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How Arsenic Chemistry Determines Remediation Efficacy as well as Fate and Transport

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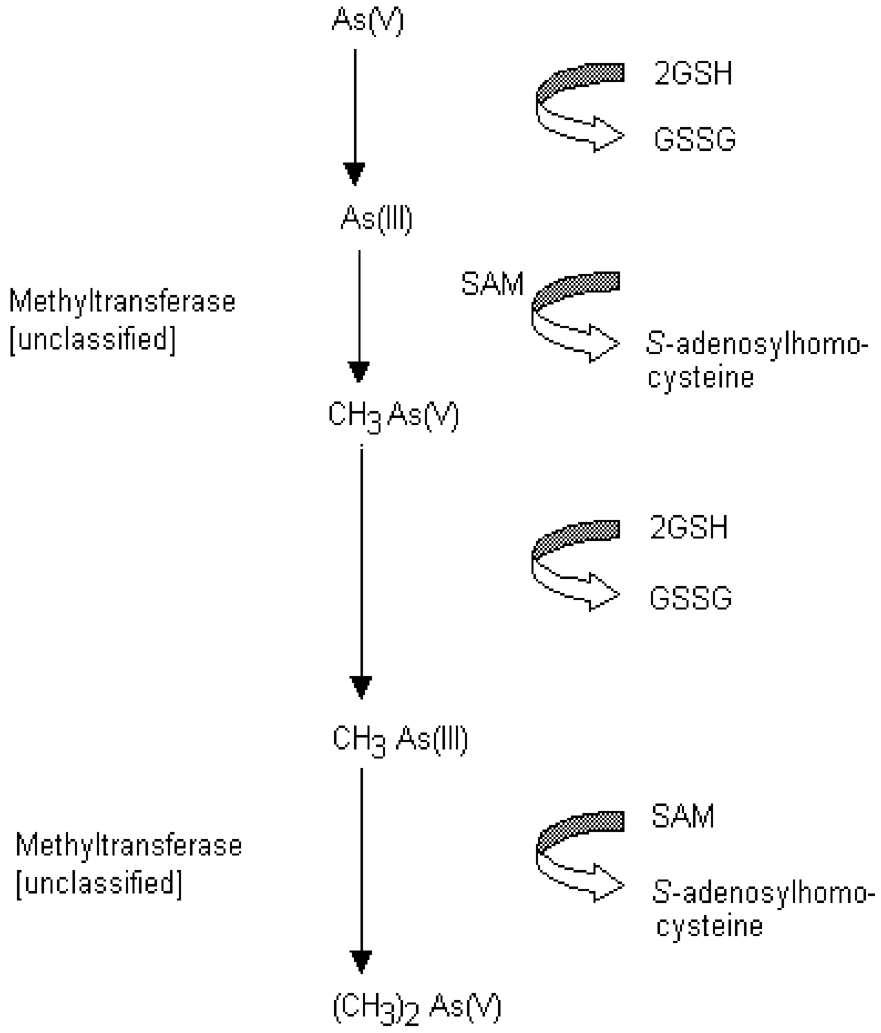
Arsenic Uses/Sources

- Mining and Smelting (Au, U, Cu, Mn, Pb) (inorganic arsenic and methylated species)
- Electronics manufacturing (semiconductor, microwave devices as GaAs)
- Biocides
- Wood preservation (CCA, Cheminite)
- Herbicides (cotton desiccants, weed control) (MMAs, DMAs, As_2O_3)
- Insecticide (MMAs)
- Orchards (Pb-arsenate)
- Feed additives for livestock to control coccoidal intestinal parasites:
  - P-arsanilic acid (4-amino-phenyl arsonic acid)
  - Roxarsone (3-nitro-hydroxyphenylarsonic acid)
- Coal combustion (fly ash) (Arsenate, MMAs)

Arsenic Species in “Typical Waters”

- Arsenite
- Arsenate
- Monomethyl arsenate, MMAs(V)
- Dimethyl arsenate, DMAs(V)

Mechanism of Arsenic Methylation



Environmental Chemistry of Arsenic

Major arsenic species in water:

Arsenite As(III)

$H_2AsO_3^{-}$ $pKa_1 = 9.2$
$HAsO_3^{-2}$ $pKa_2 = 12.7$

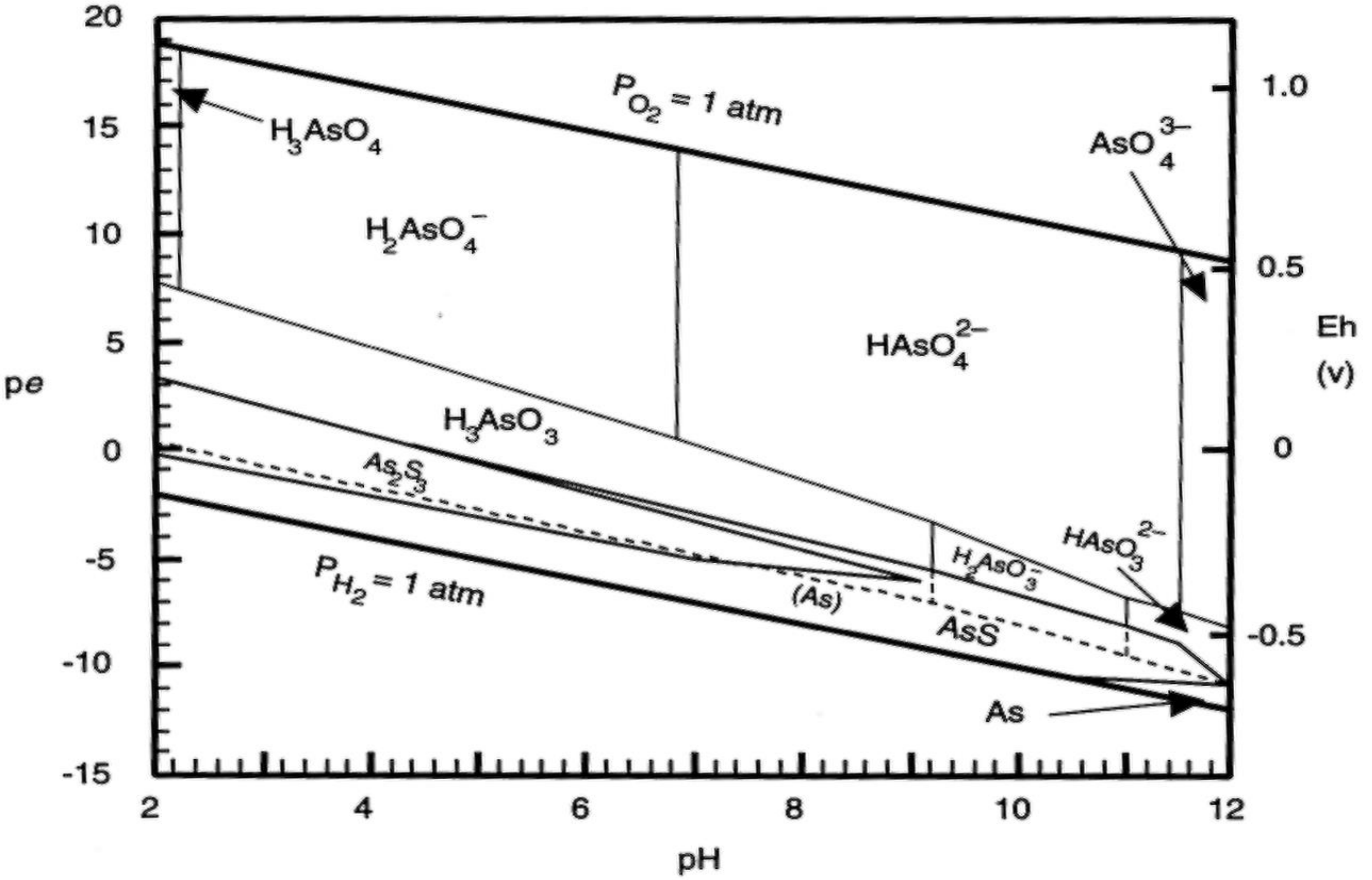
- Normally neutral molecule (weak acid)
- Easily oxidized but kinetics relatively slow
- Does not bind much to FeOOH
- Not similar to common anions
- Presumed to be more mobile

Arsenate As(V)

$H_2AsO_4^{-}$ $pKa_1 = 2.3$
$HAsO_4^{-2}$ $pKa_2 = 6.8$
AsO_4^{-3} $pKa_3 = 11.6$

- Strong acid
- Normally anion
- Very stable
- Binds strongly to FeOOH
- Similar to phosphate
- Presumed to be less mobile

Arsenic Eh-pH Diagram



Arsenic Species in “Unusual Chemical Systems”

- Thio-arsenic compounds
- Arsenic fluoride complexes

Arsenic in Reducing Environments

- Redox potential **and** reaction kinetics determine distribution between arsenite and arsenate in moderately oxic systems
- In anaerobic conditions, oxyanions react with free sulfide and form (oxy)thioanions
  - $As(OH)_3 + SH^- \rightarrow As(OH)_2SH + OH^-$ etc.
  - $AsO(OH)_3 + SH^- \rightarrow AsO(OH)_2SH + OH^-$ etc.

Arsenic in Sulfur Enriched Environments

Redox potential **and** reaction kinetics determine distribution between arsenite and sulfur in geothermal vents, mine sites, landfills, swamps, etc.

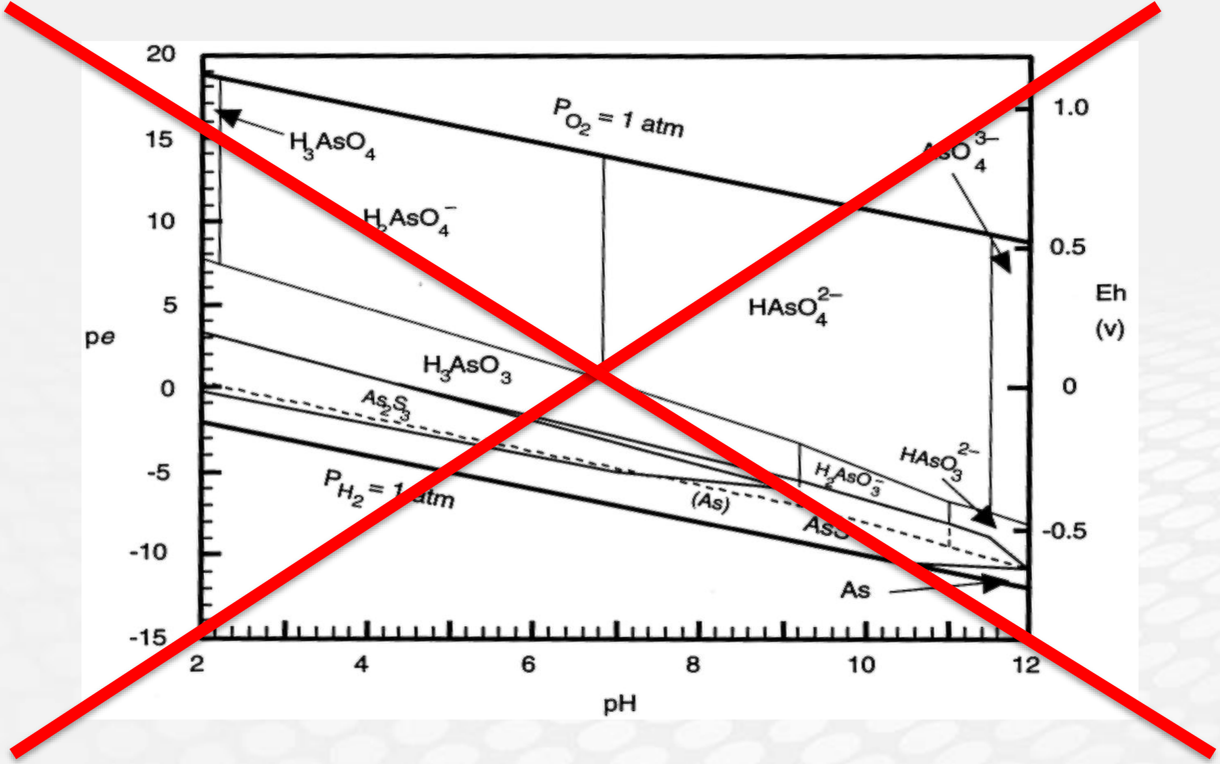
S/As	Charge (0)	Charge (1-)	Charge (2-)	Charge (3-)
0	$As(OH)_3^0$	$As(OH)_2O^-$	$As(OH)O_2^{2-}$	AsO_3^{3-}
1	$As(OH)_2(SH)^0$	$As(OH)_2S^-$	AsO_2HS^{2-}	AsO_2S^{3-}
2	$As(OH)(SH)_2^0$	$As(OH)S_2H^-$	$As(OH)S_2^{2-}$	$AsOS_2^{3-}$
3	$As(SH)_3^0$	$AsS_3H_2^-$	AsS_3H^{2-}	AsS_3^{3-}
4	$As(SH)_4H^0$	$As(SH)_4^-$	$As(SH)_3S^{2-}$	$As(SH)_2S_2^{3-}$

Arsenate is not typically thermodynamically favored for thio arsenical formation but can exist

Arsenic in Sulfur Enriched Environments

Pourbaix diagrams are no longer valid…

Thus, modeling programs have a high probability of failure



Arsenic-Fluoro Complexes

$[AsF_6]^{3-}$

- Extremely stable
- Does not form hydrides: “hidden arsenic”

Reactions of Arsenic Species

- As(III) oxidation by O_2 is very slow!
- As(III) is typically catalytically oxidized by OH• or chemically by Fe(III)
- As(III)/As(V) are often in thermodynamic disequilibrium

- Thio-arsenicals can form under acidic conditions

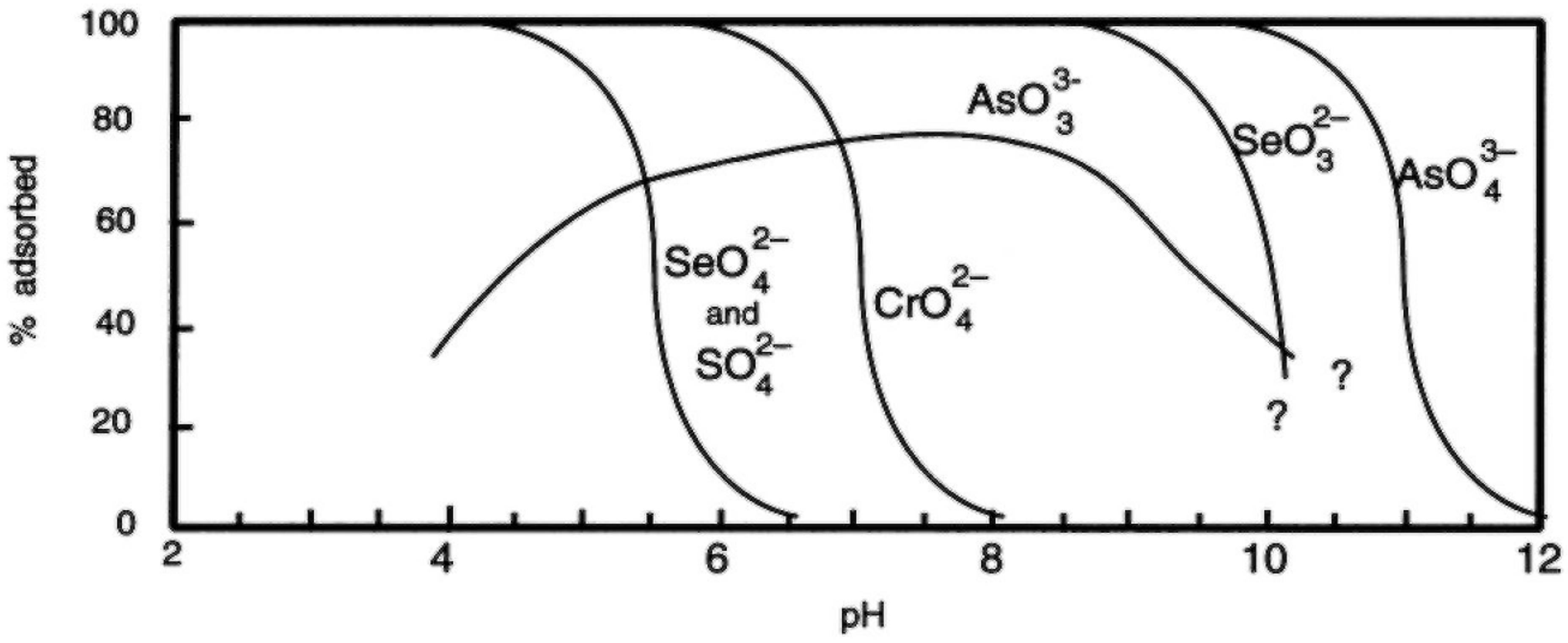
Arsenic Species in Soils/Sediments

- As-sulfide minerals
- As bound to Fe and Mn oxyhydroxides
- As bound to organic matter?

Arsenic Adsorption on Surfaces

- Arsenate is an anion, and adsorbs **strongly** on clay minerals, particularly FeOOH at pH 3-5
- Arsenite is a neutral compound and adsorbs **weakly** to non-polar materials, e.g. NOM
- DMAs and MMAs have weak interactions with FeOOH
- Trimethylarsine oxide and tetramethyl arsonium also have limited interaction with FeOOH
- $[AsF_6]^{3-}$ has weak interactions with FeOOH

Arsenic Adsorption on HFO



Solubility of Arsenic Minerals (The Unwelcome Guests)

Arsenic forms three significant sulfide minerals:

- Orpiment (As_4S_6)
- Realgar (As_4S_4)
- Arsenopyrite (FeAsS)
    - These minerals are insoluble under acidic and neutral conditions, but soluble in alkaline environments

- $FeAsO_4$: logK = 20.2, but typically not formed
- Fe(III)-minerals with bound As: scorodite, jarosite etc.: dissolve under reducing conditions and/or acidic pH to release As
    - $Ca_3(AsO_4)_2$: logK = 18.9
    - $Ba_3(AsO_4)_2$: logK = 50.1

But, arsenic containing minerals are readily solubilized by microbial activity and hydrocarbon releases

How do we Control the Mobility of Arsenic?

Anthropogenic activity and natural weathering of arsenic bearing minerals will inherently mobilize arsenic into the environment

How can this be mitigated?

Arsenic Removal from Groundwater

- Traditional approaches to arsenic removal by adsorption or co-precipitation is highly dependent on:
  - pH (what most scientists monitor)
  - Molecular form of arsenic (speciation)
  - ORP (usually ignored)
  - Concentration of everything else in solution
    - PO_4^{-3}, S^{-2}, SO_4^{-2}, Cl^-, Br^-, DOC, Ca, Mg
- Either competitively bind or scale solid phase treatment

Arsenic Remediation in Soils

- Phytoremediation (ferns, grasses, etc.)
- Immobilization by iron addition and oxidation
- Immobilization by formation of concrete
- Zero valent iron (ZVI) reactive barriers
- In situ soil flushing (pump and treat)
- Ion exchange

Questions???

Your attention was greatly appreciated!!