATER	SECONDARY EFFLUENT	RECLAIMED WATER	EPA DRINKING WATER STANDARDS
Sodium (mg/l)	41.0	40.1	96.7	112	122	None
Fluoride (mg/l)	0.39	0.36	0.425	0.80	0.93	4.0 (MCL)
Total Dissolved Solids (mg/l)	210	282	611	547	655*	500 (SMCL)
Hardness (as CaCO3) (mg/l)	84	129	266	141	217	None
Alkalinity (as CaCO3) (mg/l)	124	129	105	229	222	None
pH	8.1	8.0	8.12	7.35	7.0	6.5-8.5 (SMCL)
Total Trihalomethanes	No Data	<5.0	<1.83	<3.24	<11.4	100 (MCL)

*Reclaimed water includes groundwater recovered from the Sweetwater US&R Facility. Ambient groundwater is high in TDS.
MCL–Maximum Contaminant Level (EPA Primary Standard) SMCL–Secondary Maximum Contaminant Level

Sources Adapted from Regional Recharge Committee Technical Report, Arizona Department of Water Resources, Tucson Active Management Area, 1996.



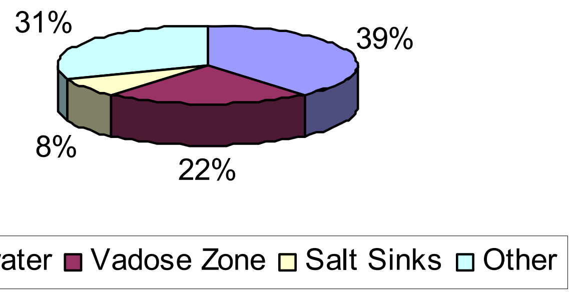
Water Quality and the Central Arizona Salinity Study (CASS)

Estimated Annual Salt Balance in Phoenix Metropolitan Area

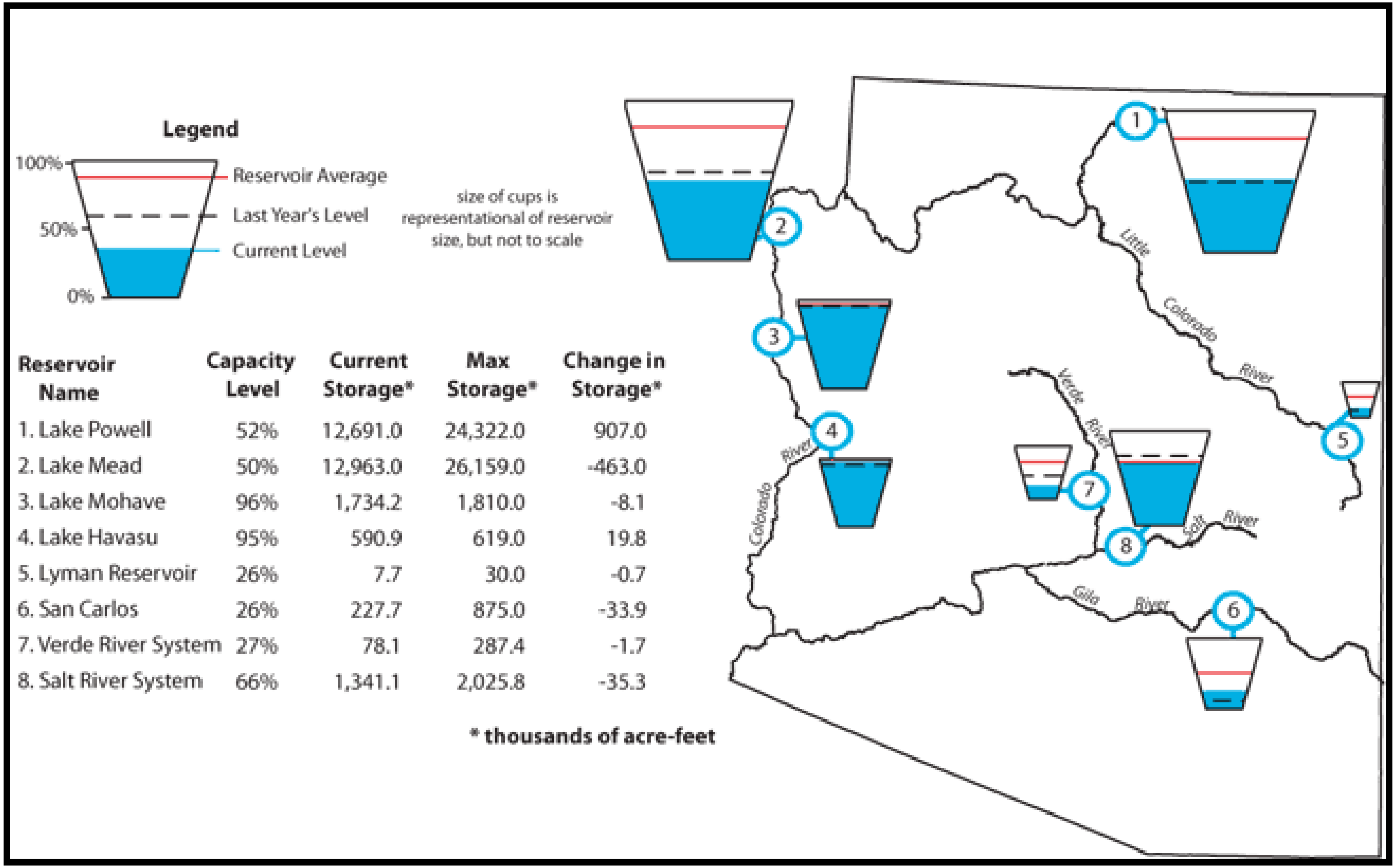
Entering Phoenix Metro	Volume (ac-ft)	TDS (mg/L)	Salt (tons)
Groundwater	37,000	680	34,218
SRP	810,000	480	528,768
CAP	752,000	650	664,768
Gila River	90,000	550	67,320
Agua Fria River	50,000	400	27,200
Society	290,000	300	118,320
Agricultural fertilizer			22,500
Total			**1,463,094**

Exiting Phoenix Metro	Volume (ac-ft)	TDS (mg/L)	Salt (tons)
Groundwater	28,000	1,100	41,888
Gila River	100,000	2,370	322,320
Total			**364,208**
Salt Load			1,098,886

Projected final location of salts imported into the Phoenix Metro area



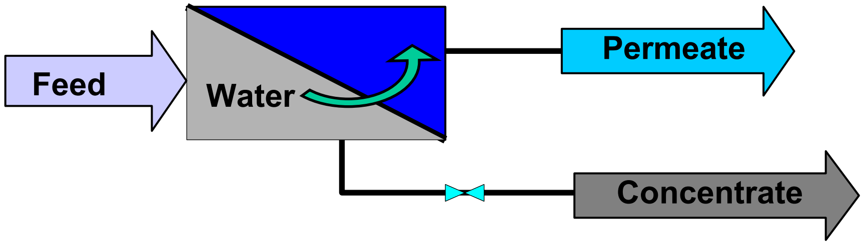
Arizona Reservoir Levels in May 2007



Reservoir Name	Capacity Level	Current Storage*	Max Storage*	Change in Storage*
1. Lake Powell	52%	12,691.0	24,322.0	907.0
2. Lake Mead	50%	12,963.0	26,159.0	-463.0
3. Lake Mohave	96%	1,734.2	1,810.0	-8.1
4. Lake Havasu	95%	590.9	619.0	19.8
5. Lyman Reservoir	26%	7.7	30.0	-0.7
6. San Carlos	26%	227.7	875.0	-33.9
7. Verde River System	27%	78.1	287.4	-1.7
8. Salt River System	66%	1,341.1	2,025.8	-35.3

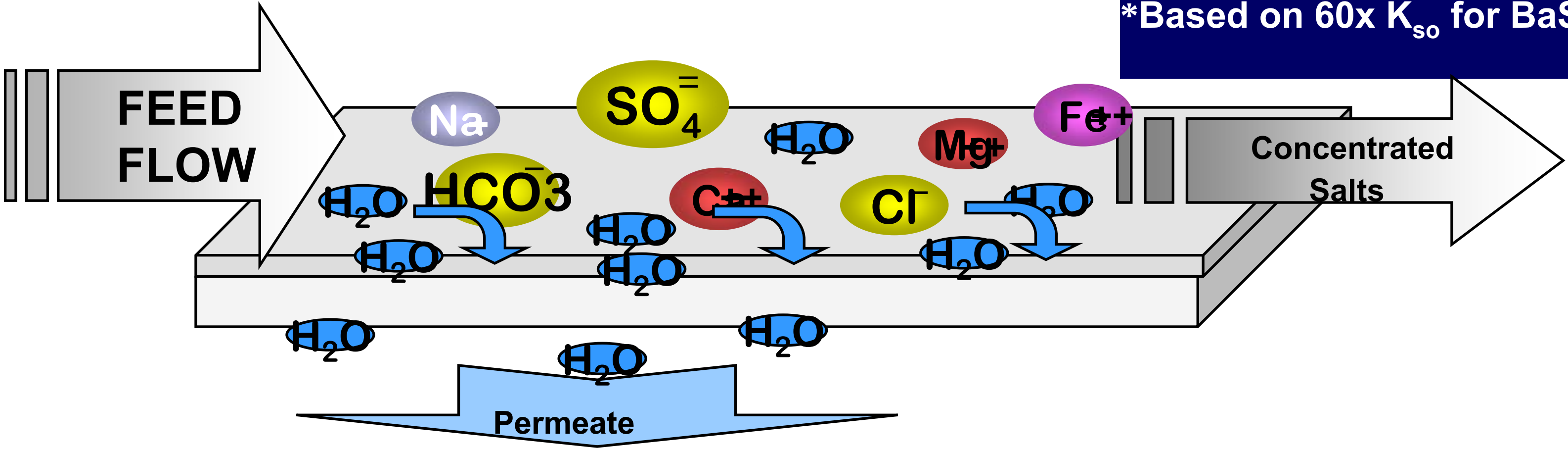
* thousands of acre-feet

What Limits Water Recovery?



$$\% \text{ Recovery} = \frac{\text{Permeate Flow}}{\text{Feed Flow}} \times 100$$

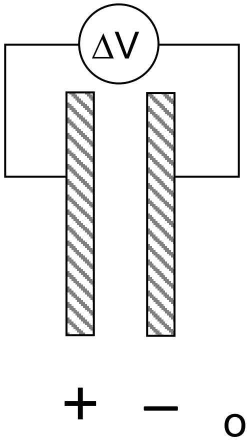
*Based on 60x K_{so} for $BaSO_4$



Augmenting Arizona’s Water Supplies

- ❖ In-State Options
  - ✓ Increased reuse of reclaimed water
  - ✓ Additional transfers of Colorado River supplies
- ❖ Out-of-State Options
  - ✓ Interbasin transfer of Columbia River Basin water via Colorado River Basin
  - ✓ Water exchange with California – Pacific Ocean desalinated water for Colorado River water
  - ✓ Water exchange with Mexico – Gulf of Mexico desalinated water for Colorado River water

Back to EC….. The Reactions



(+)
Anode Reactions

$$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^{-}$$
$$Al_{(s)} \rightarrow Al^{3+}_{(aq)} + 3e^{-}$$

metal dissolution

$$2H_2O \rightarrow O_2 + 4H^{+} + 4e^{-}$$
$$2OH^{-} \rightarrow O_2 + 2H^{+} + 2e^{-}$$

water oxidation

(–)
Cathode Reactions

oxygen & water reduction

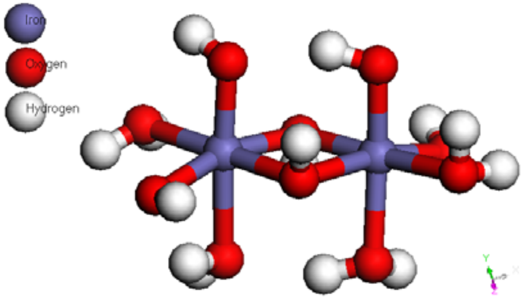
$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O$$
$$2H_2O + 2e^{-} \rightarrow H_2 + 2OH^{-}$$
$$2H^{+} + 2e^{-} \rightarrow H_2$$

Precipitation Reactions, e.g.

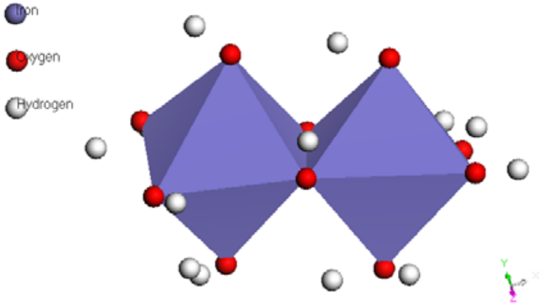
$$Fe^{3+}_{(aq)} + 3OH^{-} \rightarrow Fe(OH)_{3(s)}$$
$$Al^{3+}_{(aq)} + 3OH^{-} \rightarrow Al(OH)_{3(s)}$$

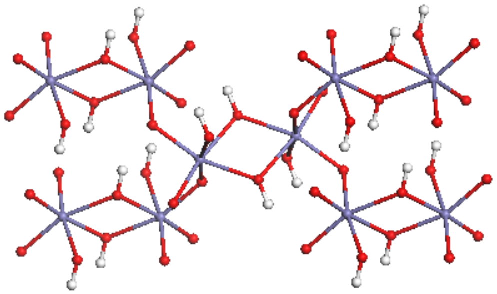
Contaminant Removal Mechanisms

Fe(III) & Al(III) Hydroxides form Charged Octahedral Structures

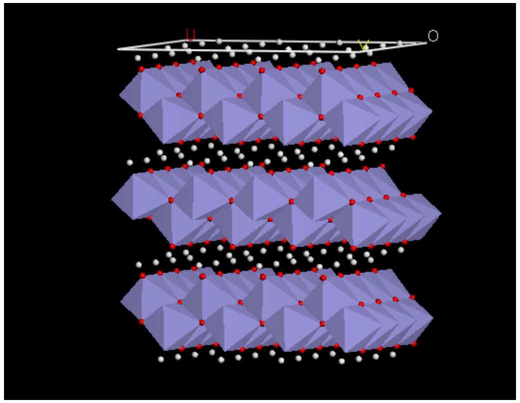


Ferric hydroxide precipitates





α-FeOOH (goethite)



γ-FeOOH (lepidocrocite)

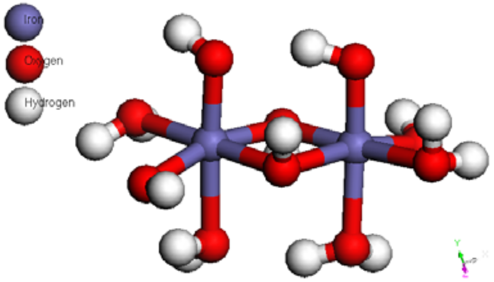
Octahedral structures combine to form amorphous precipitates or crystalline solids

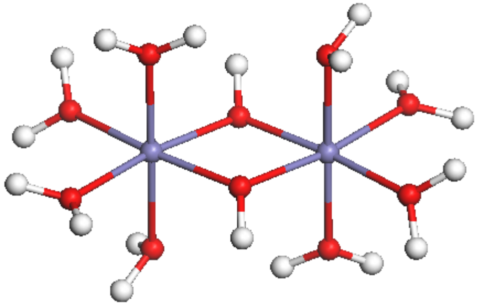
Contaminant Removal Mechanisms

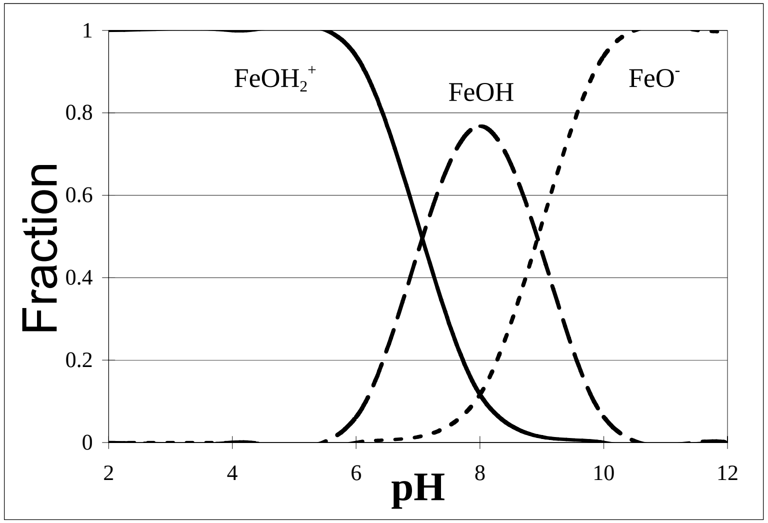
Ferric hydroxides bind and release protons according to the two reactions:

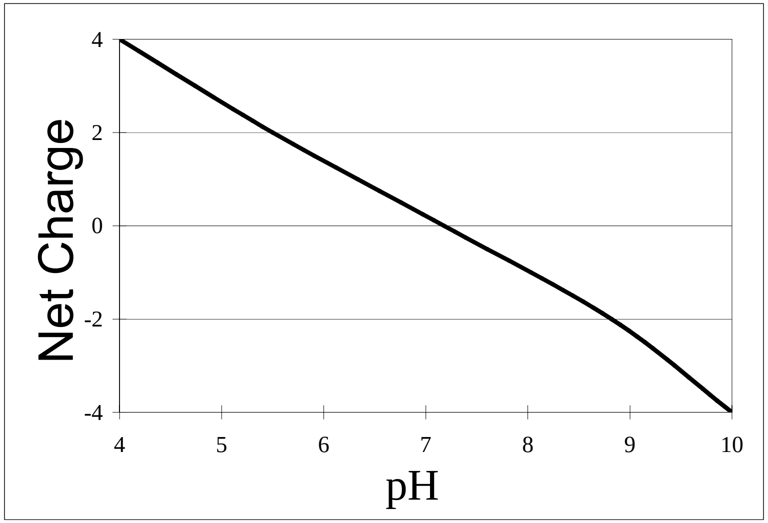
$$FeOH + H^+ \rightleftarrows FeOH_2^+ \qquad K_{a1} = 10^{-7.18}$$

$$FeOH \rightleftarrows FeO^- + H^+ \qquad K_{a2} = 10^{-8.82}$$

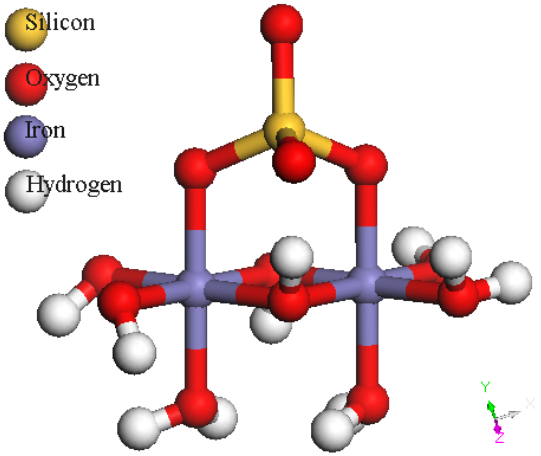


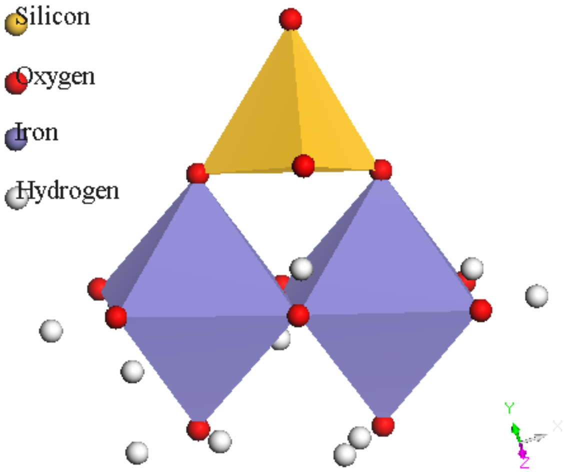






Contaminant Removal Mechanisms





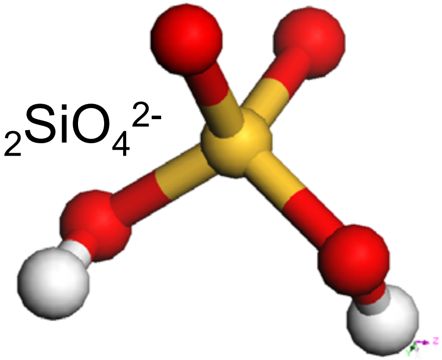
Orthosilicate anion (SiO_4^{4-}) chemically adsorbed to ferric hydroxide binding site. The chemical reaction involves replacing the two OH- ions at the top of the structure with SiO_4^{4-}

Oxyanions that are tetrahedrally coordinated (*e.g.*, SiO_4^{4-}) form bidentate corner sharing complexes with ferric hydroxide octahedra

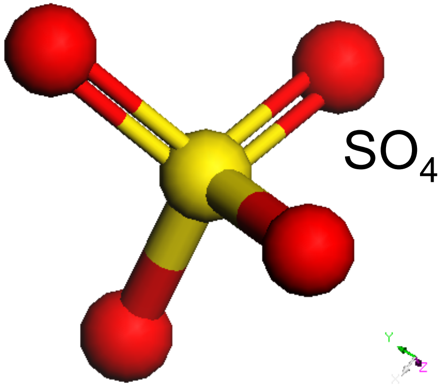
$$2(\equiv FeOH) + H_4SiO_4 + H^+ \leftrightarrow \equiv Fe_2H_3SiO_4^+ + 2H_2O \qquad K = 10^{-10.03}$$

Examples of oxyanions that are removed via chemical adsorption include: orthosilicate, arsenate, *etc.*

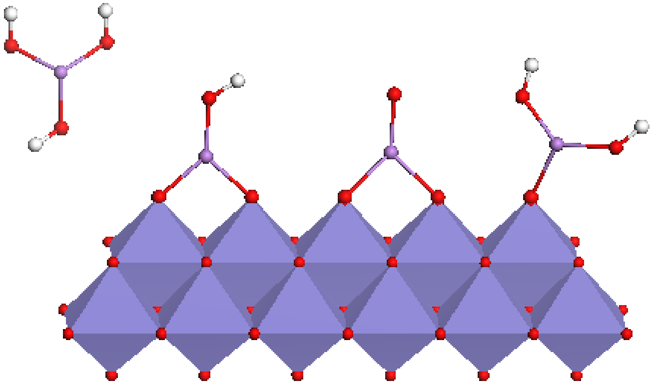
Most Oxyanions form Chemical Bonds to Fe(III) and Al(III) Hydroxides

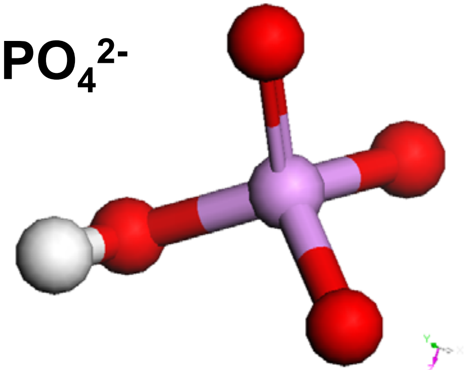


$H_2SiO_4^{2-}$

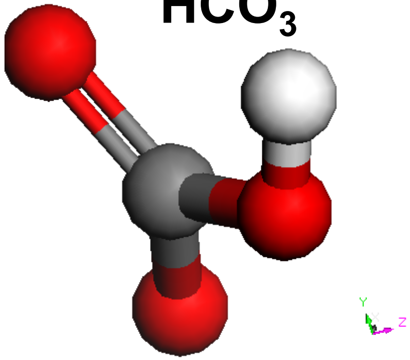


SO_4^{2-}





HPO_4^{2-}

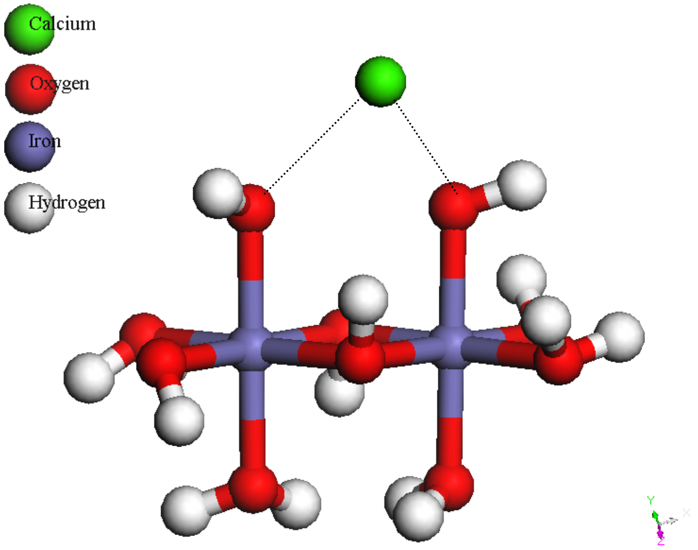


HCO_3^-

Others:

chromate, nitrate, arsenate, etc.

Alkaline Earth (+2) Cations Physically Adsorb to Charged Sites on Fe(III) and Al(III) Hydroxides



Calcium ion physically adsorbed to ferric hydroxide via electrostatic attraction to oxygen atoms that carry a partial negative charge

Removal Mechanisms

Physical adsorption - hydrophobic organic solvents, microorganisms, polyvalent cations, oils, grease

- ion adsorption is very sensitive to pH (charge on the solids)
- hydrophobic organic adsorption is insensitive to pH

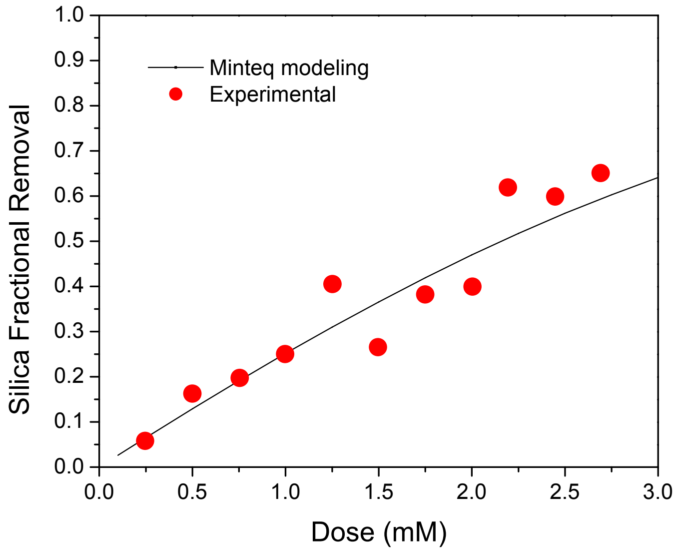
Chemical adsorption - oxyanions, natural organic matter (humic acids), metal oxides

- pH sensitivity less than for physical adsorption

Minteq Modeling

Silica removal

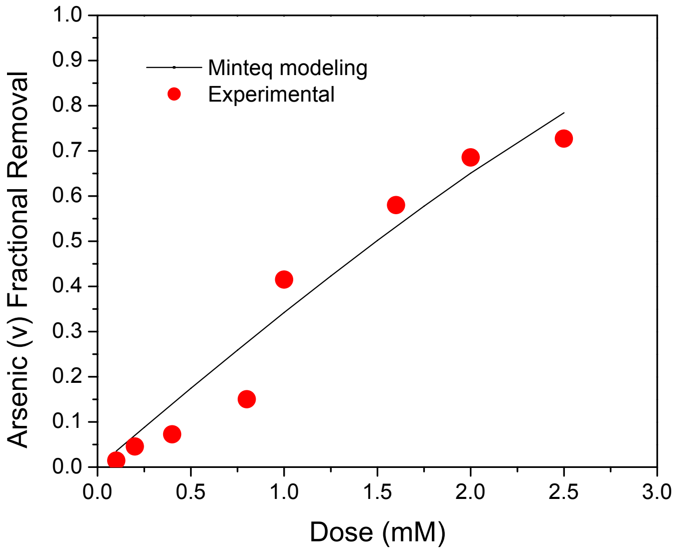
(initial concentration: 1.8 mM)



Site density: 6 sites/nm^2

Arsenic (v) removal

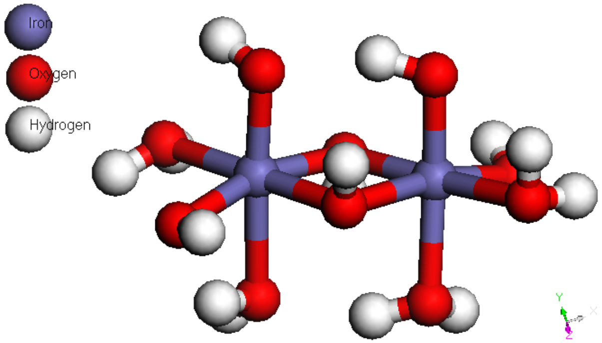
(initial concentration: 1.8 mM)

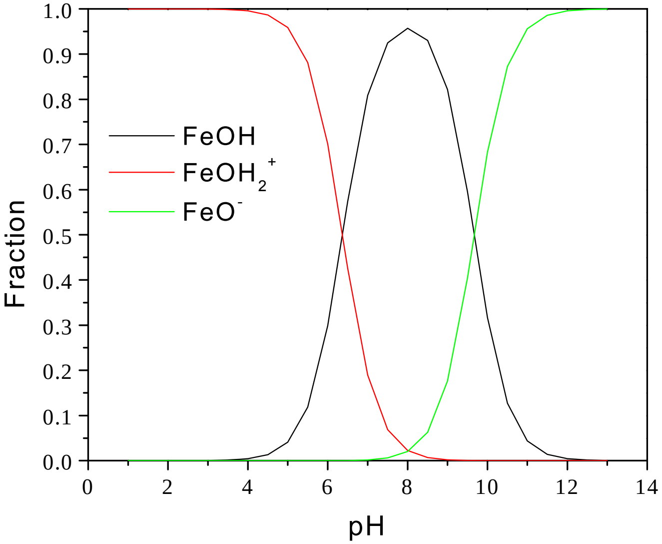


Site density: 13 sites/nm^2

- Model: Ferrihydrite triple plane model from Minteq database. Specific Surface Area: 750 m^2/g; inner capacitance: 1.3 F/m^2; outer capacitance: 5 F/m$^{2.}$
- Site density need to be adjusted to fit the experimental data for silica and arsenate removal.

Quantum Chemistry Modeling of Oxyanion Removal: Protonation of Binding Sites as a Function of pH



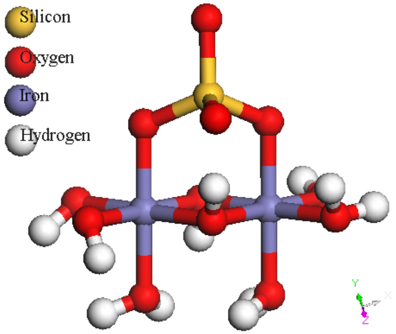


$$FeOH + H^+ \rightleftarrows FeOH_2^+ \qquad K_{a1} = 10^{-6.37}$$

$$FeOH \rightleftarrows FeO^- + H^+ \qquad K_{a2} = 10^{-9.67}$$

From quantum chemistry calculation: ΔG_f for FeOH, $FeOH_2^+$ and FeO^- are -415.72, -424.41, -402.52 kcal/mol, respectively.

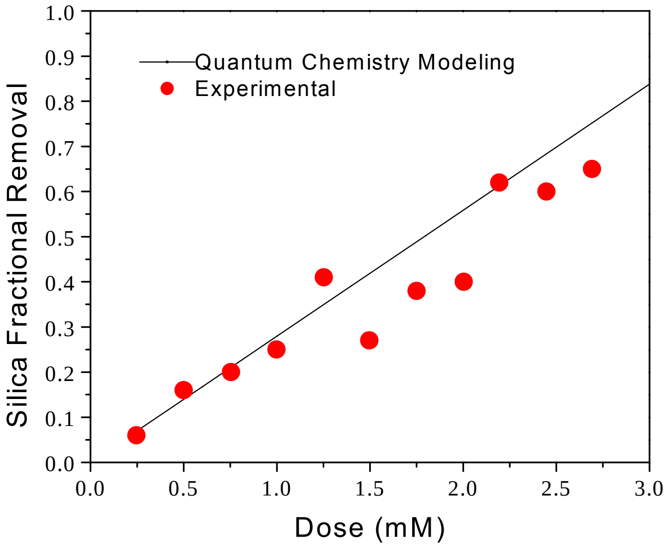
Quantum Chemistry Modeling of Oxyanion Removal



$$2(\equiv FeOH) + H_4SiO_4 + H^+ \leftrightarrow \equiv Fe_2H_3SiO_4^+ + 2H_2O$$

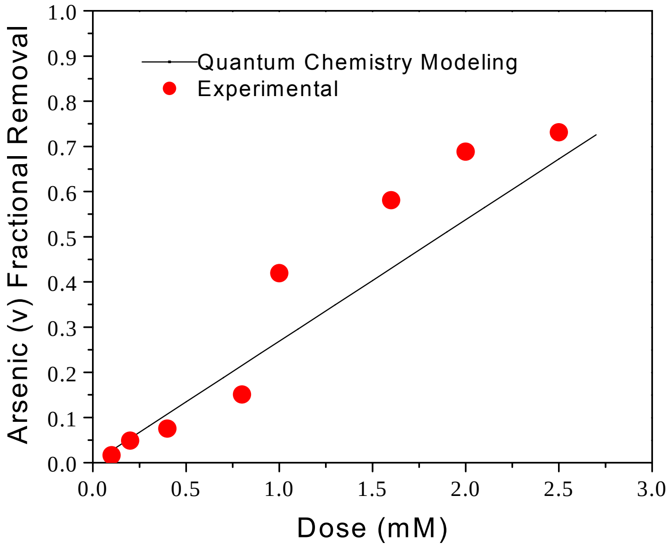
Silica removal

(initial concentration: 1.8 mM)



Arsenic (v) removal

(initial concentration: 1.8 mM)



No other parameters need to be adjusted to fit the experimental data for silica and arsenate removal

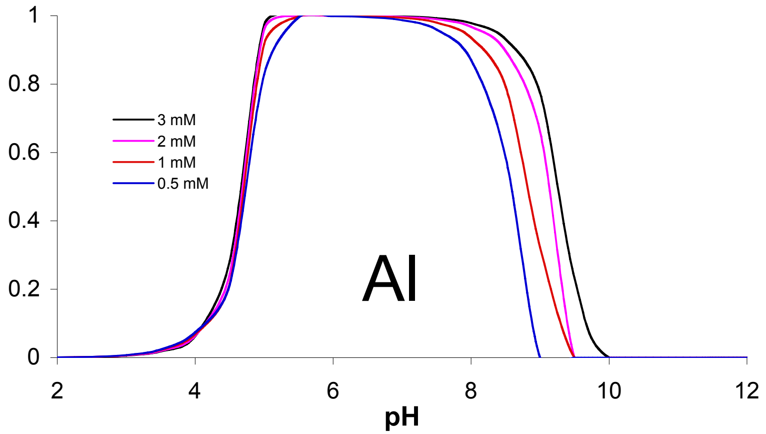
Contaminant Removal Experiments: Parameters to Consider

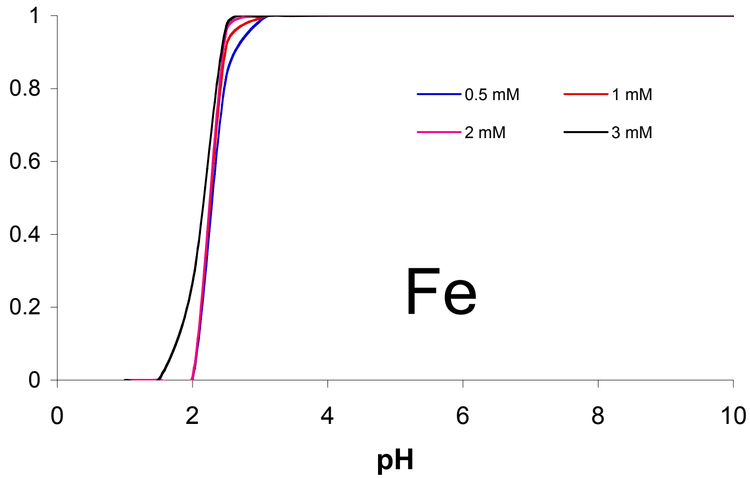
Operational variables that may affect EC performance are:

- Coagulant dose and type (e.g. Al vs. Fe)
- pH value (5-7-9; CTB 7.5-8.0; ROR 7.8-8.2)
- Post EC clarification or filtration method
- Organic compound concentrations (CTB additives)
- Solution ionic strength
- Hydraulic residence time (rate of dosing)
- Degree of mixing
- Scale of the EC reactor (1 L/min vs. 20 L/min)

Precipitate Stability Range

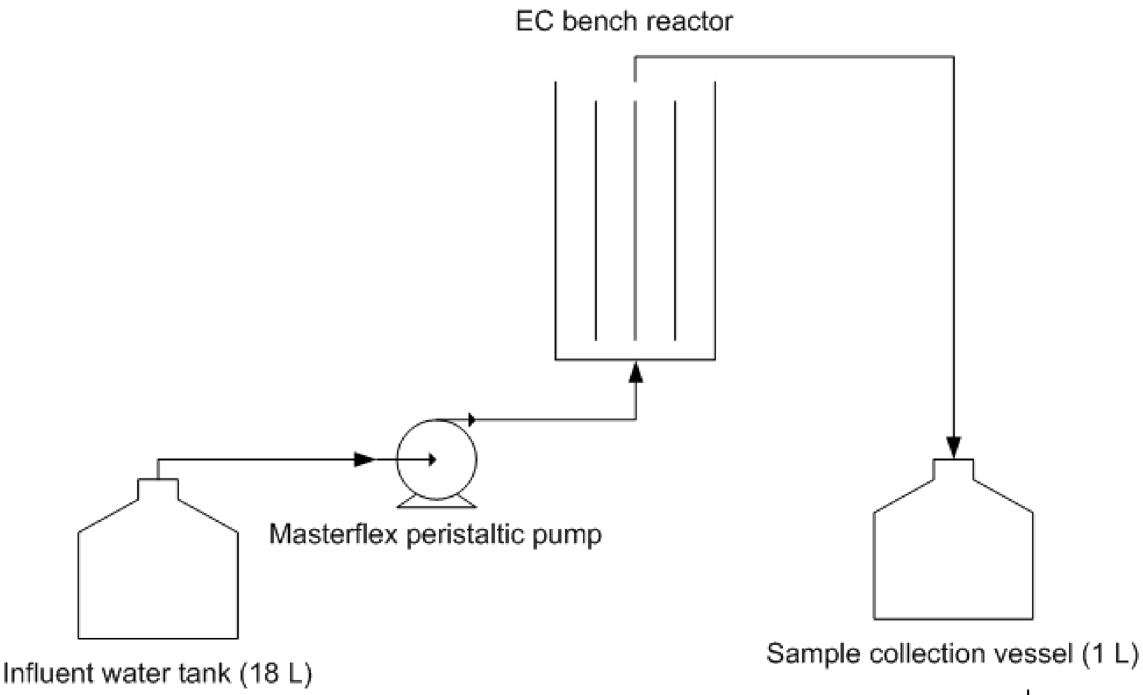
Fraction of total Al or Fe that precipitates as a function of pH for total metal doses of 0.5, 1, 2 and 3 mM

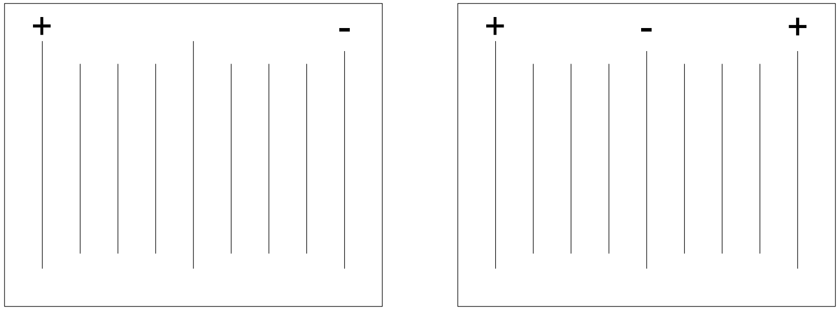




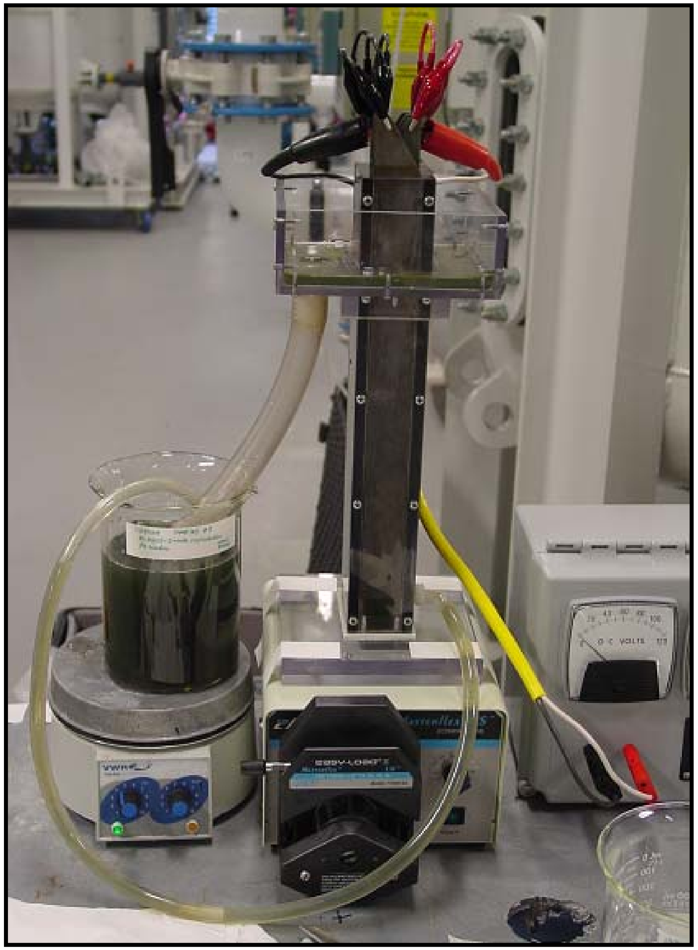
- Ideal Al pH range: 5.8 to 7.8
- Ideal Fe pH range: > 4

Bench Tests: 1 L/min EC Device





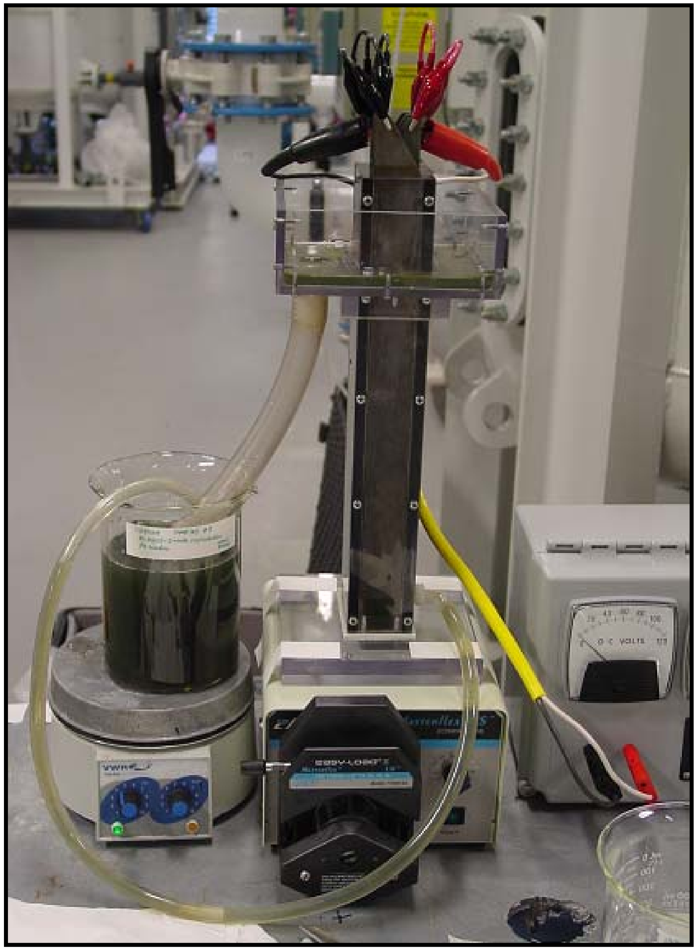
(a) (b)



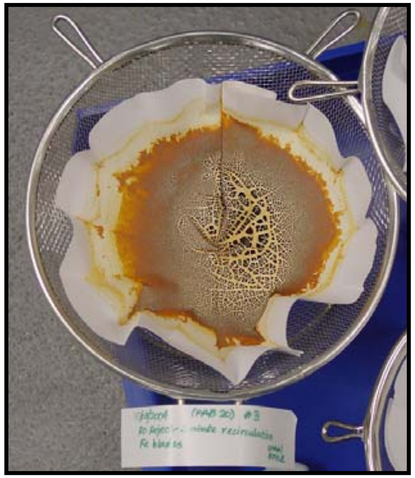
effluent gravity-settled or filtered (0.45μm, 0.8μm, 10μm)

Bench Tests: 1 L/min EC Device

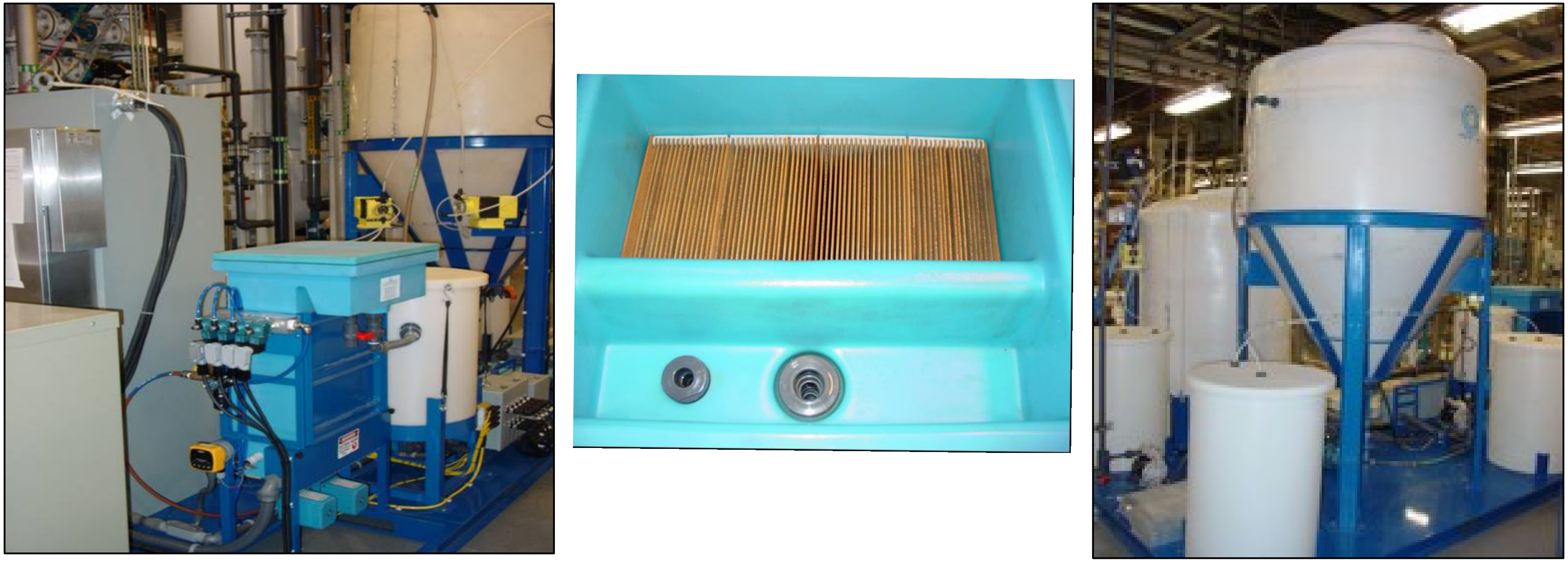
- Working electrode dimensions: 3.178 cm × 34.04 cm
- Space between electrodes: 0.4 cm
- Nominal† electrode thickness: 0.318 cm
- Working volume: 0.35 L
- Applied current: 0.1–0.8 A
- Volumetric flow rate: 0.35 LPM
- Residence time: 60 sec
- Number of electrodes/channels: 9/8

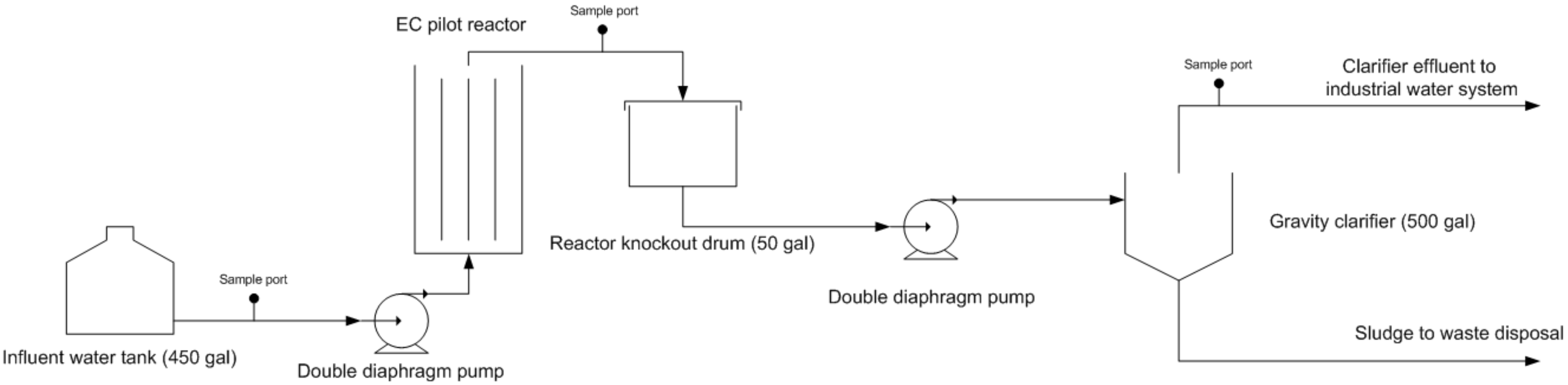


effluent gravity-settled or filtered (0.45μm, 0.8μm, 10μm)



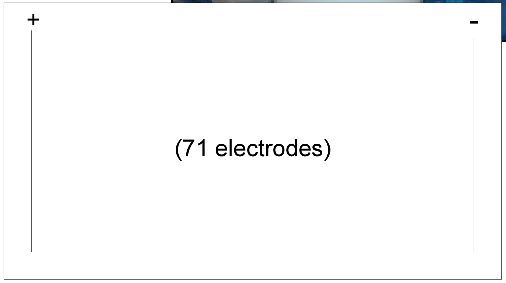
20 L/min Pilot (Intel site @ Ronler Acres,OR)



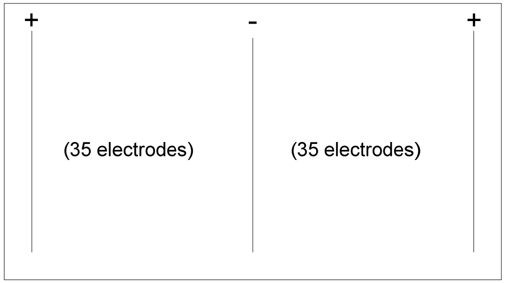


20 L/min Pilot (Intel site @ Ronler Acres,OR)

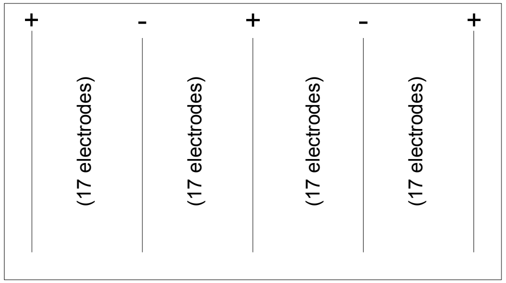
- Working electrode dimensions: 20.3 cm × 50.8 cm
- Space between electrodes: 0.4 cm
- Nominal† electrode thickness: 0.318 cm
- Working volume: 22.7 L
- Applied current: 1.0–16.0 A
- Volumetric flow rate: 11.35/18.92 LPM
- Residence time: 72 or 120 sec
- Number of electrodes/channels: 73/72



(a)

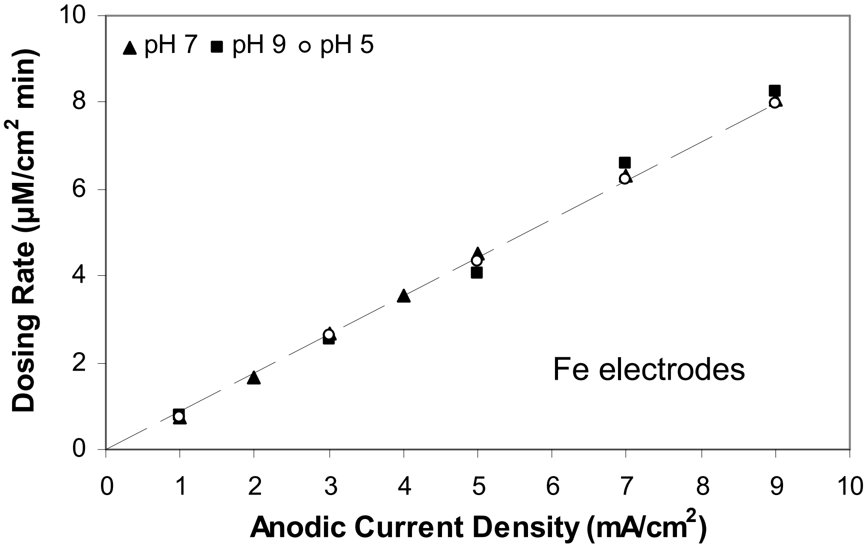


(b)



(c)

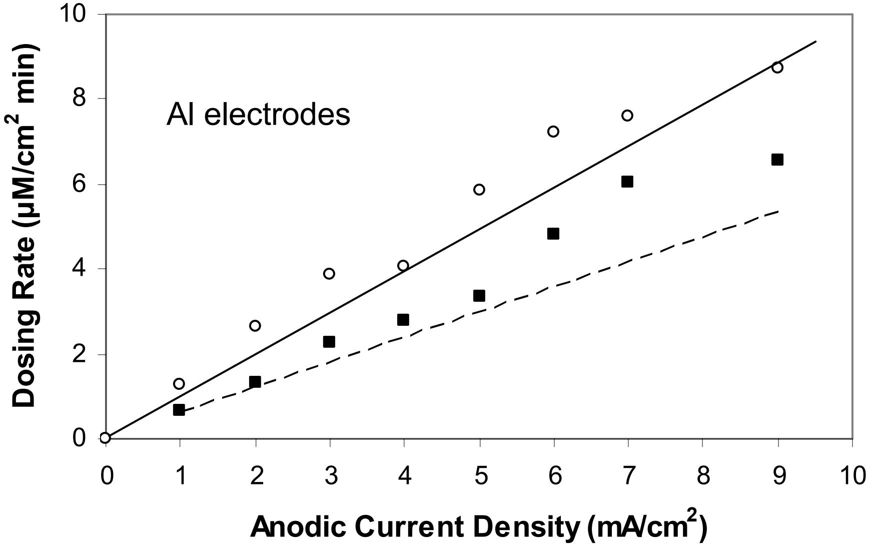
Dosing Tests



Dissolution rate of iron as a function of anodic current density using weight loss measurement under pH values of 5, 7 and 9.

- Primary anodic reaction is metal dissolution.
- Negligible O_2 evolution.
- Results from these tests indicate that dose can be controlled by the current.
- Results can be used to set desired dosing rates in pilot and larger units.

Dissolution rate of aluminum (square: anode; circle: anode + cathode) as a function of anodic current density using weight loss measurement.



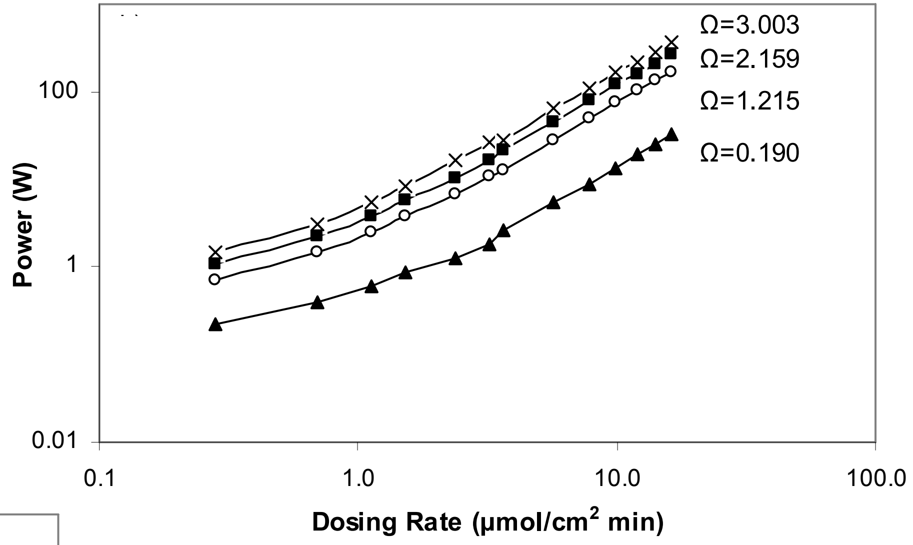
anodic current density = (current) / (electrode area)

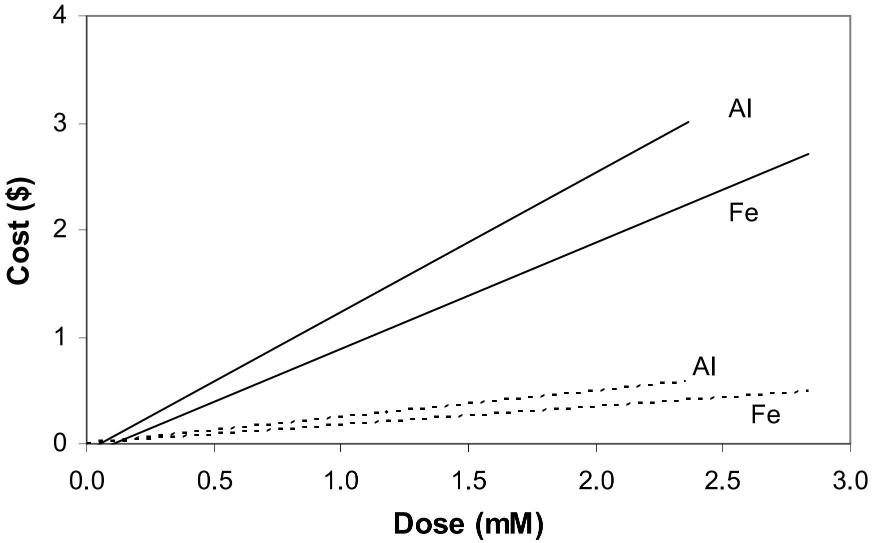
dose = (dose rate) x (electrode area) x (hydraulic detention time)

Power and Cost per Unit Dose of Coagulant

Power consumption (logarithmic) as a function of dosing rate (logarithmic) at different Ω for iron electrodes.

$$\Omega = \frac{\text{electrode spacing (cm)}}{\text{solution conductivity (mS/cm)}}\left[\frac{\text{V cm}^2}{\text{mA}}\right]$$

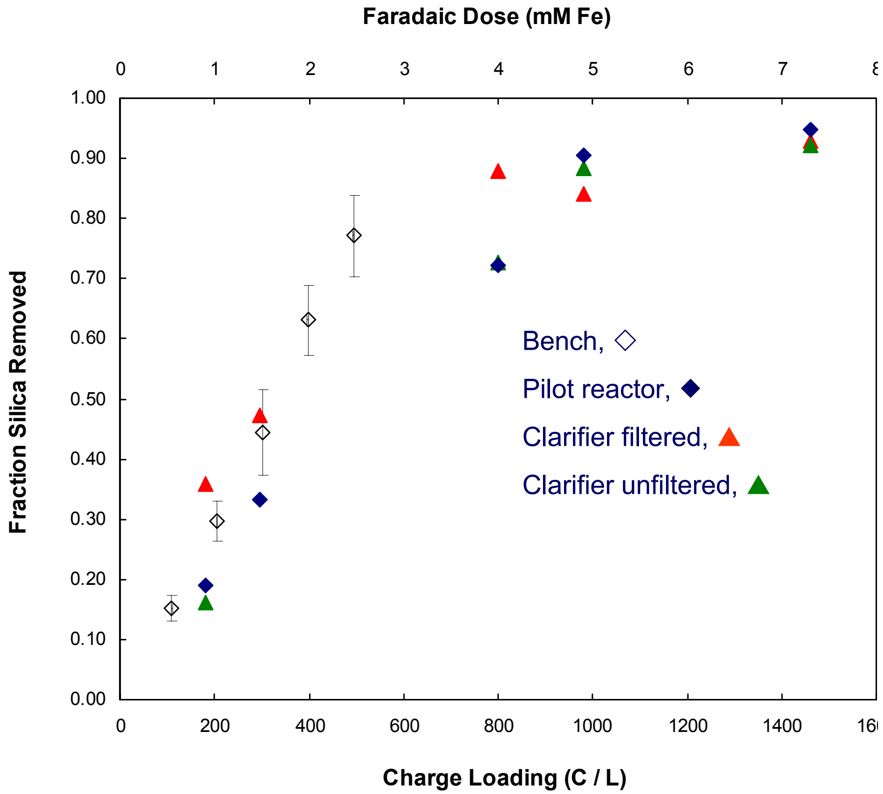




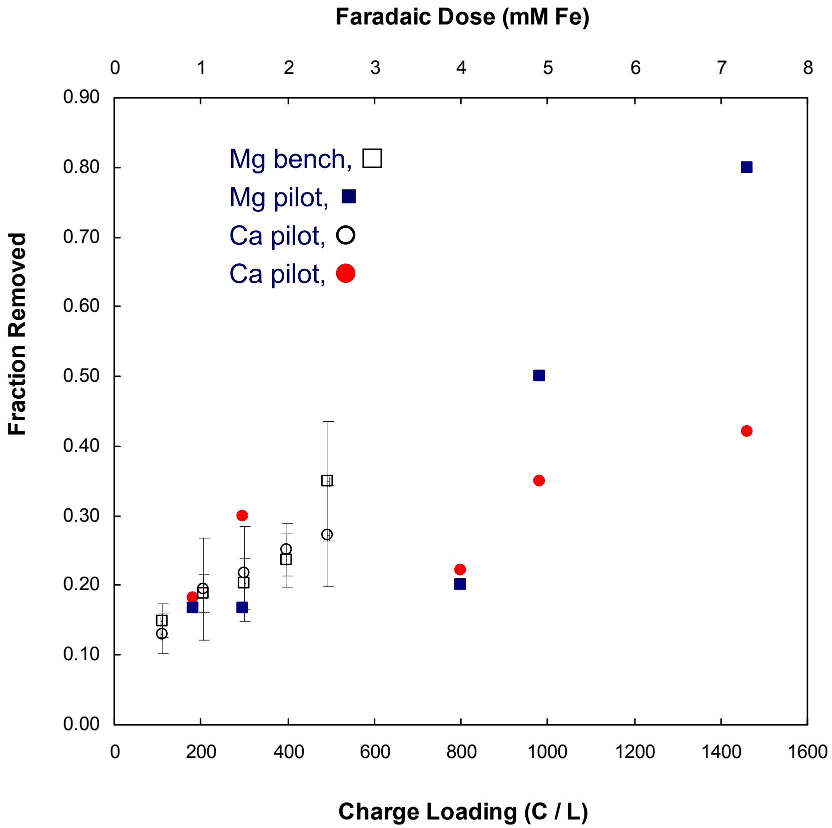
Electrode cost (dashed line) and total operation cost to treat 1000 gallon of water using electrocoagulation as a function of dose using aluminum or iron electrodes (energy: \$0.1/kWh; aluminum: \$2.40/kg; iron: \$0.80/kg).

- Power requirements are dominated by Ohmic losses in solution.
- Lower power requirement for Fe versus Al at a fixed Ω.

Fe Dose Response: Pilot vs. Bench



Silica removal from CTB

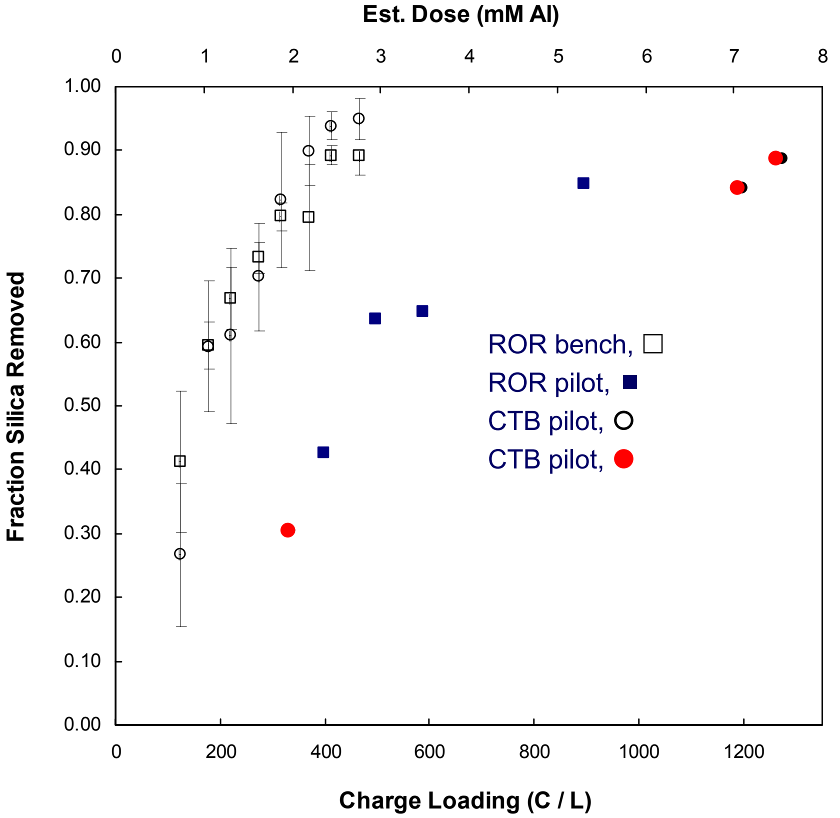


Ca, Mg removal from CTB

- Agreement between results in bench and pilot units on CTB w/ Fe
- Implication is that scale-up can be based on dose (bench ~60x bigger)
- Ca, Mg removal is but 10 to 30% at economically feasible doses

Al Dose Response: Pilot vs. Bench

Silica removal from CTB and ROR



cathode fouling in pilot unit

- Fouling of cathodic surfaces encountered
- Aluminosilicates?

Summary

- Oxyanions are cost effectively removed by Al or Fe electrodes; we have examined the removal of silica, phosphate and arsenic and obtained >90% removal
- Effective coagulant dose levels are on the order of 1-3 mM for the waters tested
- Hardness cations can be removed by anodically generated iron and aluminum hydroxide precipitates, but typically the dose levels required are not economically justified
- Scale-up from bench to pilot EC units can be predicated on Fe-dose for the waters studied; severe fouling was encountered w/ Al electrodes
- Currently, we are developing electrochemical methods for hardness ion removal (ELIXR)

Acknowledgements

Intel - Allen Boyce, Avi Fuerst, Zoe Georgousis, Len Drago

U of A - Matt Schulz, Zheng Gu, Lily Liao, Aaron Solt, Jake Davis, Brian Weaver
Ritika Mohan, Brian Chaplin

ASU - John Crittenden, Yongshon Chen, Steven Whitten

AWI - Chuck Graf

Quantum Chemistry Calculations

- Density functional theory (DFT) calculations performed using DMOL^3 code from Accelrys.
- Unrestricted GGA calculations using VWN-BP functionals.
- All electron calculations performed with double-numeric with polarization (DNP/DMOL3) basis sets.
- Solvation effects incorporated using the COSMO-ibs polarized continuum model.

Compositions of streams (mM)

	CTB	ROR	UA Synthetic
pH	7.5-8.0	7.8-8.2	7-8
Silica	1.42-1.78	2.31-2.67	1.80
Calcium	0.42-0.57	0.75-0.87	0.99
Magnesium	0.16-0.25	0.33-0.49	0.49

EC versus Conventional Coagulation

- Chemical coagulation uses alum or ferric chloride salts
  - Alum typically sold as $KAl(SO_4)_2 \cdot 12(H_2O)$
  - Ferric chloride typically sold as $FeCl_3 \cdot 6(H_2O)$
- Alum and ferric chloride contribute salinity increasing counter-ions
  - 8.57 g of undesired solids per g of aluminum in potassium alum
  - 1.91 g of undesired solids per g of iron in ferric chloride
  - **EC adds no undesirable counter-ions**
- Alum and ferric chloride contain very little coagulant on a per mass basis
  - 114 lbs of aluminum per ton of alum
  - 413 lbs of iron per ton of ferric chloride
  - **EC yields one lb of coagulant per lb of electrode**
- Formation of precipitates from Fe and Al salts decreases pH values
  - 2 mM dose of Fe drops pH by 1.5 units
  - 2 mM dose of Al drops pH by 3 units
- Post coagulation pH adjustments are needed with Al and Fe salts
  - **Post coagulation pH adjustments are not needed with EC**