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CEE 680: Water Chemistry

Lecture #53

Redox Chemistry: Arsenic II, Geochemistry

(Stumm & Morgan, Chapt.8)

Benjamin; Chapter 9

Arsenic Geology

- 20th in Abundance in Earth's Crust
- Typically Associated with Igneous or Sedimentary Rocks
  - Arsenic Concentrations Tend to be High in Igneous Rocks Containing Iron Oxides
- Often Associated with Sulfidic Ores

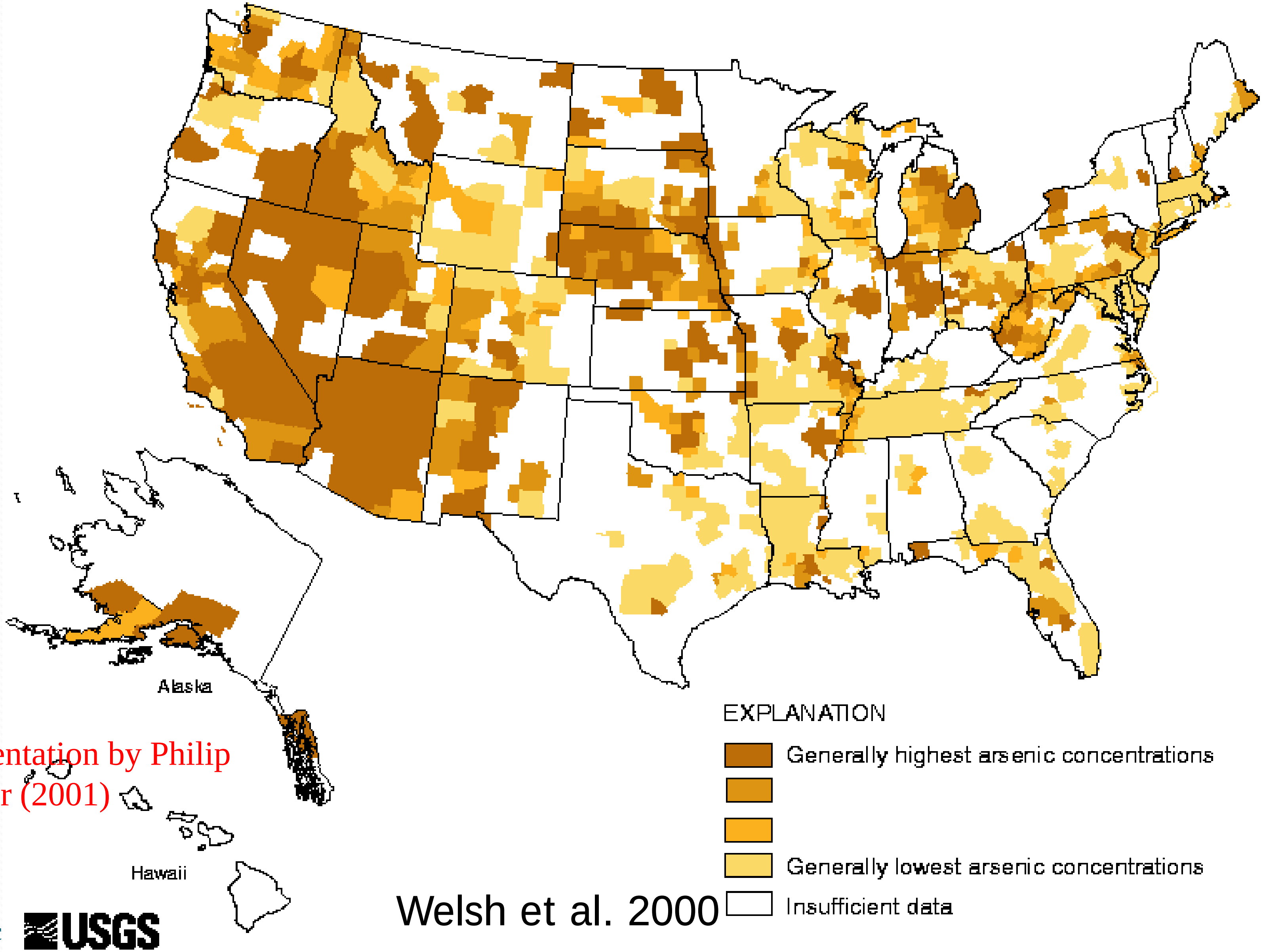
From presentation by Philip Brandhuber (2001)

Geology (cont.)

- Approximately 245 Arsenic Bearing Minerals have been Identified
- Some Common Arsenic Bearing Minerals
  - Realgar (AsS)
  - Orpinent (As_2O_3)
  - Arsenopyrite (FeAsS)
  - Scorodite ($FeAsO_4 \cdot H_2O$)

From presentation by Philip Brandhuber (2001)

National Distribution of Arsenic in Groundwater



From presentation by Philip Brandhuber (2001)

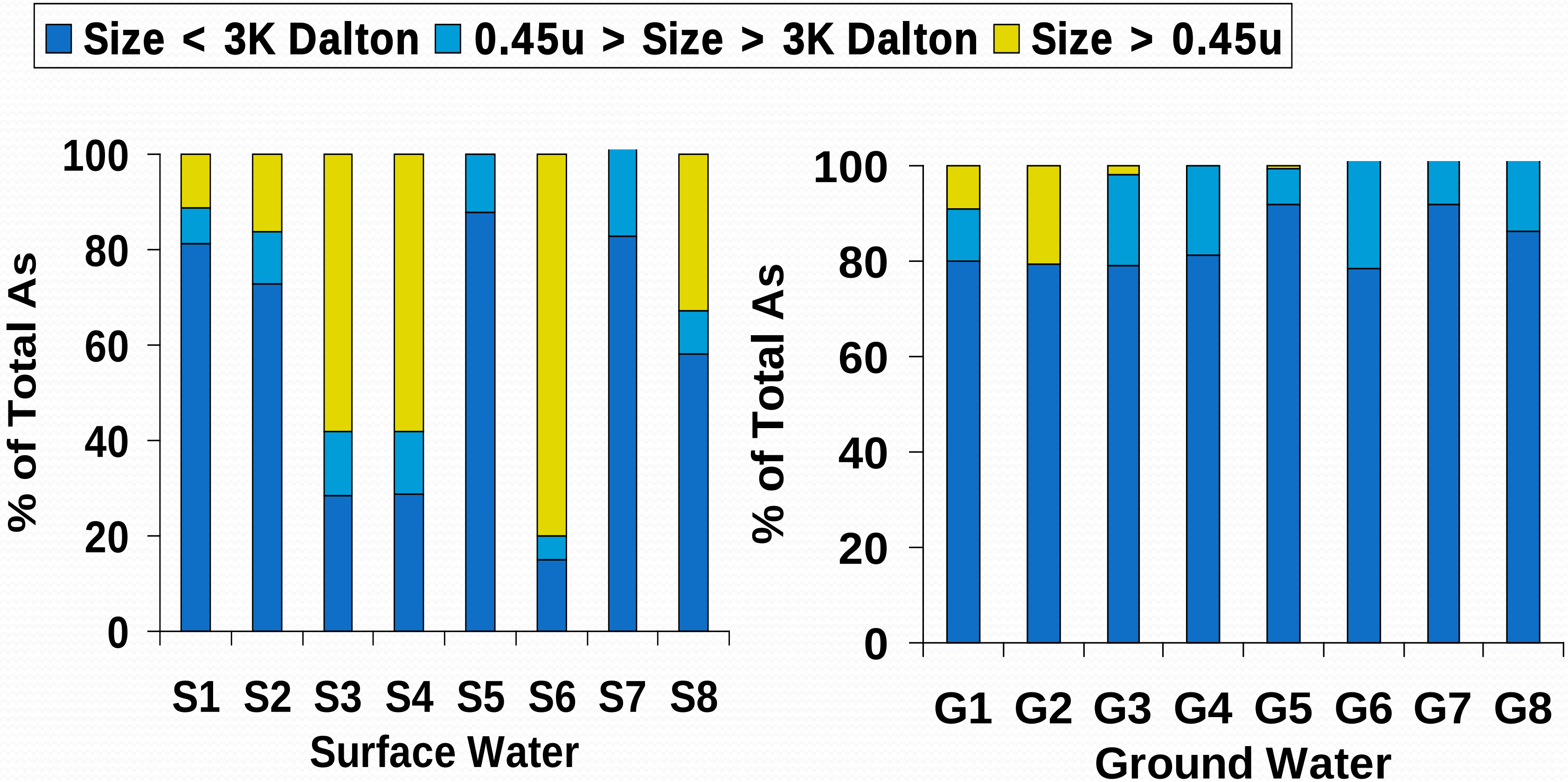
Welsh et al. 2000

Arsenic Mobility

- Theoretically As(III) tends to be more Mobile than As(V)
  - As(V) will Strongly Sorb to Iron Oxides
  - To a lesser Extent, As(V) will Sorb to Manganese Oxides
- However, As(VI) Associated with Iron Oxides may be Transported (Colloidal As)
- Changes in Redox Conditions may Mobilize Arsenic

From presentation by Philip Brandhuber (2001)

Arsenic Size Distribution



From presentation by Philip Brandhuber (2001)

Reference: Brandhuber and Amy 1998

Equilibrium constants used in the computer modeling

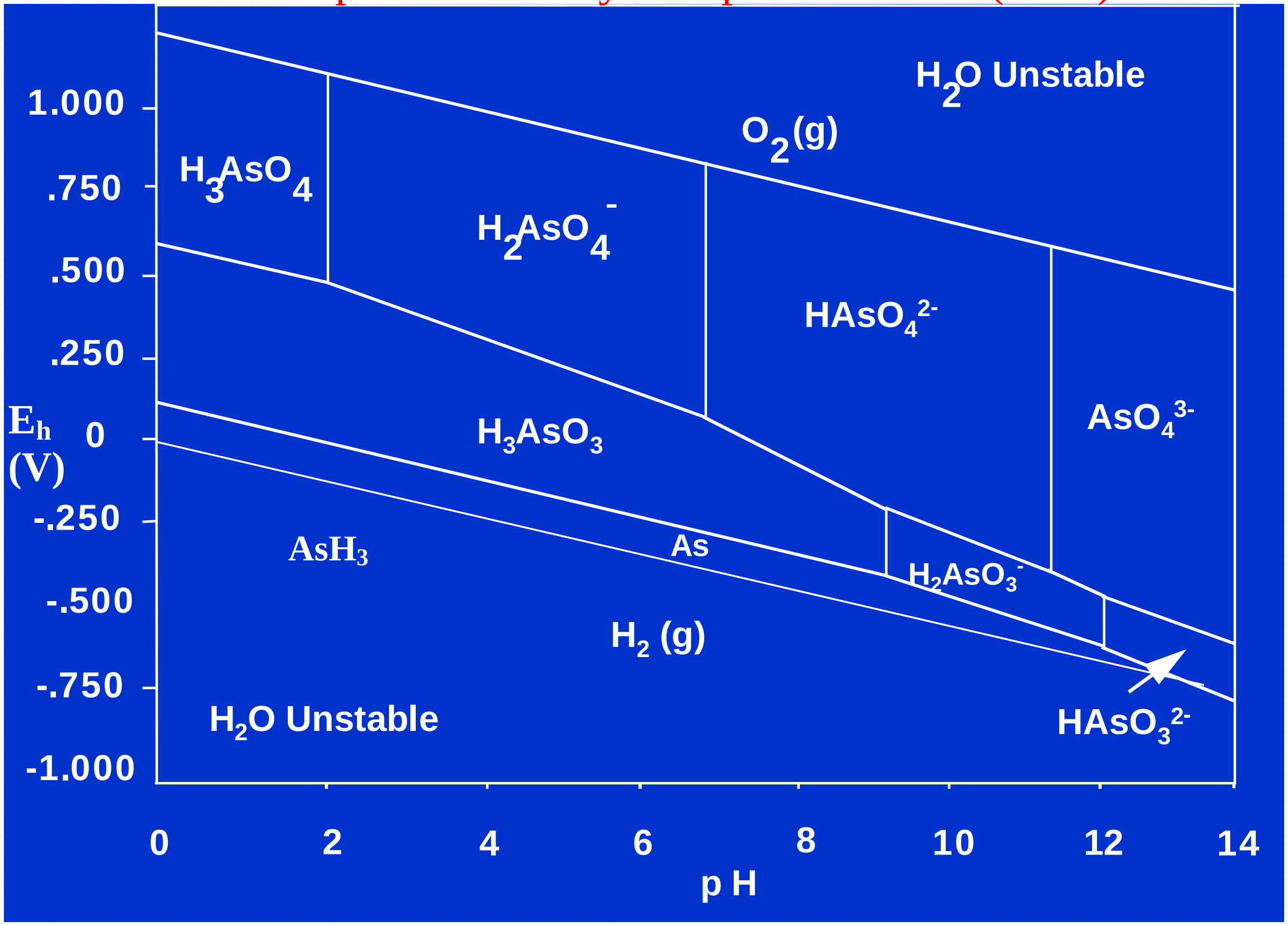
Acid-Base Reactions	log K
$AsO_4^{3-} + H^+ = HAsO_4^{2-}$	11.60
$AsO_4^{3-} + 2H^+ = H_2AsO_4^-$	18.35
$AsO_4^{3-} + 3H^+ = H_3AsO_4$	20.60
$AsO_3^{3-} + H^+ = HAsO_3^{2-}$	13.41
$AsO_3^{3-} + 2H^+ = H_2AsO_3^-$	25.52
$AsO_3^{3-} + 3H^+ = H_3AsO_3$	34.74

Surface Reactions (Intrinsic Adsorption Constants)	$\log K^{int}$
$\equiv Fe^{w,s}OH + H^+ = \equiv Fe^{w,s}OH_2^+$	7.29
$\equiv Fe^{w,s}OH = \equiv Fe^{w,s}O^- + H^+$	–8.93
$\equiv Fe^{w}OH + Ca^{2+} = \equiv Fe^{w}OCa^+ + H^+$	–5.85
$\equiv Fe^{s}OH + Ca^{2+} = \equiv Fe^{s}OHCa^{2+}$	4.97
$\equiv Fe^{w,s}OH + SO_4^{2-} + H^+ = \equiv Fe^{w,s}SO_4^- + H_2O$	7.78
$\equiv Fe^{w,s}OH + SO_4^{2-} = \equiv Fe^{w,s}OHSO_4^{2-}$	0.79
$\equiv Fe^{w,s}OH + PO_4^{3-} + 3H^+ = \equiv Fe^{w,s}H_2PO_4 + H_2O$	31.29
$\equiv Fe^{w,s}OH + PO_4^{3-} + 2H^+ = \equiv Fe^{w,s}HPO_4^- + H_2O$	25.39
$\equiv Fe^{w,s}OH + PO_4^{3-} + H^+ = \equiv Fe^{w,s}PO_4^{2-}$	17.72
$\equiv Fe^{w,s}OH + AsO_4^{3-} + 3H^+ = \equiv Fe^{w,s}H_2AsO_4 + H_2O$	29.31
$\equiv Fe^{w,s}OH + AsO_4^{3-} + 2H^+ = \equiv Fe^{w,s}HAsO_4^- + H_2O$	23.51
$\equiv Fe^{w,s}OH + AsO_4^{3-} = \equiv Fe^{w,s}OHAsO_4^{3-}$	10.58
$\equiv Fe^{w,s}OH + AsO_3^{3-} + 3H^+ = \equiv Fe^{w,s}H_2AsO_3 + H_2O$	40.20

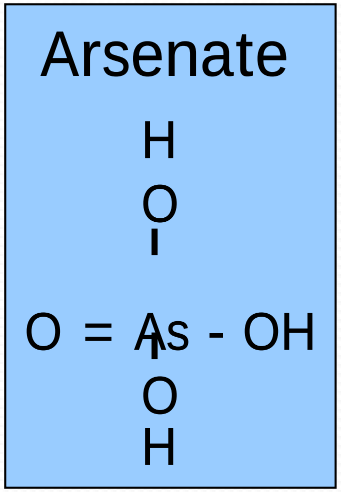
From: Hering & Elimelech, 1996; AWWARF Report

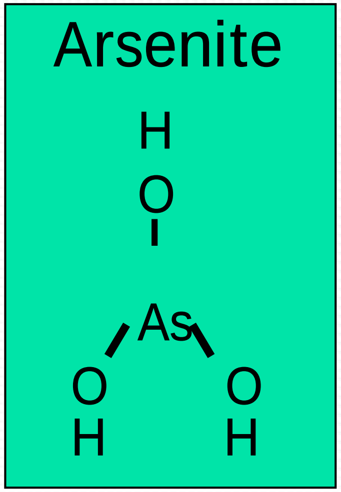
Arsenic E_h - pH Diagram in Pure Water

From presentation by Philip Brandhuber (2001)



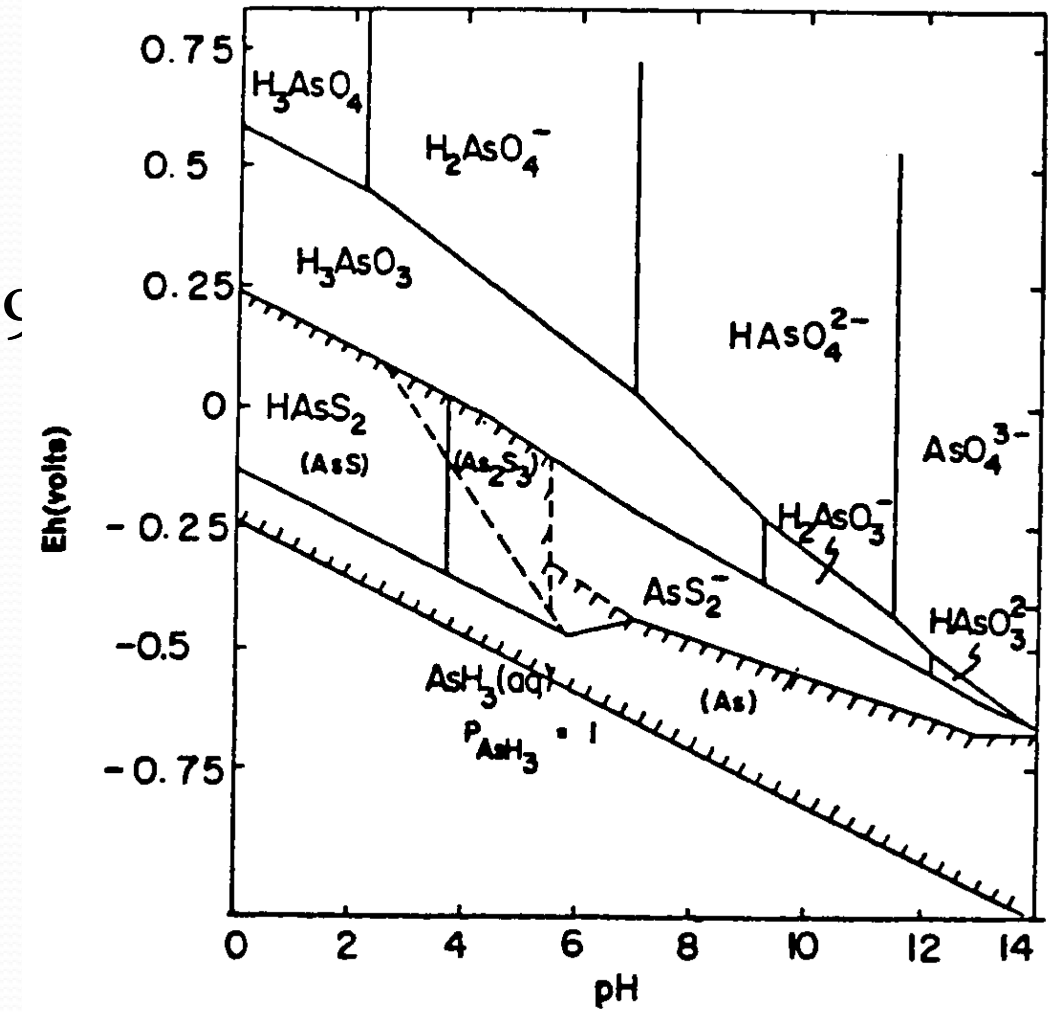
Reference: Ferguson and Garvis (1972)





As and S

- Ferguson & Gavis, 1972 [Wat. Res. 6:1259
  - $As_T = 10^{-5}$ M
  - $S_T = 10^{-3}$ M
  - Solids in ()



From: Evangelou, 1998, Environmental Soil and Water Chemistry, Wily Publ.

Regulatory Dates I

- 1942, Public Health Service Establishes 50 ppb Standard
- 1975, EPA formalizes 50 ppb Standard
- 1989, EPA misses the First of Several Deadlines for Revising Rule
- June 22, 2000, EPA Proposes MCL of 5 ppb
- January 22, 2001, EPA Publishes Final Rule, MCL of 10 ppb

From presentation by Philip Brandhuber (2001)

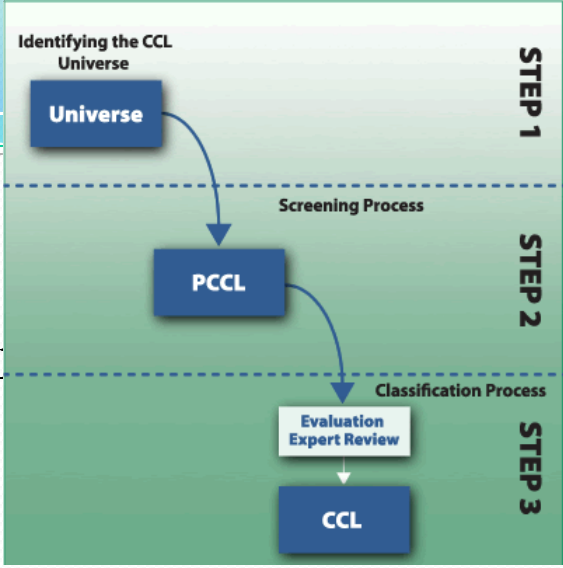
Regulatory Dates II

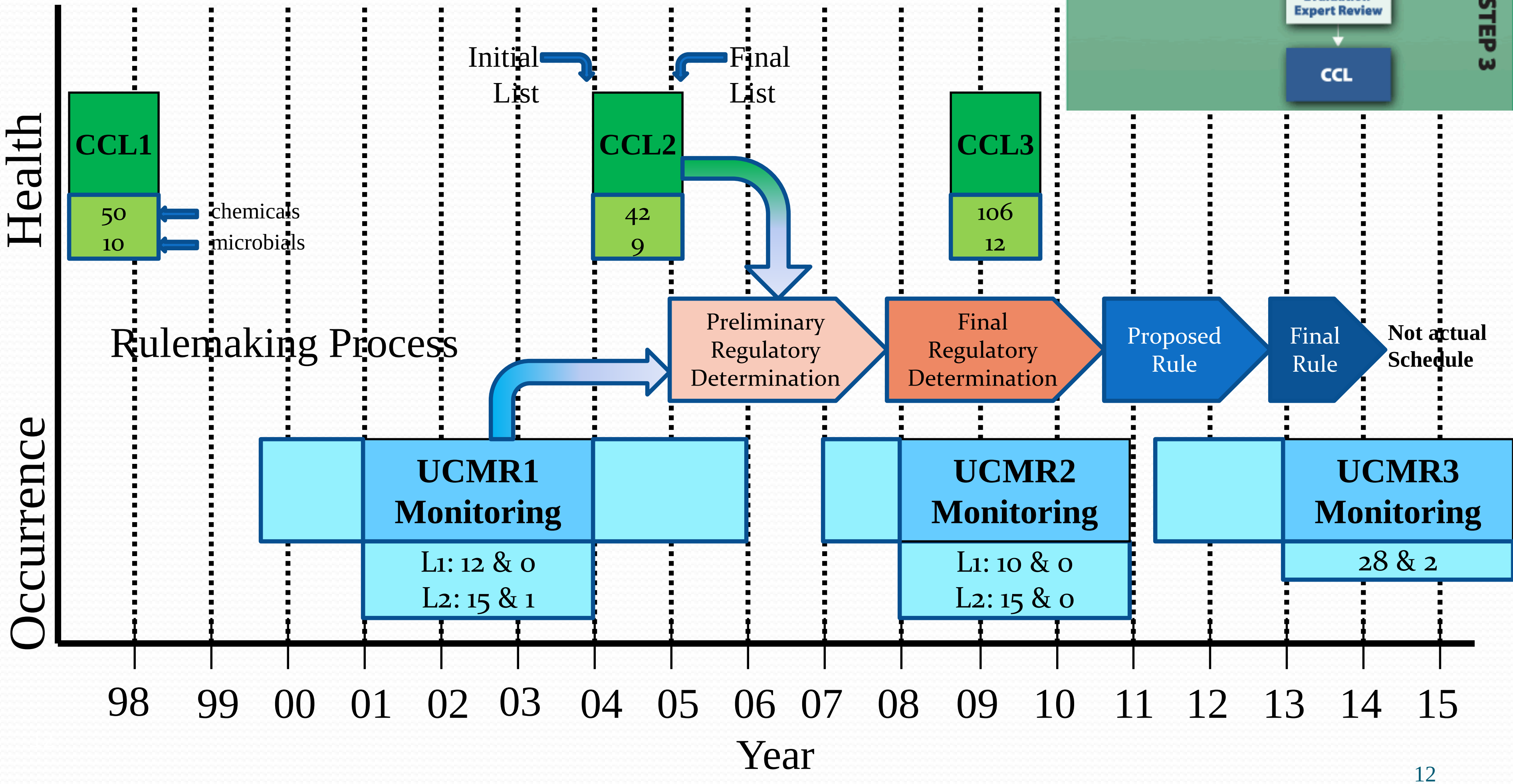
- March 20, 2001, EPA Announces it will "Reassess" Costs and Scientific Issues, Delay Rule 60 Days
- April 23, 2001, EPA Announces Additional Delay of Nine Months
- May 22, 2001, EPA Announces Delay Until February 22, 2002
- July 19, 2001, EPA Request Comment on MCL's of 20, 5 and 3 as Alternative to 10 ppb
- October 31, 2001, EPA announces that As standard will be 10 ppb (effective 2006?)

From presentations by Brandhuber (2001) & Kempic (2001)

New regulated contaminants

- UCMR: 12 months of sampling within w





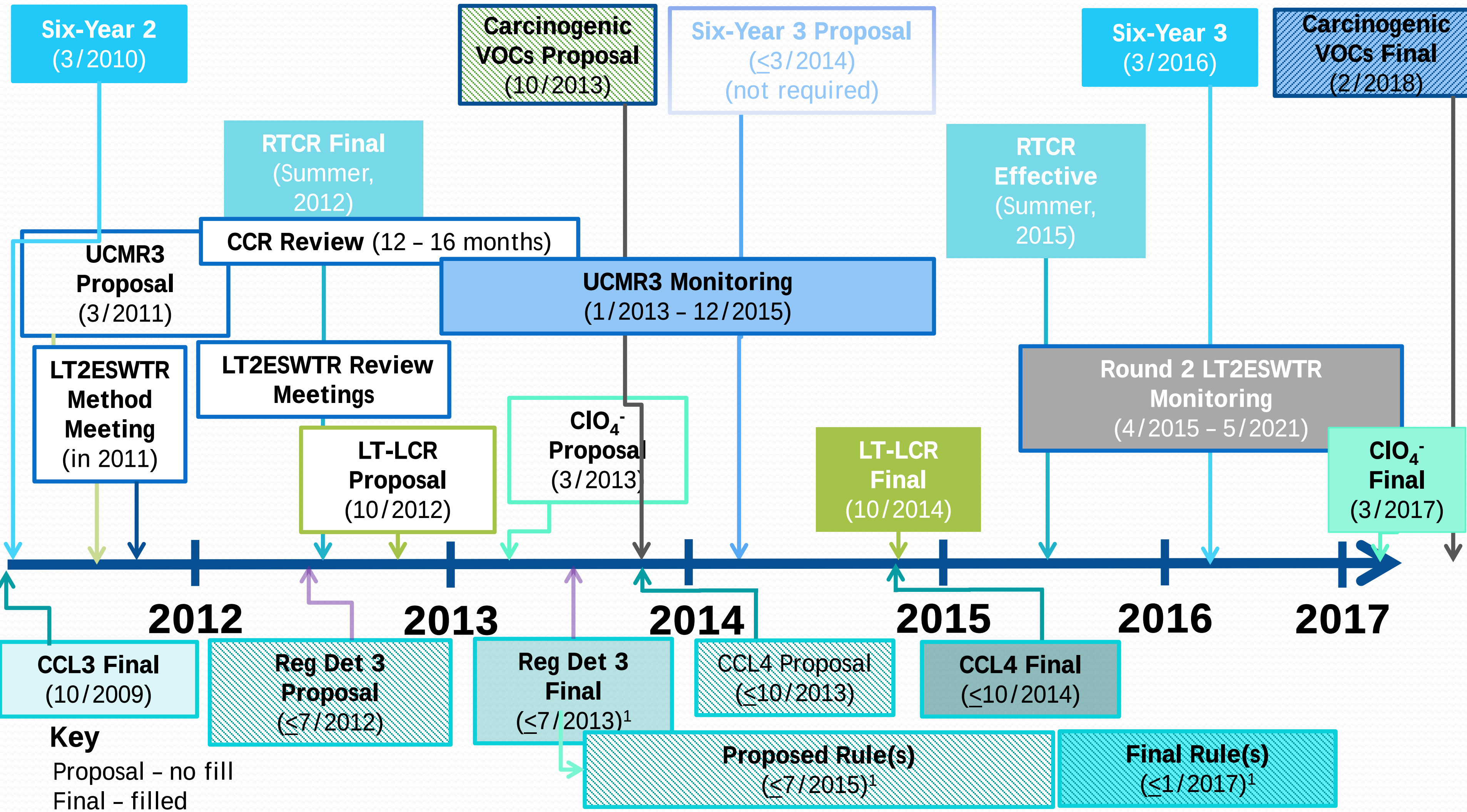
Other new or revised rules expected

- Revised TCR
  - *E. coli* in; fecal coliforms out <5% positive for TC as before
  - Published: Feb 13, 2013 with Apr 1, 2016 effective date
    - http://water.epa.gov/lawsregs/rulesregs/sdwa/tcr/regulation_revisions.cfm
- Revised Pb/Cu Rule
  - New site selection criteria & sampling procedures
    - no flushing or removal or aerators
  - Same 0.015 mg/L & 1.3 mg/L action levels (in 10% of samples)

Revised LCR: not before 2020

- Perchlorate (ClO_4^-)
  - Peer review in 1/2017; Proposed rule is delayed
    - States: MA @ 2μg/L; CA @6μg/L; others advisory @1-18μg/L
- Chlorate (ClO_3^-)
  - Could be a problem for on-site hypochlorite generation (Stanford, 2014)
- Hexavalent Chromium
  - Currently regulated as total Cr
  - Likely carcinogen: Final health assessment: end of 2011
  - Late addition to UCMR 3 (2013-2015)

A “simple” view of what’s happening

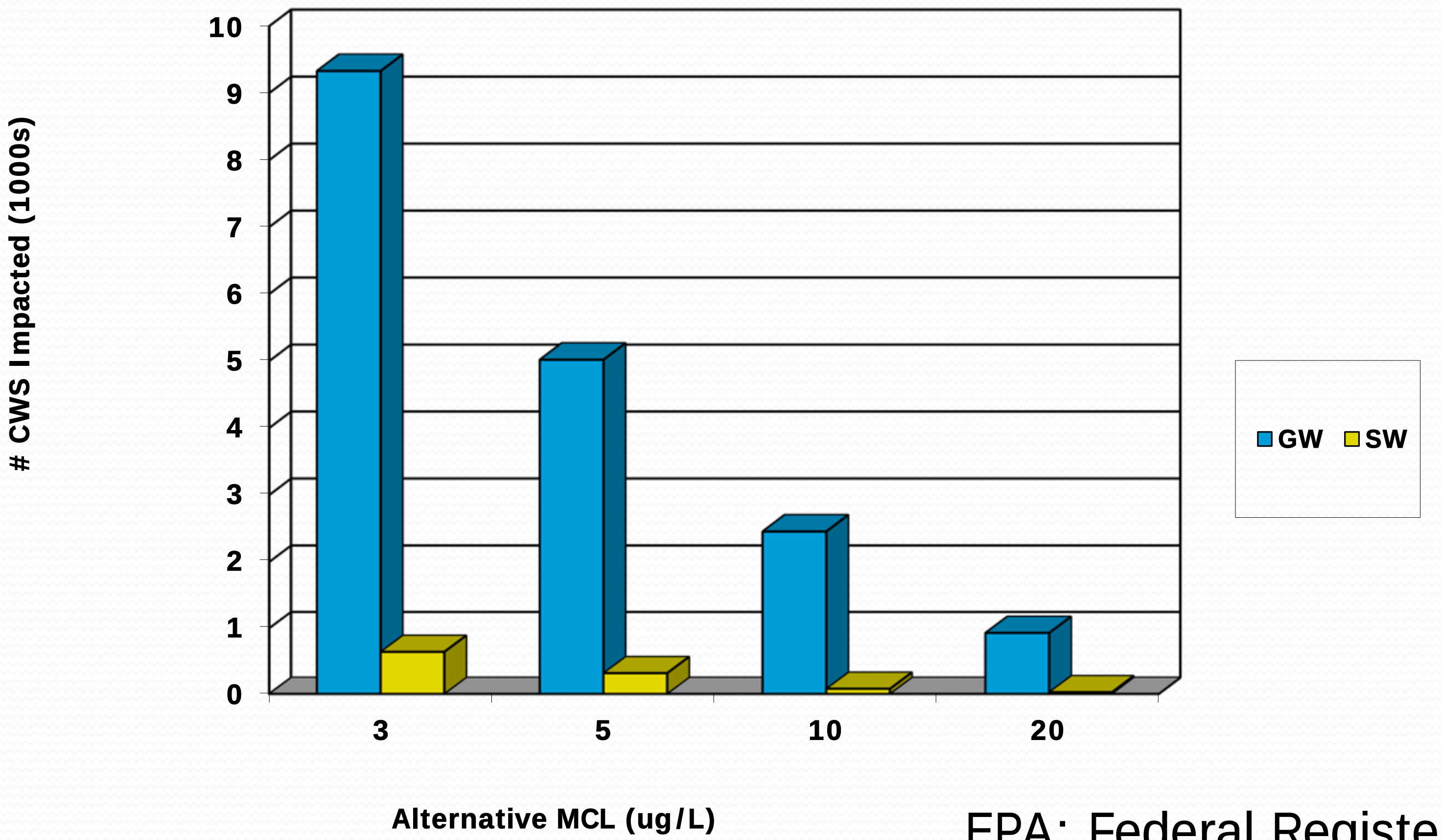


Key
Proposal – no fill
Final – filled
Uncertain – cross hatched
Unique color for related regulatory actions

Note: As yet unassigned (fluoride, acrylamide, epichlorohydrin, total chromium / Cr(VI))

Modified from: Steve Via, AWWA

Impact to Utilities, Alternative MCL's



EPA: Federal Register 65(121):38888

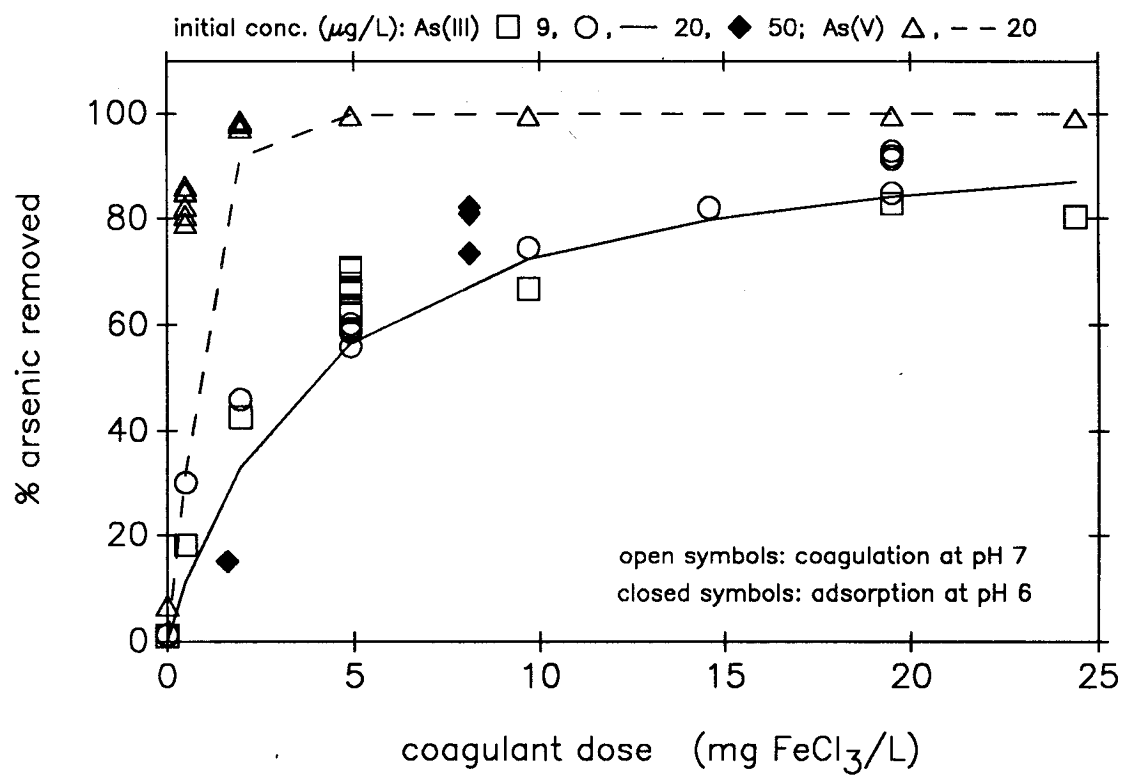
From presentation by Philip Brandhuber (2001)

- Key Features of Arsenic's Chemistry in Water
  - Present in two Oxidation States
  - Behaves as an Acid
- Arsenate (As(V))
  - H_3AsO_4 => $H_2AsO_4^-$ => $HAsO_4^{2-}$ => AsO_4^{3-}
- Arsenite (As(III))
  - H_3AsO_3 => $H_2AsO_3^-$ => $HAsO_3^{2-}$

From presentation by Philip Brandhuber (2001)

Coagulation

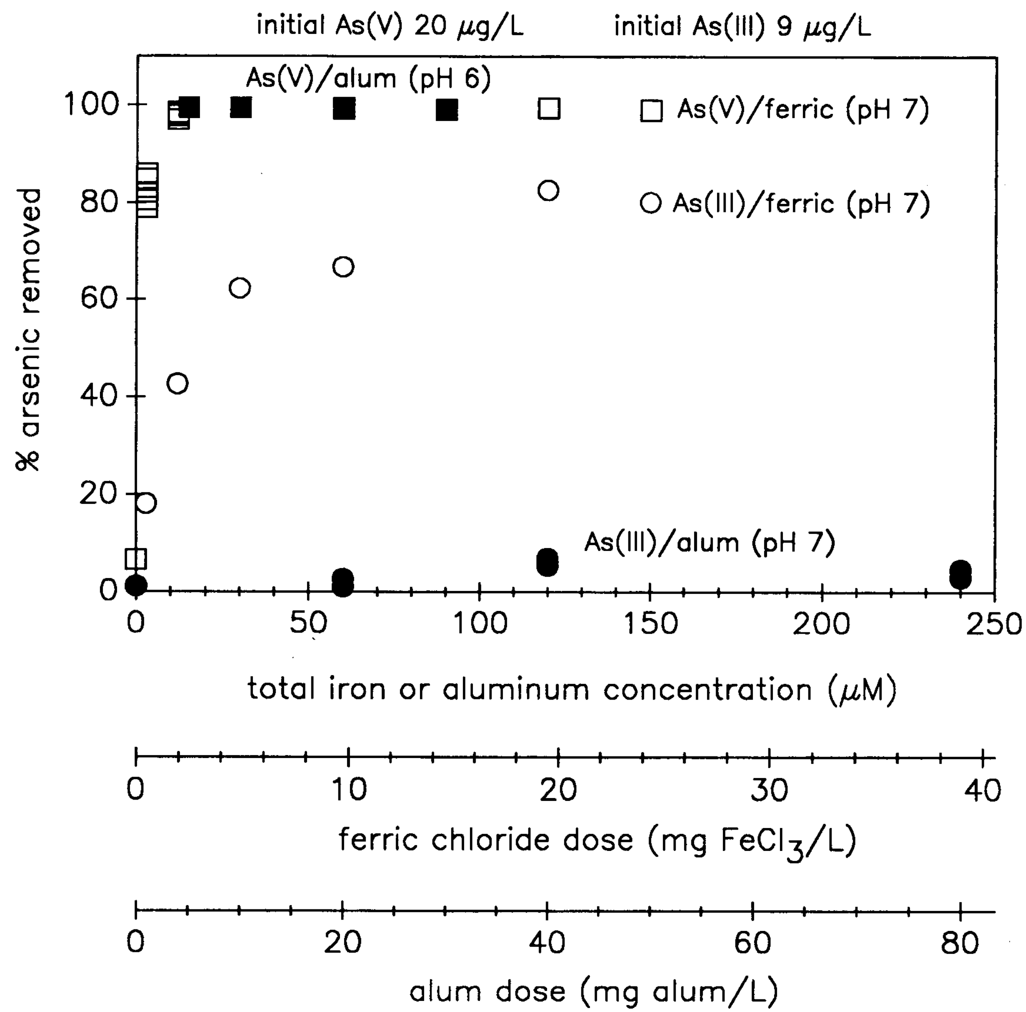
- As(V) is much better removed than As(III)



From: Hering & Elimelech, 1996; AWWARF Report

Coagulation

- Alum vs Ferric
  - Fe(III) is clearly better
  - Why?



From: Hering & Elimelech, 1996; AWWARF Report

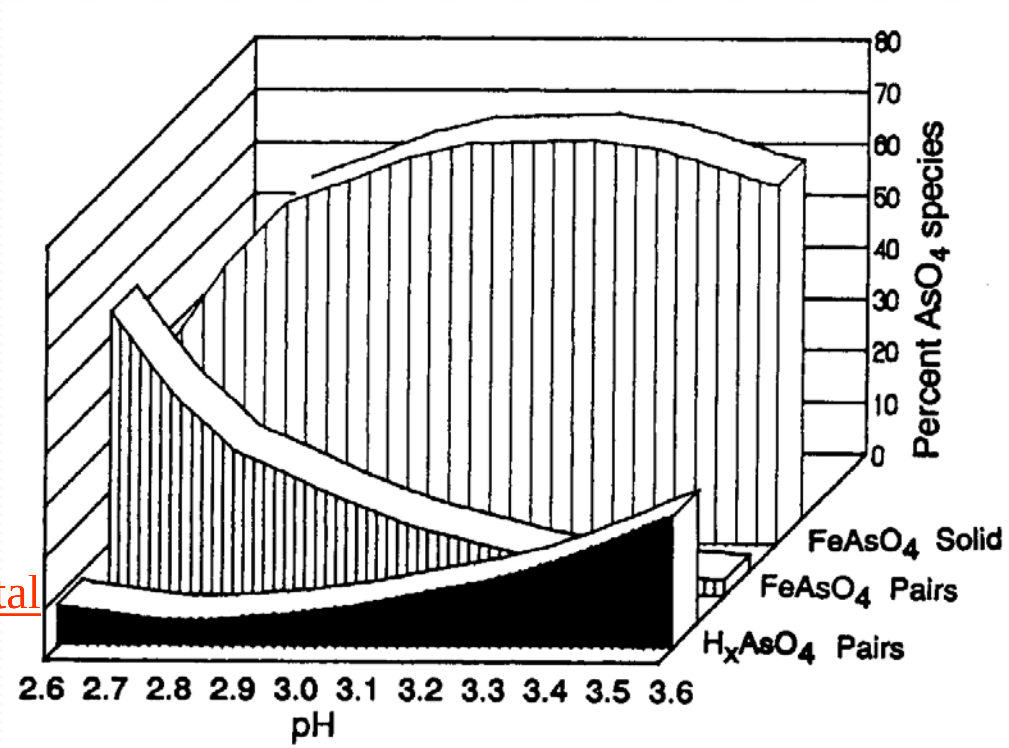
- <u>Oxidize</u>
  - \- Cl_2 - MnO_4^- - O_3
- <u>Treat</u>
  - \- RO/NF - Coagulation/MF - Activated Alumina - Ion Exchange - Greensand - Iron media (GFH)
- <u>Dispose of Residual</u>
  - \- POTW - Dewater - Landfill

From presentation by Philip Brandhuber (2001)

Ferrous Arsenite

- Initial Arsenite:Fe ratio of 1:1
  - From GEO-CHEM-PC

From: Evangelou, 1998, Environmental Soil and Water Chemistry, Wily Publ.



- To next lecture

DAR