An Overview of Arsenic Treatment Methods

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  - Ganesh Ghurye, Jean Tong, Manxue Wu, Tony Tripp, C. C. Lin.

Outline

- Forms of arsenic in water
- List of arsenic treatment processes
- Sorption onto alumina and iron
  - Selectivity sequence
  - Importance of Oxidation state and pH
- Ion exchange for As(V) removal
  - Selectivity sequence
  - Influence of sulfate on peaking and run length
  - Regeneration and reuse of brine
- Coagulation-filtration and C-MF
  - Basically the same Fe/Al sorption processes
  - Influence of mixing, filter size, pH, silica
- Comparison of processes

Arsenic in Water

- MCL = 10 µg/L, 3500 violations USA
- Soluble or Particulate
- Inorganic or Organic
- As(V), Arsenate species of H_3AsO_4
  - $H_2AsO_4^-$ monovalent at pH < 7.0
  - $HAsO_4^{2-}$ divalent at pH > 7.0
- As(III), Arsenite species of H_3AsO_3
  - H_3AsO_3 uncharged at pH < 9.2
  - $H_2AsO_3^-$ anionic at pH > 9.2

Arsenic Removal Processes

- Activated Alumina Adsorption, AAl
- Fe(III)-Based Adsorbents (e.g. GFH, GFO)
- Anion Exchange w Cl^- Form SBA, IX
- Fe(III) Coagulation-MicroFiltration, C-MF, C-F

- Conventional Coagulation Filtration
- Adsorption using Zr, Ti, Humates, Polyelectrolytes
- Lime Softening w Fe, Mg addition
- Reverse Osmosis and Nanofiltration
  - As(III/V) 50-99% Removal, pH 5.5-8, TFC
  - Pressure: 50-250 psig (3.4-17 bar, 50-1700kPa)
  - Extensive pretreatment, high cost
- Phytoremediation

Disposable Alumina or GFH/ GFO

Raw Water
As(III)
As(V)

No pH adjust.
No oxidation

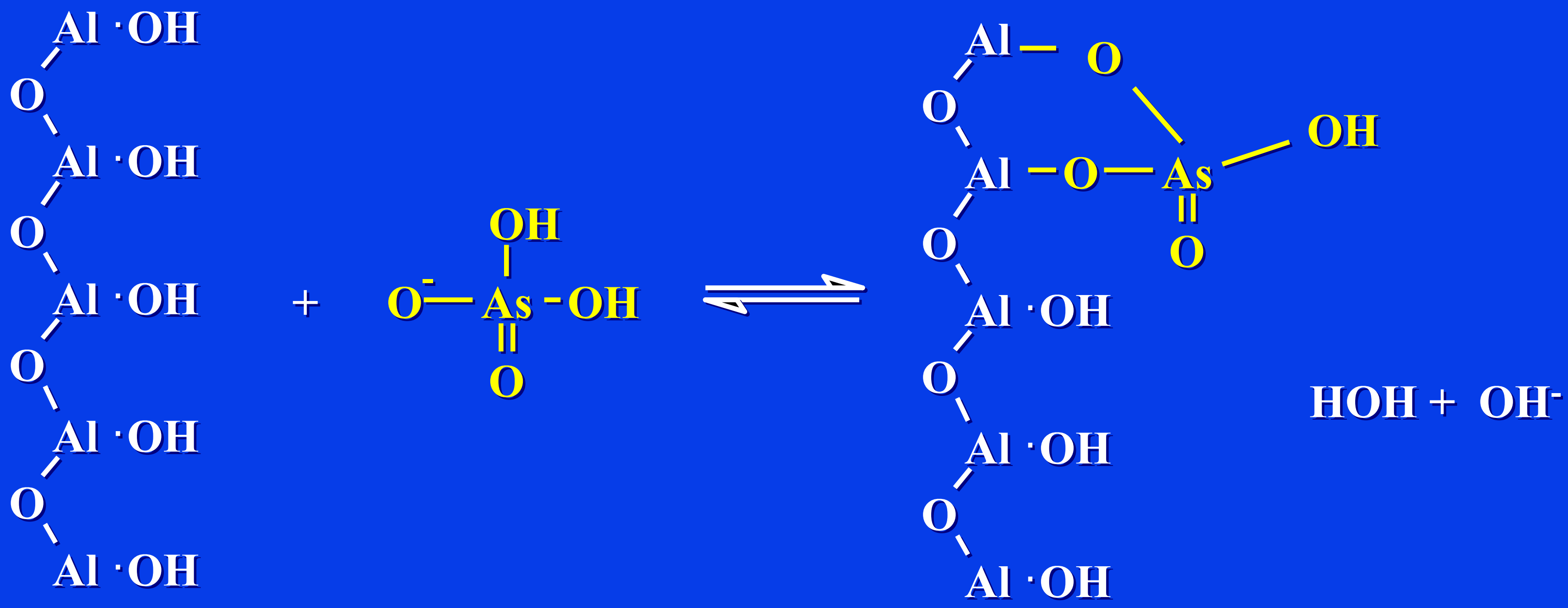
Activated Alumina or GFH Granules

0.3-0.6 mm
> 1 m deep
> 5 min EBCT

Arsenic-free treated water

- No regeneration on site
- Much shorter runs than pH 6, As(V) runs.
- Regenerate or dispose of spent alumina off site

AAl—Arsenic Ligand Exchange



Alumina
AlOOH
FeOOH
Zr, Ti oxides

Arsenic (V)
$H_2AsO_4^-$

Arsenic on
AlOOH
FeOOH

Hydroxide

Competing Ligands Sequence Activated Alumina (and GFH)

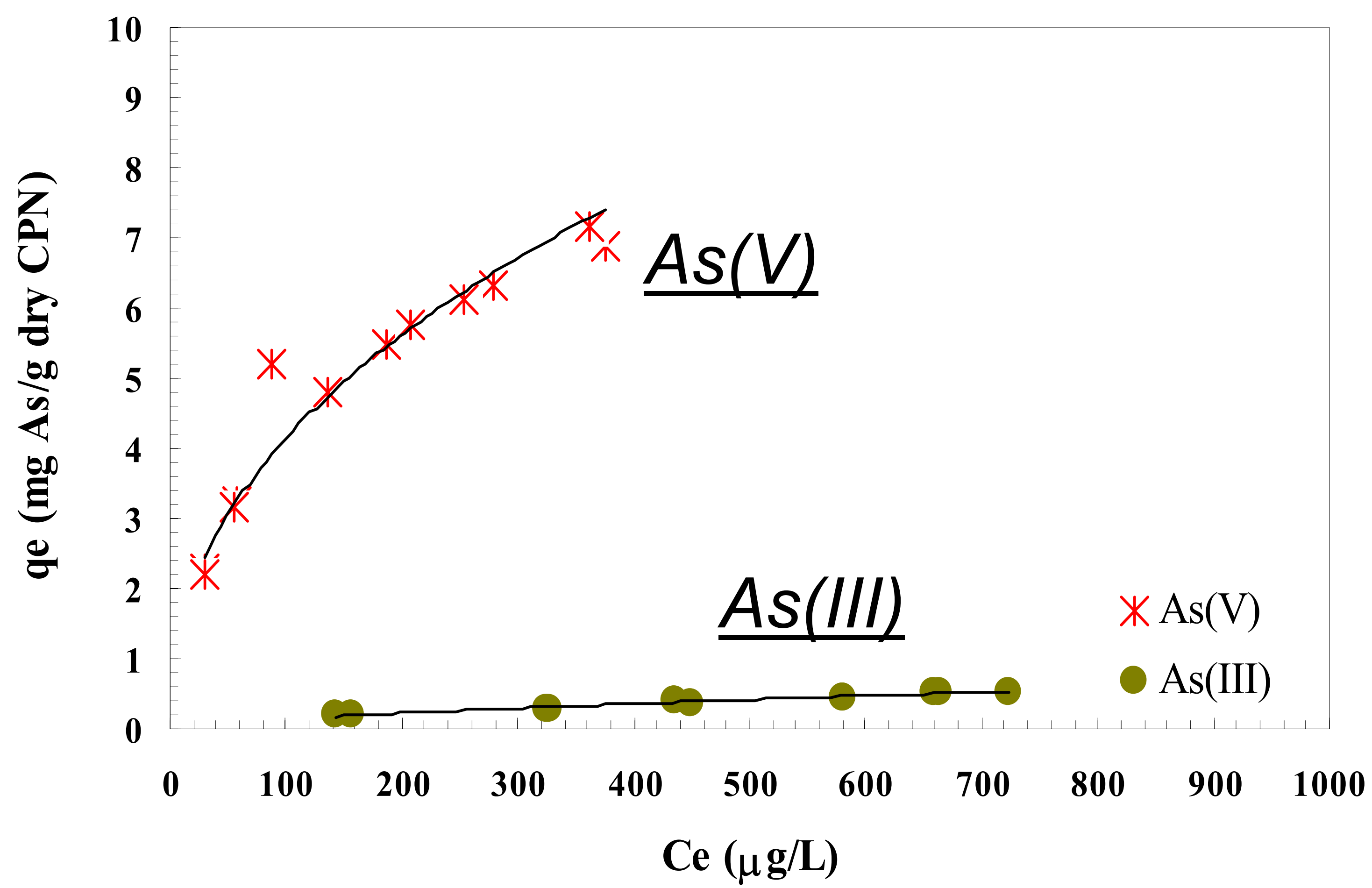
$OH^- > H_2AsO_4^- > H_2PO_4^- > Si(OH)_3O^-$

VO_4^-, MoO_4^- $> F^- > HSeO_3^- \gg TOC^-$

$> SO_4^{2-} \gg Cl^-$, NO_3^-, $HCO_3^- >$

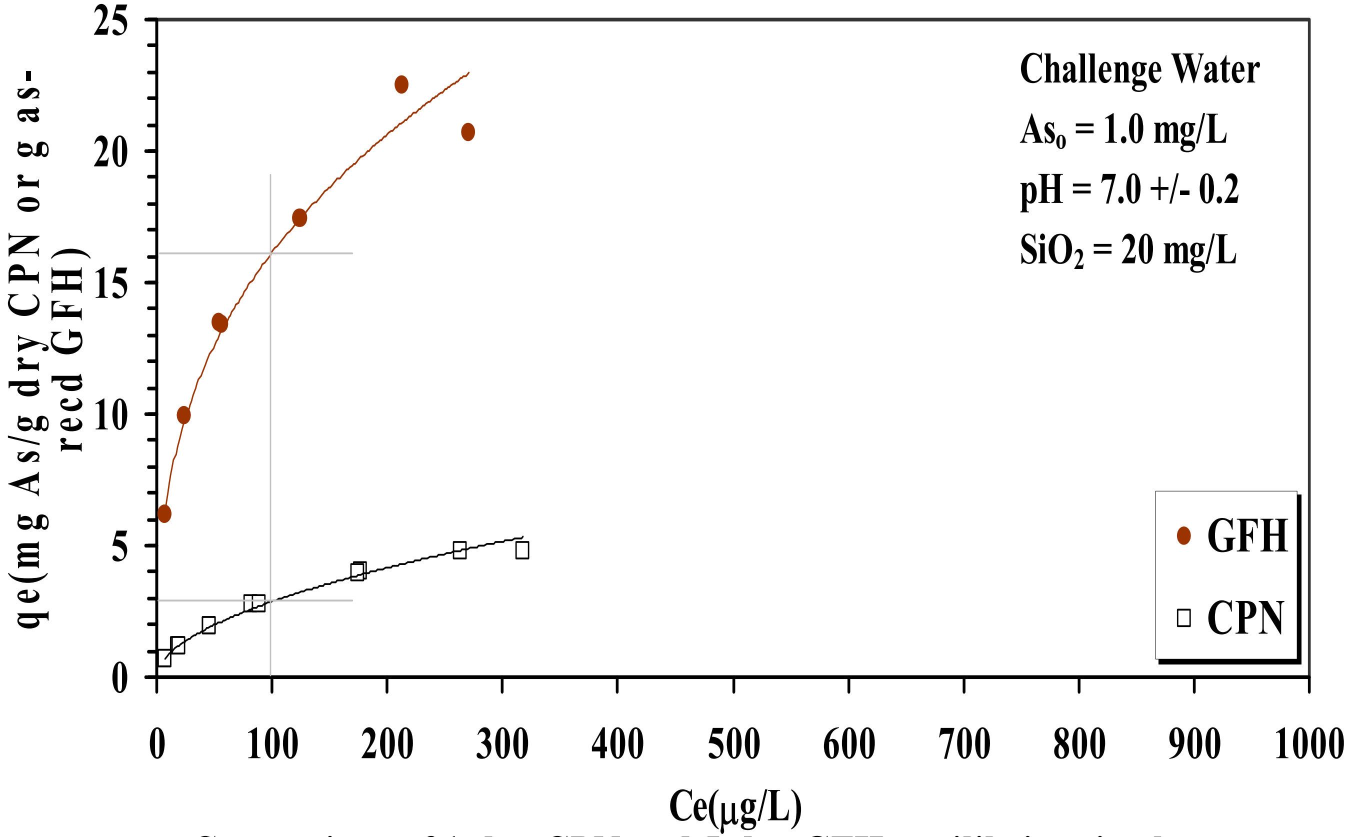
H_3AsO_3

Comparison of As(V) vs As(III) Adsorption at pH=7.0±0.2, without Si



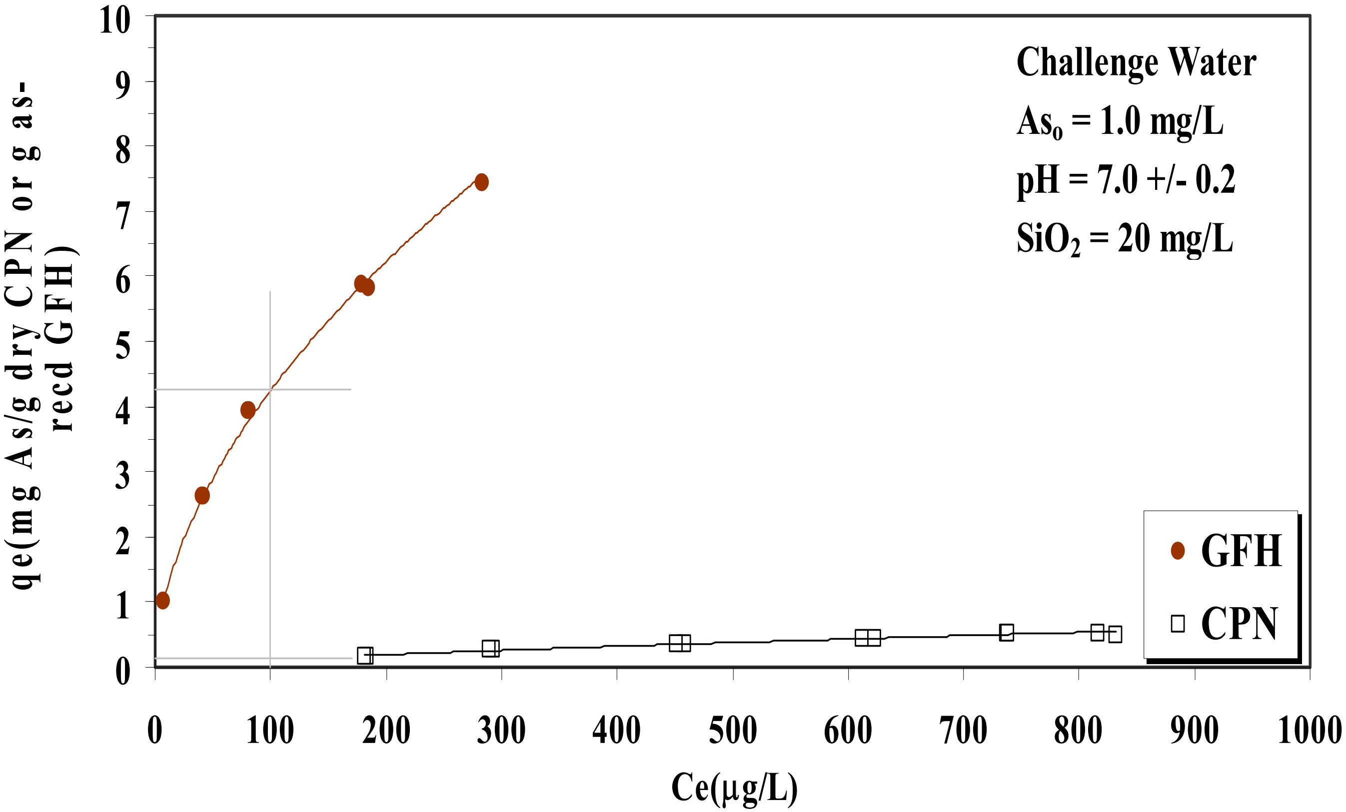
One day equilibrium isotherms for arsenic adsorption onto CPN in challenge water at pH =7.0+/-0.2, in the absence of silica

GFH vs CPN Alumina, pH 7, As(V)



Comparison of 1-day CPN and 5-day GFH equilibrium isotherms,
As(V), challenge water, pH = 7.0 +/- 0.2, with silica

GFH vs CPN Alumina, pH 7.0, As(III)



Comparison of 1-day CPN and GFH equilibrium isotherms, As(III), challenge water, pH = 7.0 +/- 0.2, with silica

As(III/V) Capacity of GFH as a Function of pH, mg As/g GFH

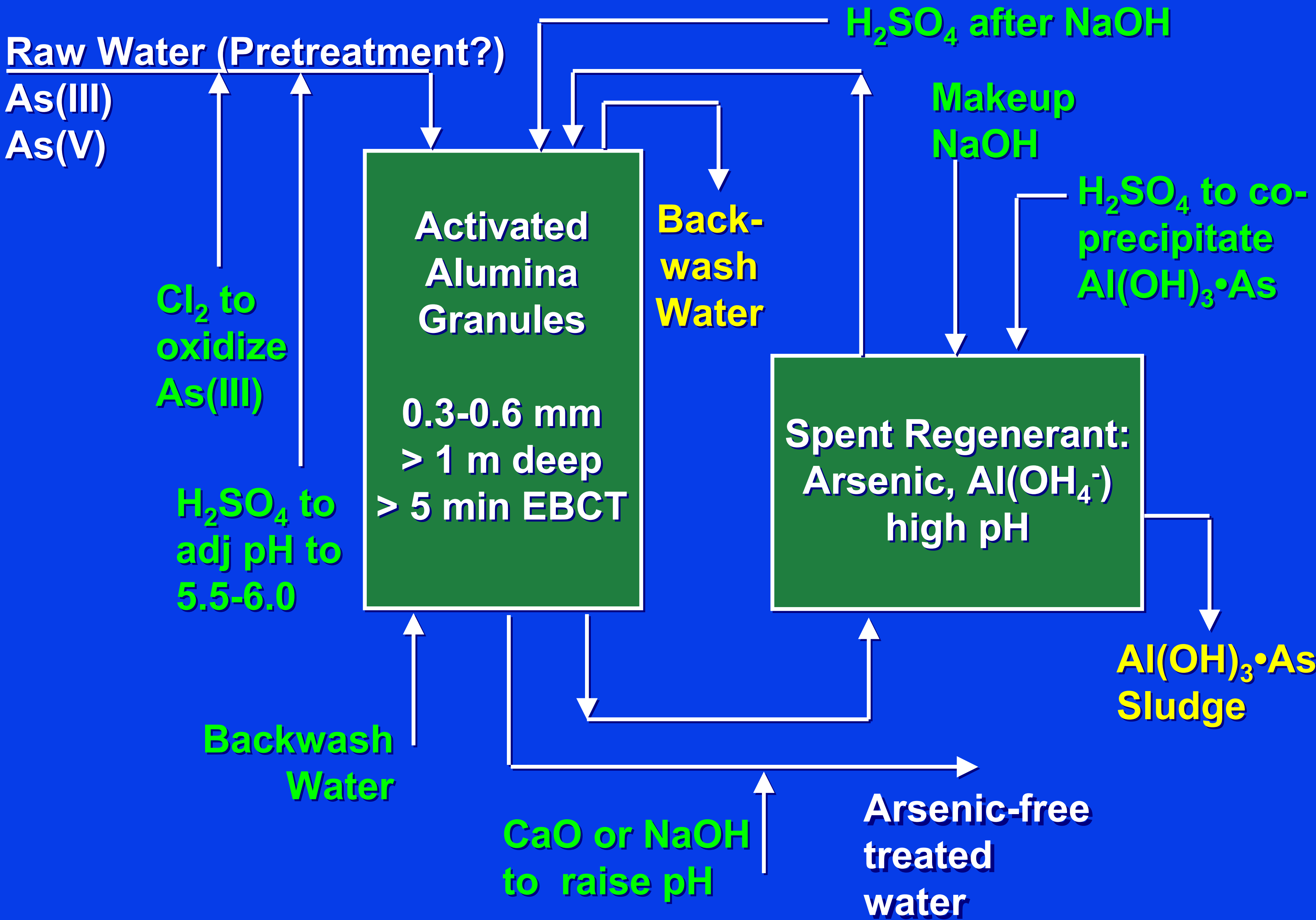
	As(III)	As(V)
pH 7.0	4.3	16.0
pH 8.4	4.7	8.0

As(III) Oxidation

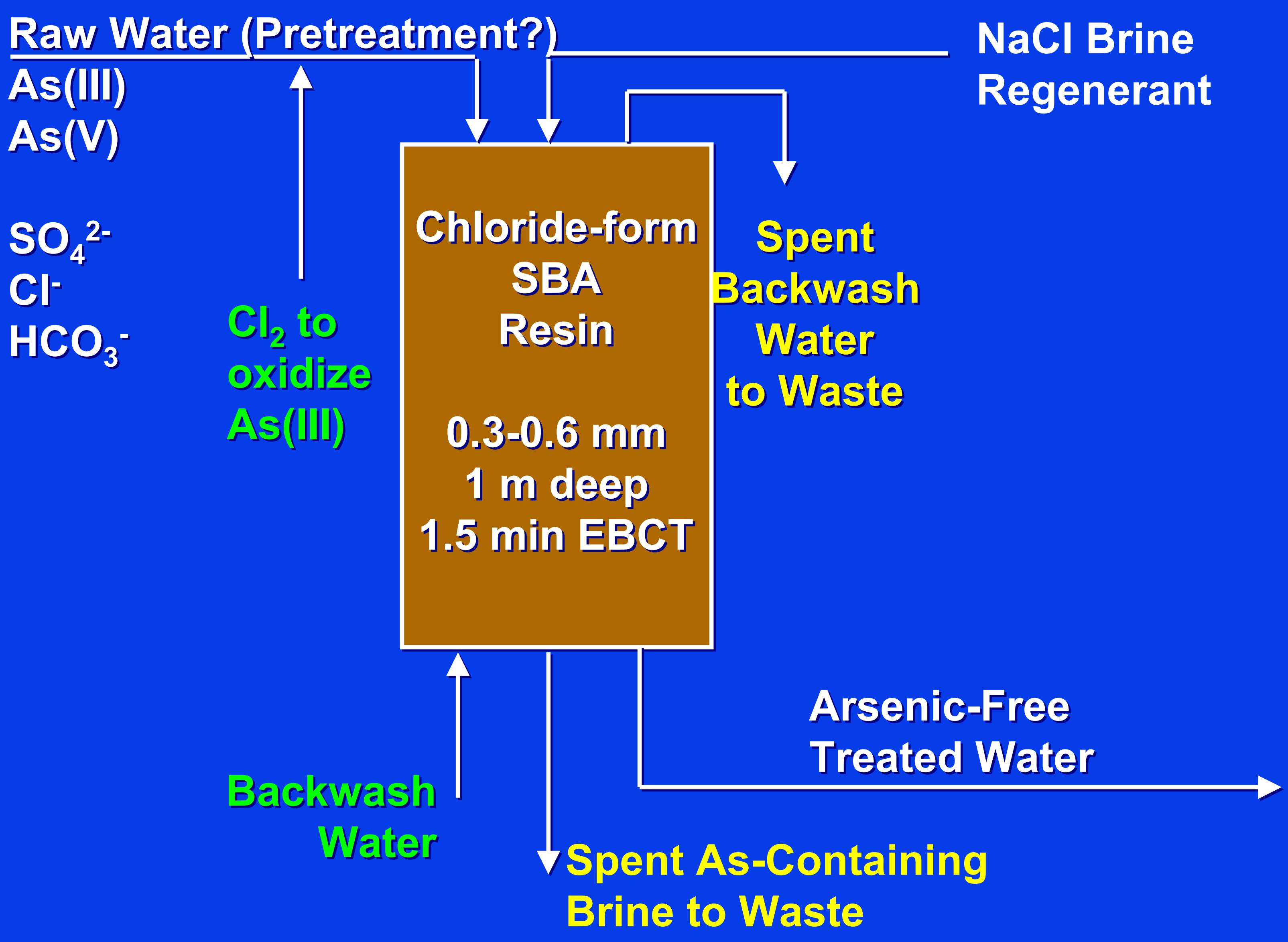
- **Effective Oxidants**
  - Chlorine
  - Hypochlorite
  - Permanganate
  - Ozone
  - Solid-Phase Media
    - Filox and Others
- **Ineffective Oxidants**
  - Chlorine Dioxide
  - Chloramines
  - UV Light Alone
- **Contaminants slow As(III) oxidation**
  - Sulfide (had the greatest effect)
  - TOC (Especially for Ozone)
  - Fe(II)

Ghurye and Clifford, 2000

Activated Alumina Process



Simple Anion-Exchange



Ion Exchange Reactions

Exhaustion

$$2RCl + HAsO_4^{2-} \text{ ----> } R_2HAsO_4 + 2\ Cl^-$$

Regeneration w xs NaCl

$$R_2HAsO_4 + 4\ Cl^- \text{ ----> } 2RCl + HAsO_4^{2-} + 2\ Cl^-$$

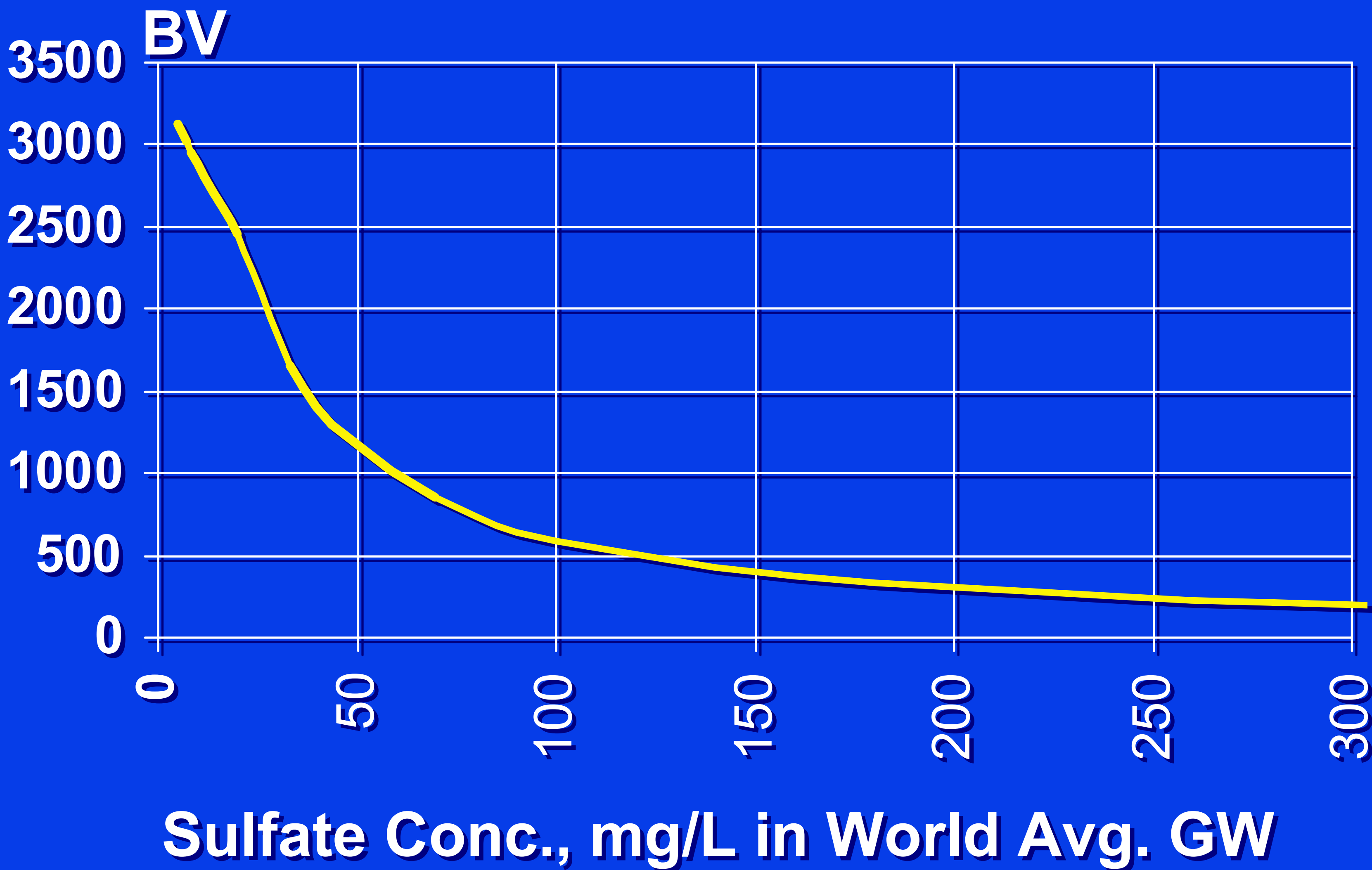
Anion Selectivity Sequence Strong-Base Anion Resins

SO_4^{2-} > $HAsO_4^{2-}$ > CO_3^{2-}, NO_3^- >

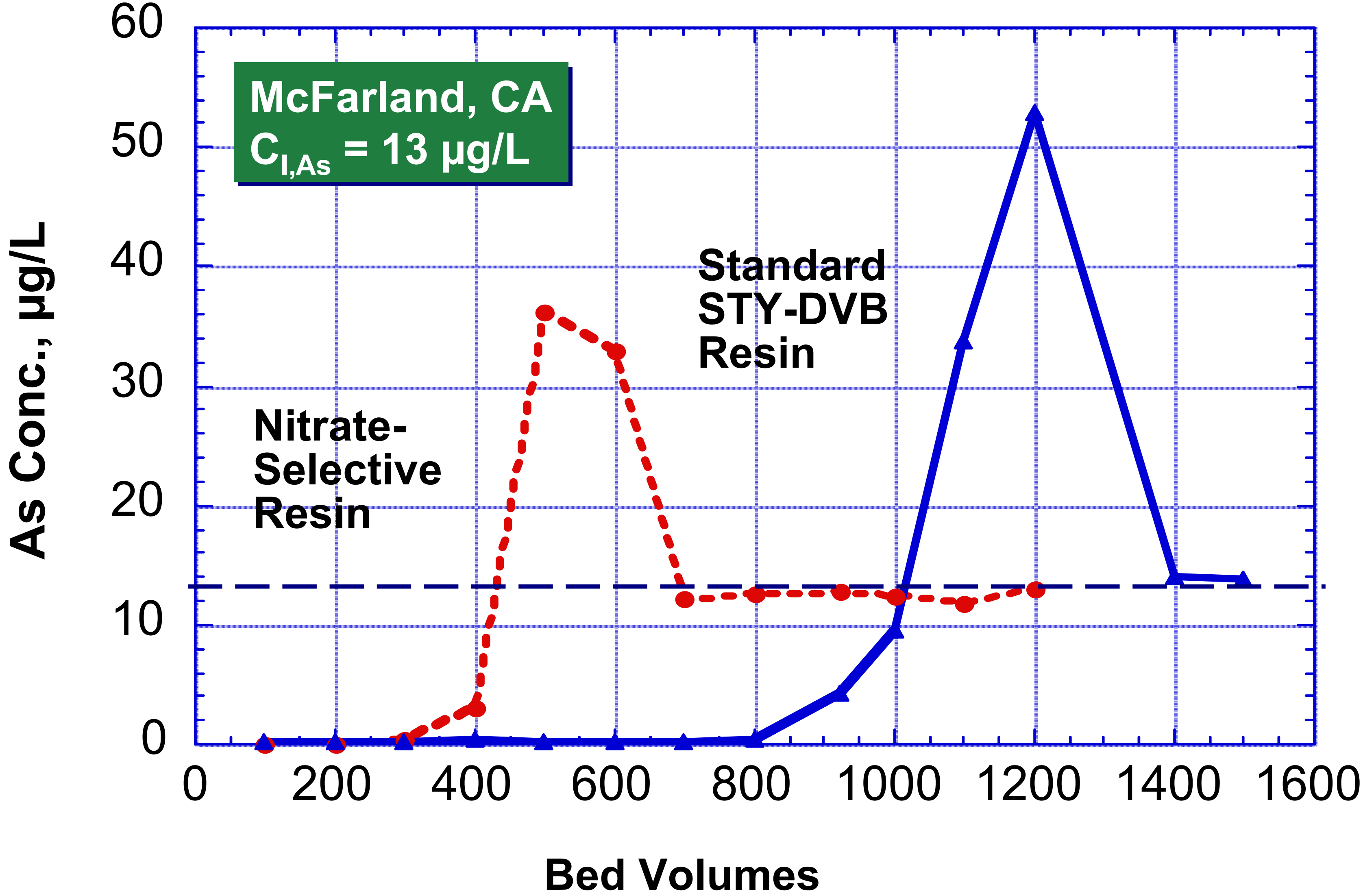
Cl^- > $H_2AsO_4^-$, HCO_3^- >>

H_3AsO_3

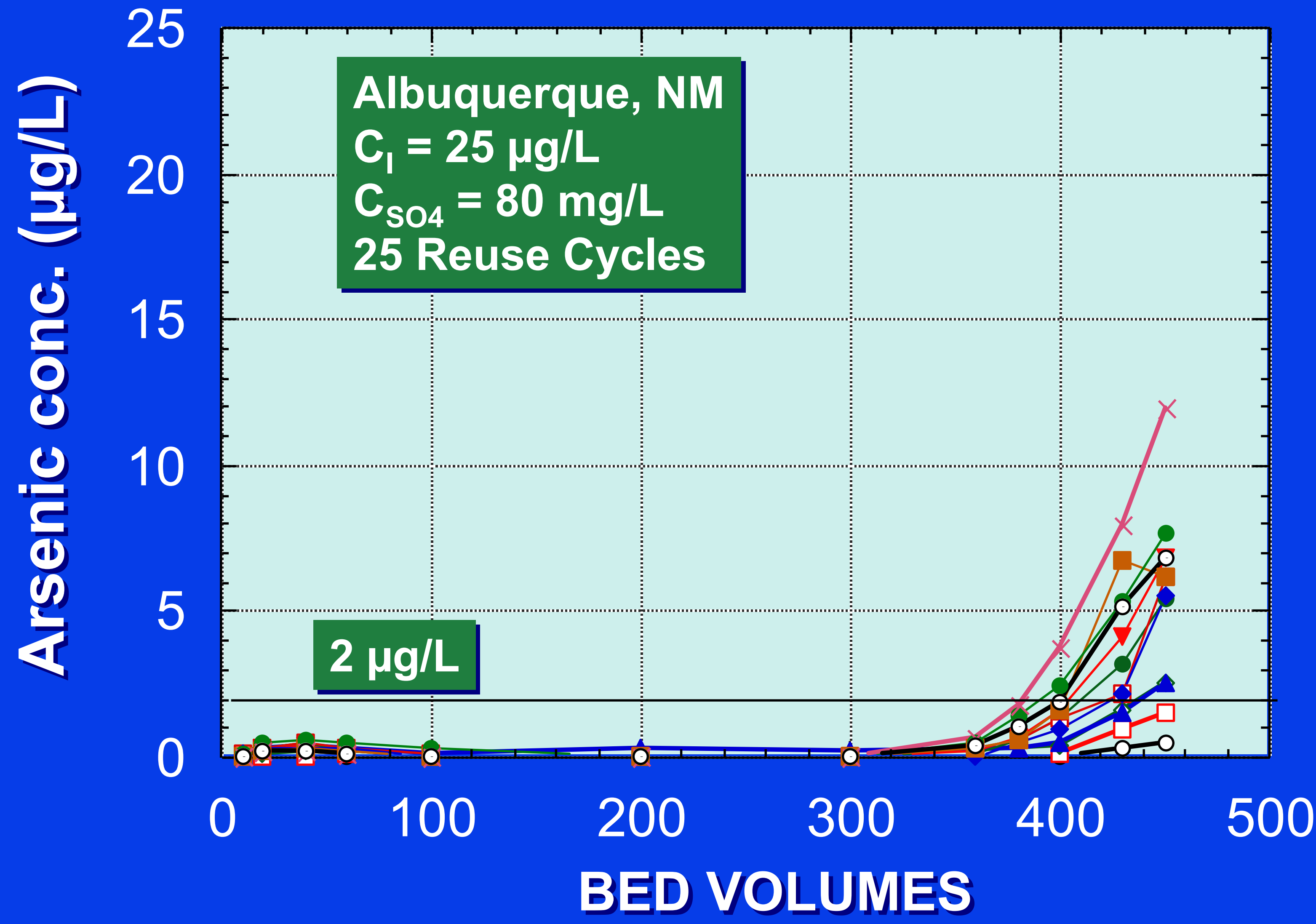
IX—Effect of SO_4^{2-} Conc.



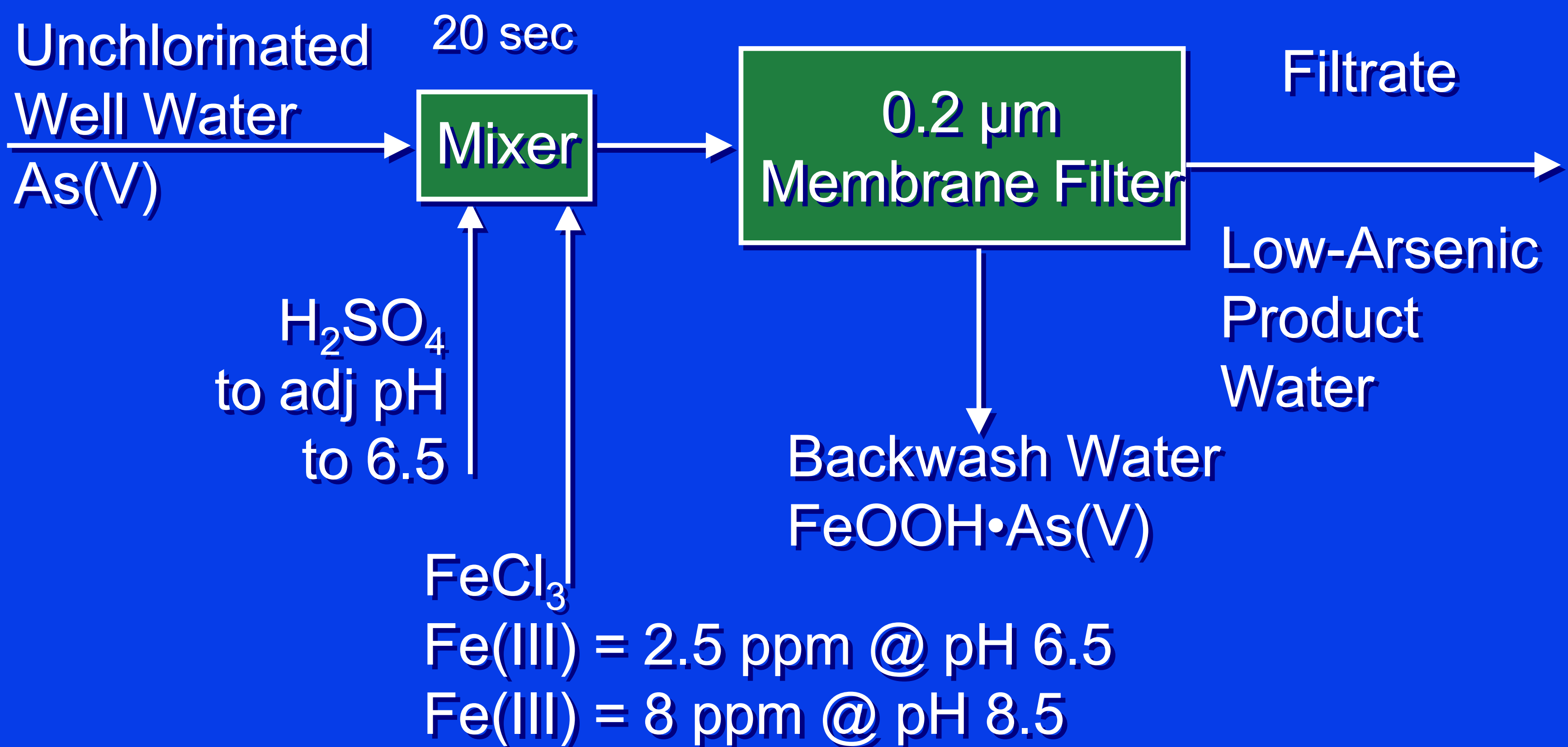
IX—Potential Arsenic Peaking



IX—Spent Brine Reuse

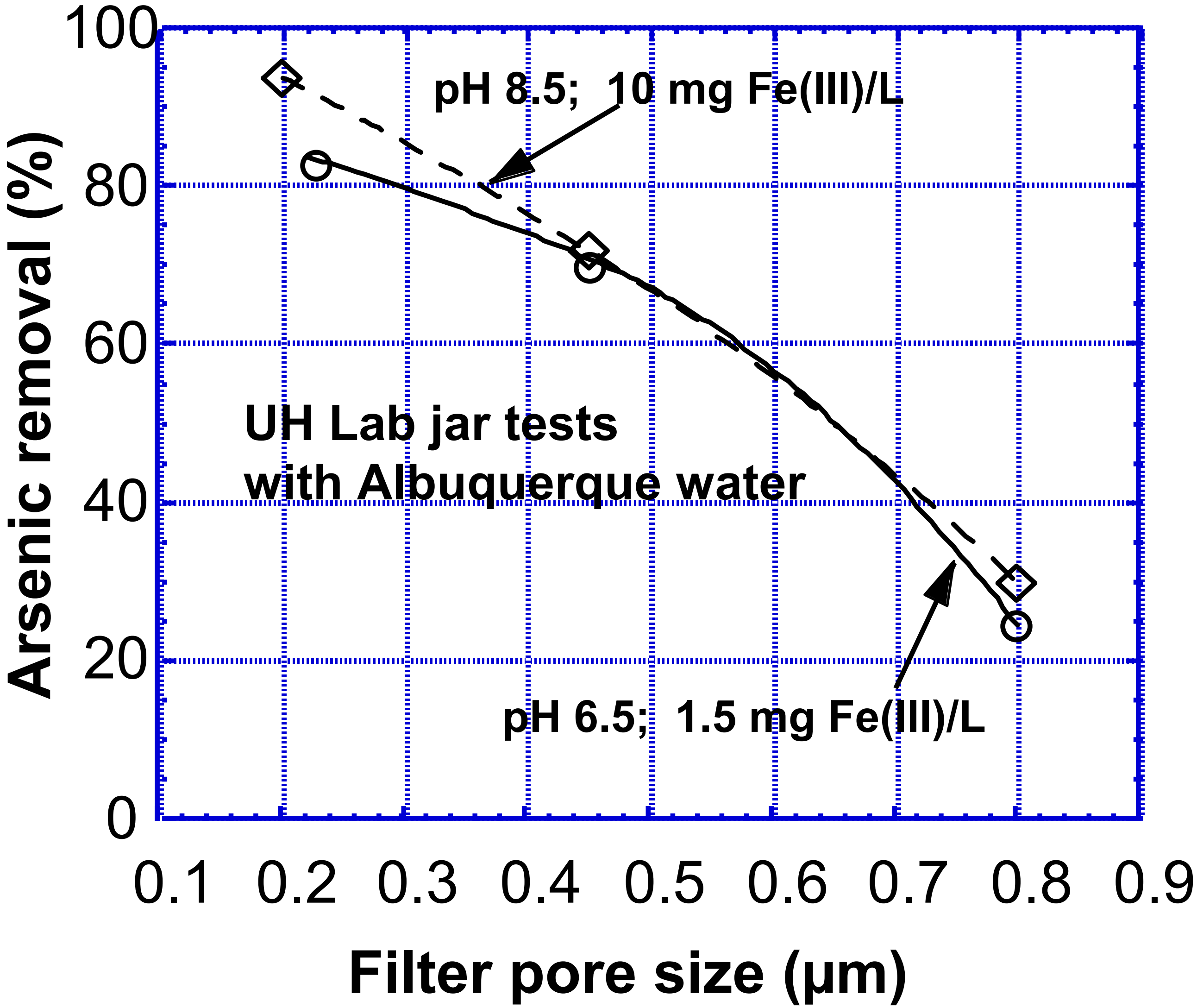


Coagulation-Microfiltration (C-MF)



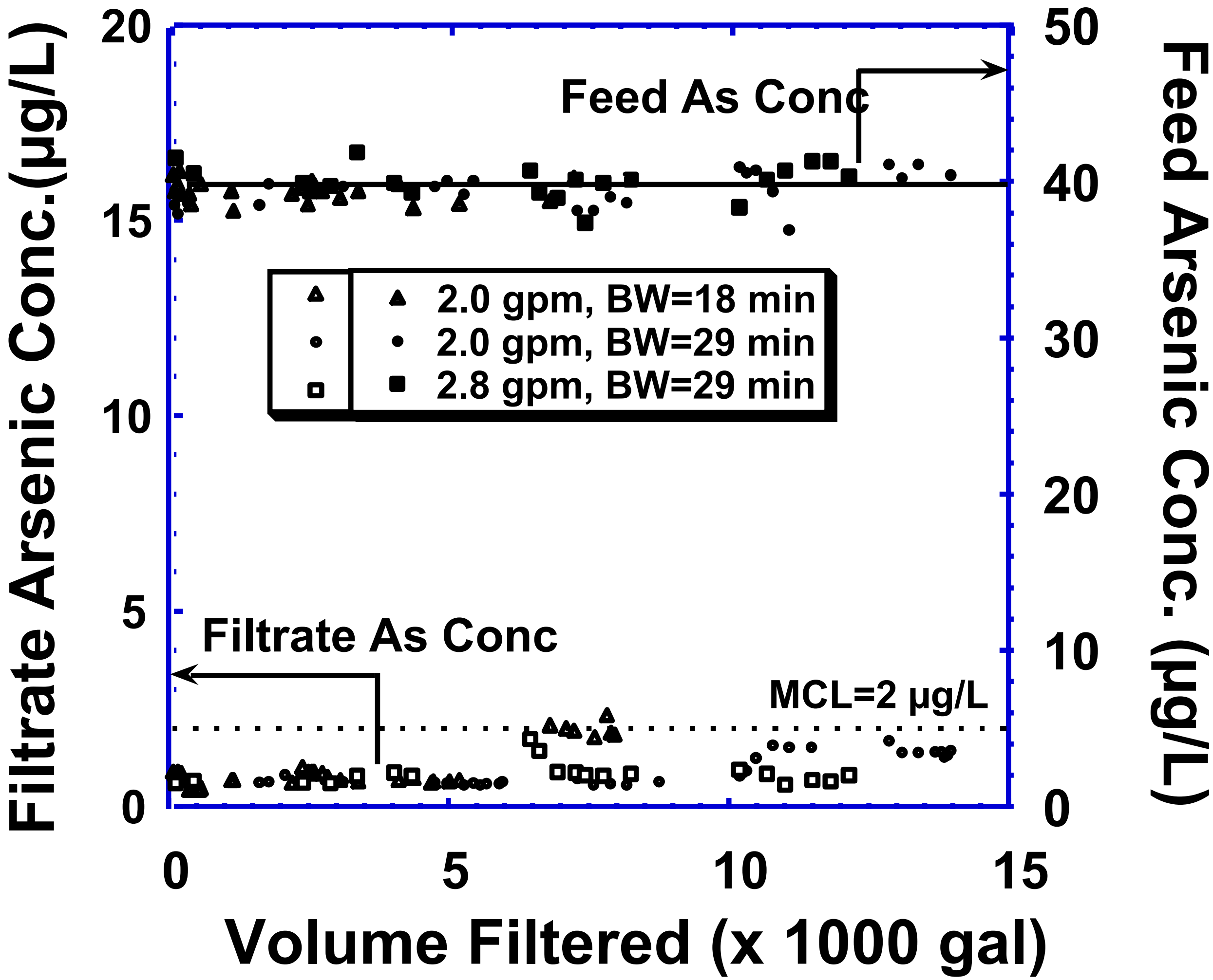
No flocculation, direct filtration, minimum space reqd.

C-MF: Effect of Filter Pore Size



10 seconds reaction time, 100 rpm.

C-MF: Field Results



5-day pilot-plant operation for arsenic removal with varying backwash intervals and flux rate. Fe (III) = 2.5 mg/L, pH = 6.35, t = 20 sec

AAl, GFH, GFO (Zr, Ti) Adsorption

+ Not sens. to TDS (sl. sens. to sulfate)

+ V. long runs possible, interruptions good.

+ Leakage < 2-3 ppb possible

- V. sens. to pH, EBCT: pH 5.5-6 best?

- Capacity decr. w Si, P, F, Mo, V, B

+ Can reuse spent regenerant directly

+ Spent regen. treatment by pH adj. to 6.5.

Chloride Anion Exchange

+ 400-4,000 BV runs possible
+ Simple NaCl regeneration w direct reuse.
+ Not sensitive to pH in 6.5-9 range.
+ < 1µg/L As routinely possible.
- TDS should be <500 mg/L
  - Sulfate should be <120 mg/L
- 200 to 2,000 lbs NaCl reqd./Mgal
+ As removal from spent regen. w $FeCl_3$, H_2SO_4
+ Multiple (2-5) parallel columns to avoid low pH, variable water quality and peaking

Fe(III) Coagulation-MF

+/- Low Fe(III) dose, but very pH sensitive

  2.5 ppm Fe(III)@ pH 6.5

  8 ppm Fe(III) @ pH 8.5

- pH sensitivity =f(SiO_2) conc.

+ 20 sec mixing, 0.2 µm pore dia.

+ Also removes U, Se, F, bact., viruses, etc.

- Limited availability of MF vendors

- Cl_2 sensitivity of membranes

+/- Produces largest amt. of $FeOH_3$•As, but most likely to pass TCLP.

Design Considerations

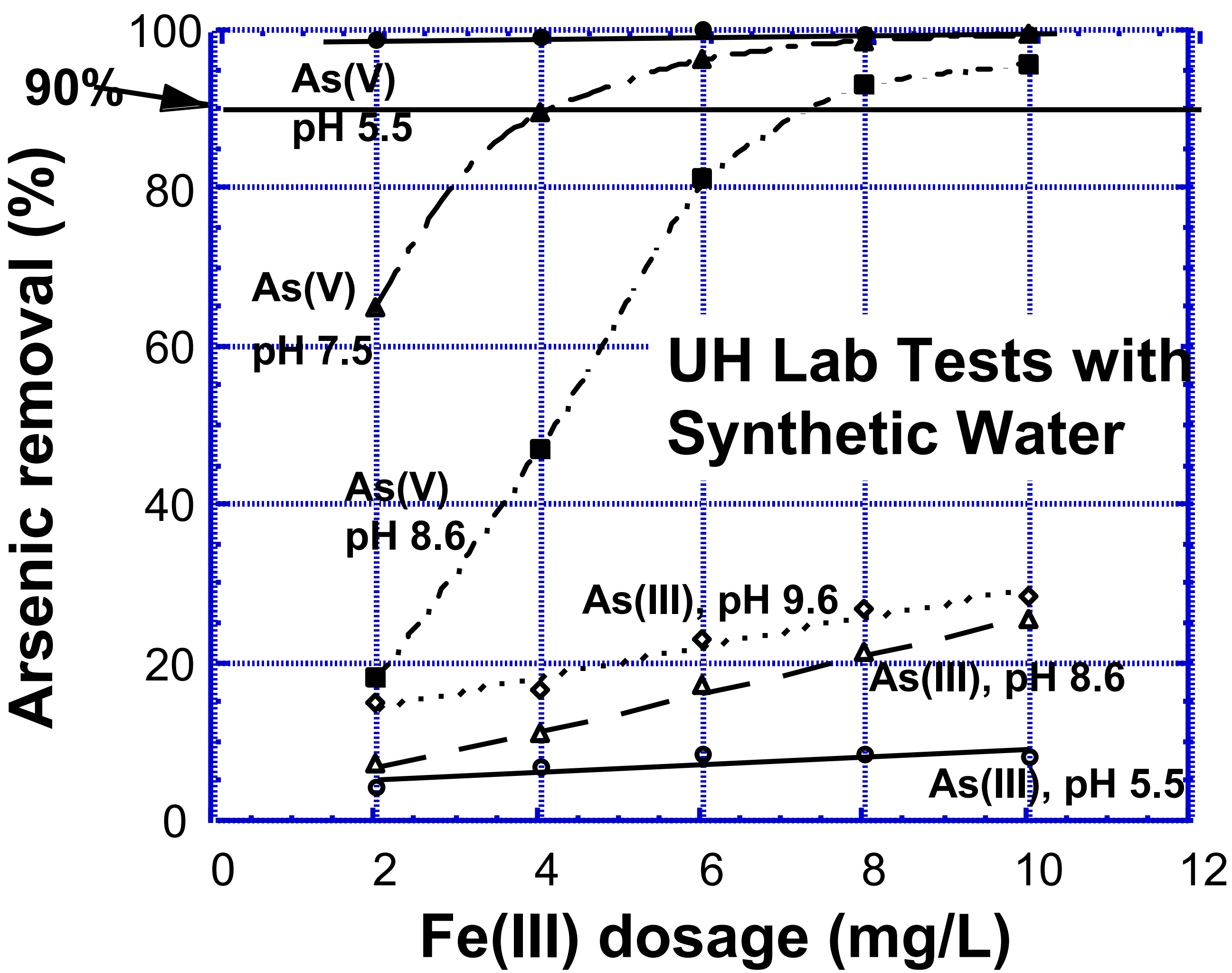
- Need to oxidize As(III) to As(V)
  - Cl_2, NaOCl, $KMnO_4$, O_3, Filox, NanoMnO_2, Interferences: S^{2-}, Fe(II), Mn(II), TOC
- Water Quality (influent and effluent)
  - SO_4^{2-},Silicate, $H_2PO_4^-$, V, M, borate.
  - TDS, Bacteria, NO_3^-, F^-, Cr, Pb, U,
- Process Complexity, (POU/POE Simple)
- Chemicals Handling / Safety
- Residuals
  - Liquid, hazardous/non hazardous
  - Solid, hazardous/non hazardous

Water Recovery

- Activated Alumina, GFH, GFO
  - 99.6% Recovery
  - 0.4% Waste Water even with regen.
- Ion Exchange
  - 98.6% Recovery
  - 1.4% Waste Water
- Fe(III) Coagulation Microfiltration
  - 99.9% Recovery
  - 0.1% Waste Water

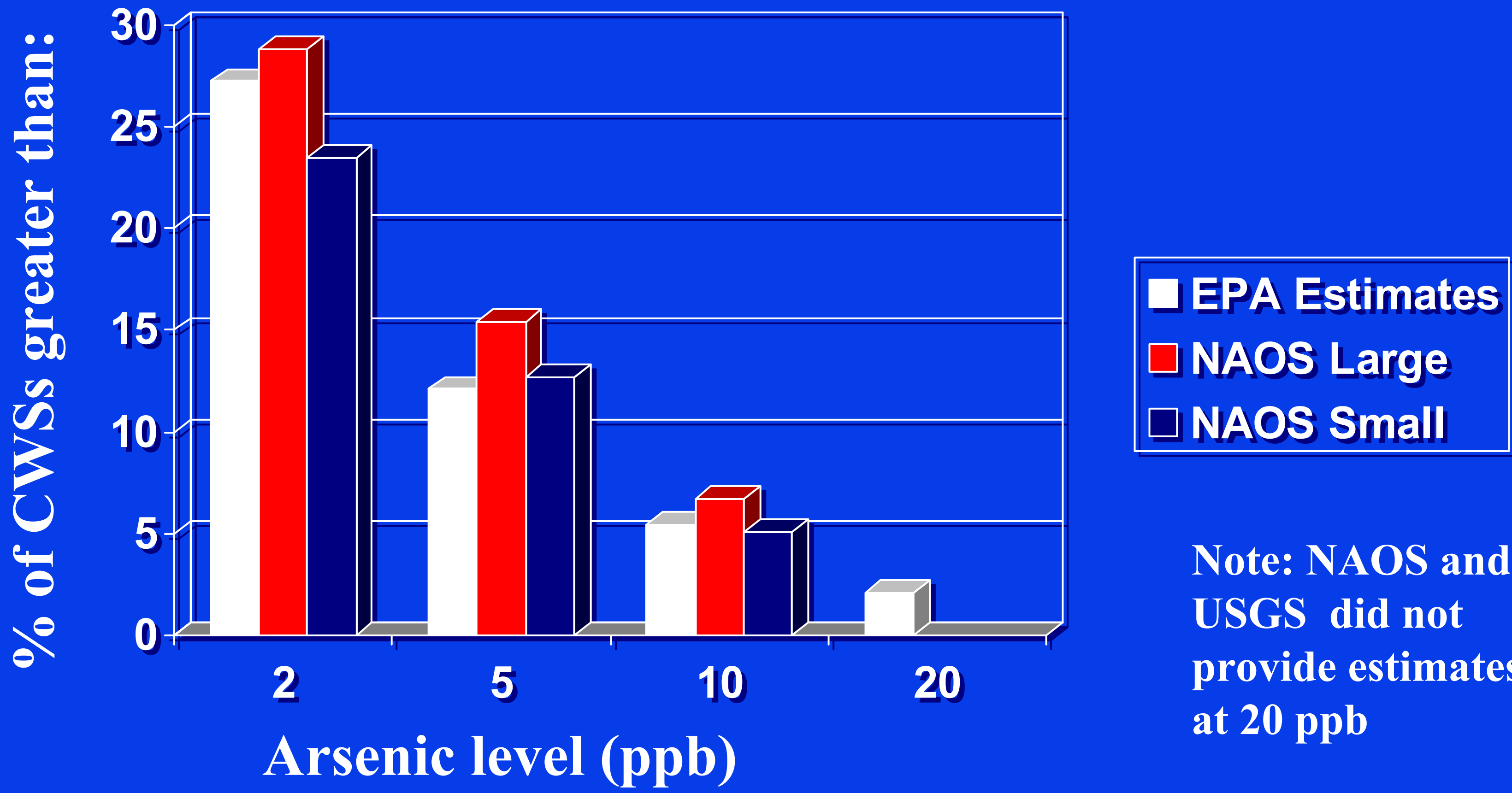
Based on Albuquerque New Mexico As Study-I Mgd

C-MF: Effect of Fe(III) Dosage on As(III/V)



10 seconds reaction time, 100 rpm, 0.2 μm filter,
initial arsenic conc.: 20 μg/L.

GW National Estimates



Note: NAOS and USGS did not provide estimates at 20 ppb

Amit Kapatia, USEPA

Comparison: As(V) and As(III) Adsorption onto Granular Ferric Hydroxide and CPN Activated Alumina

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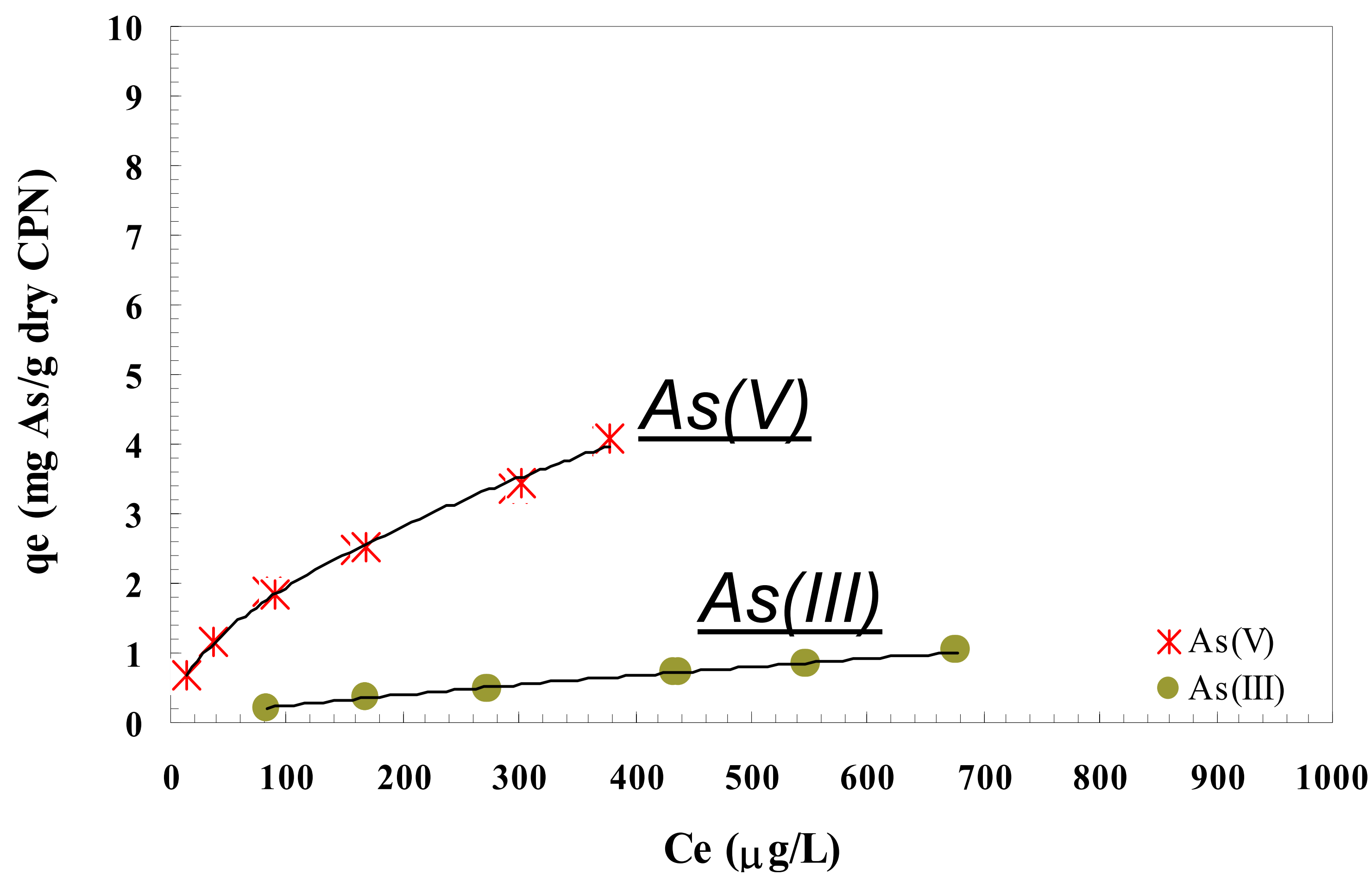
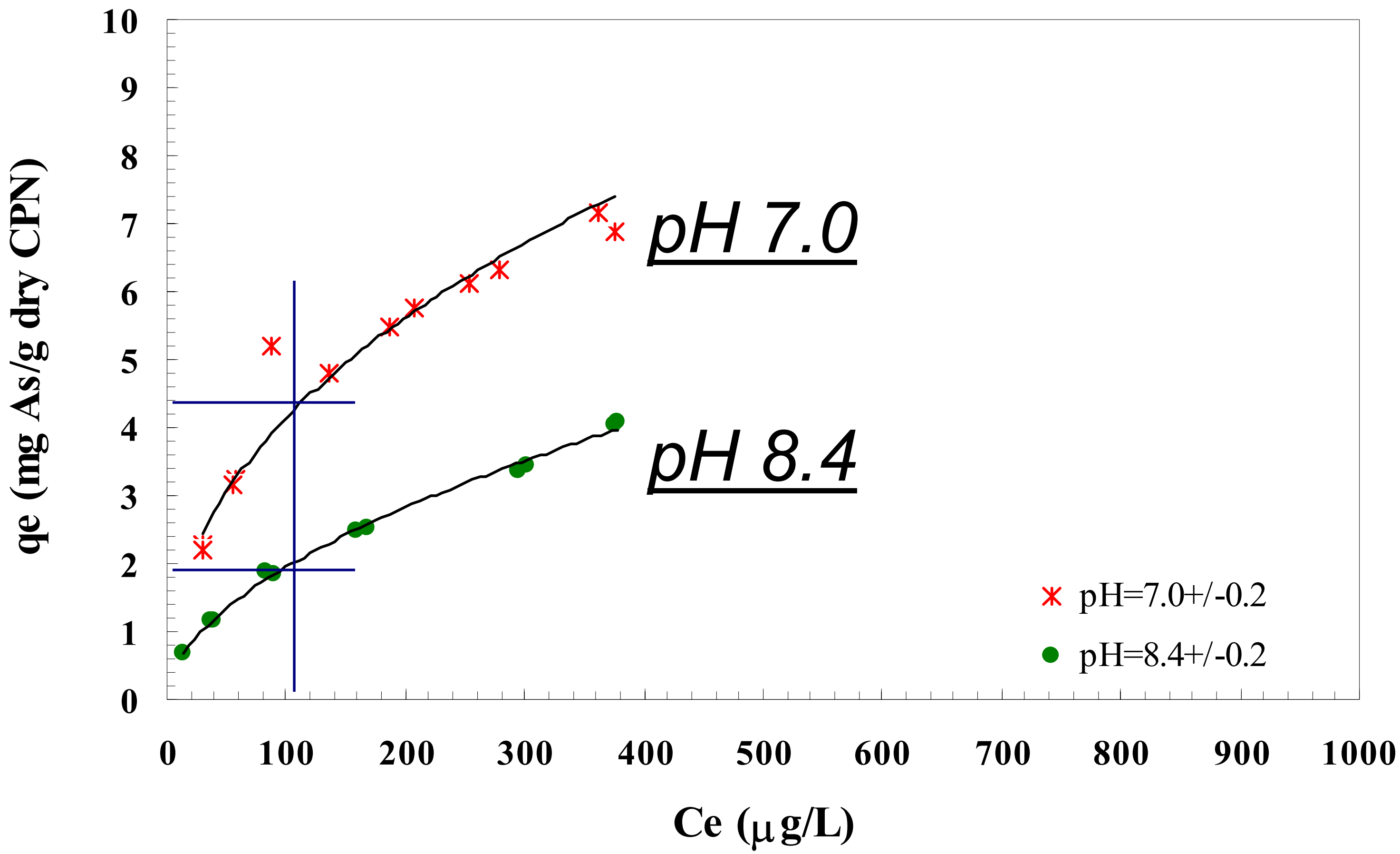
Comparison of As(V) vs As(III) Adsorption at pH=8.4±0.2, without Si



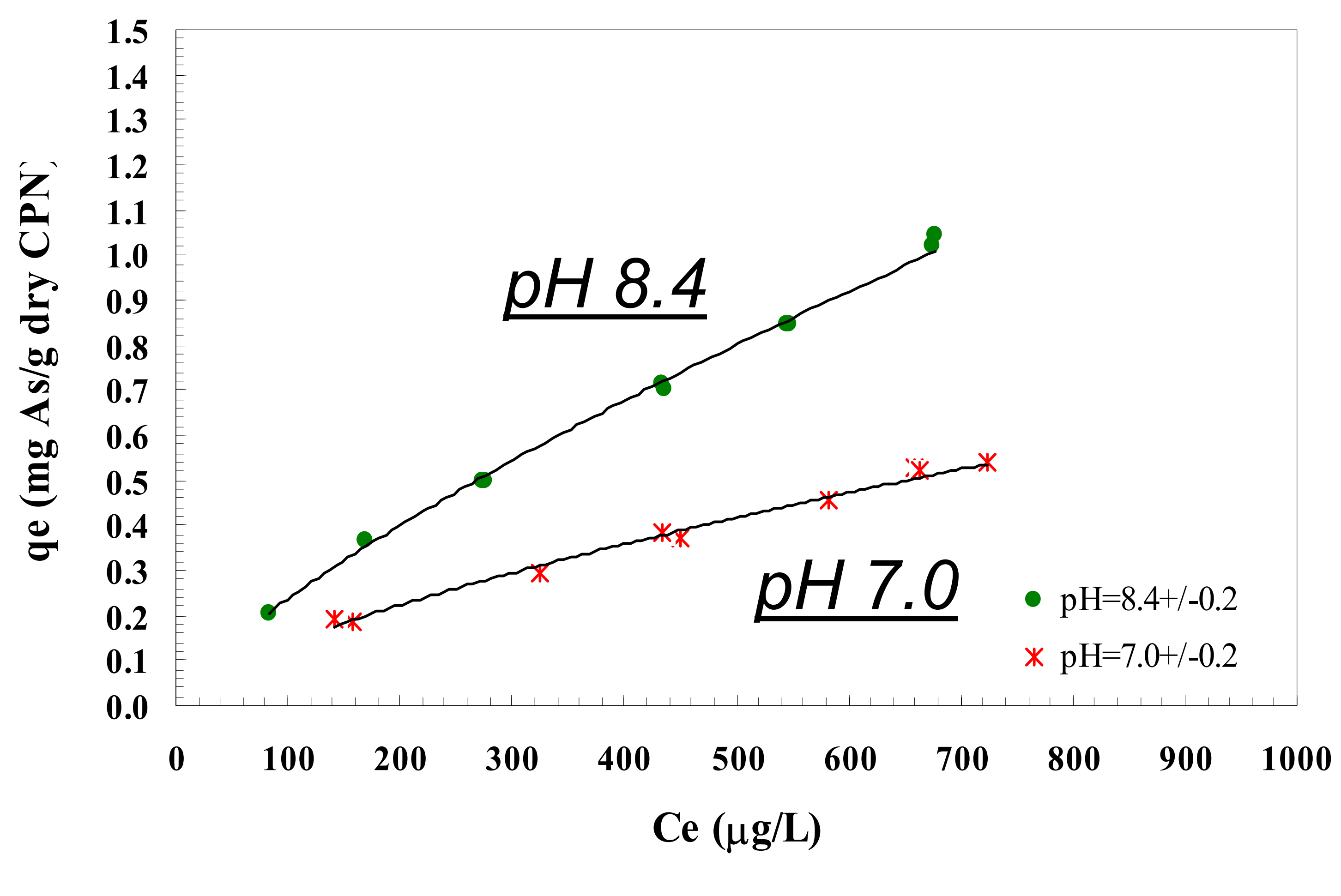
One day equilibrium isotherms for arsenic adsorption onto CPN in challenge water at pH =8.4+/-0.2, in the absence of silica

Effect of pH on As(V) Adsorption (without Si)



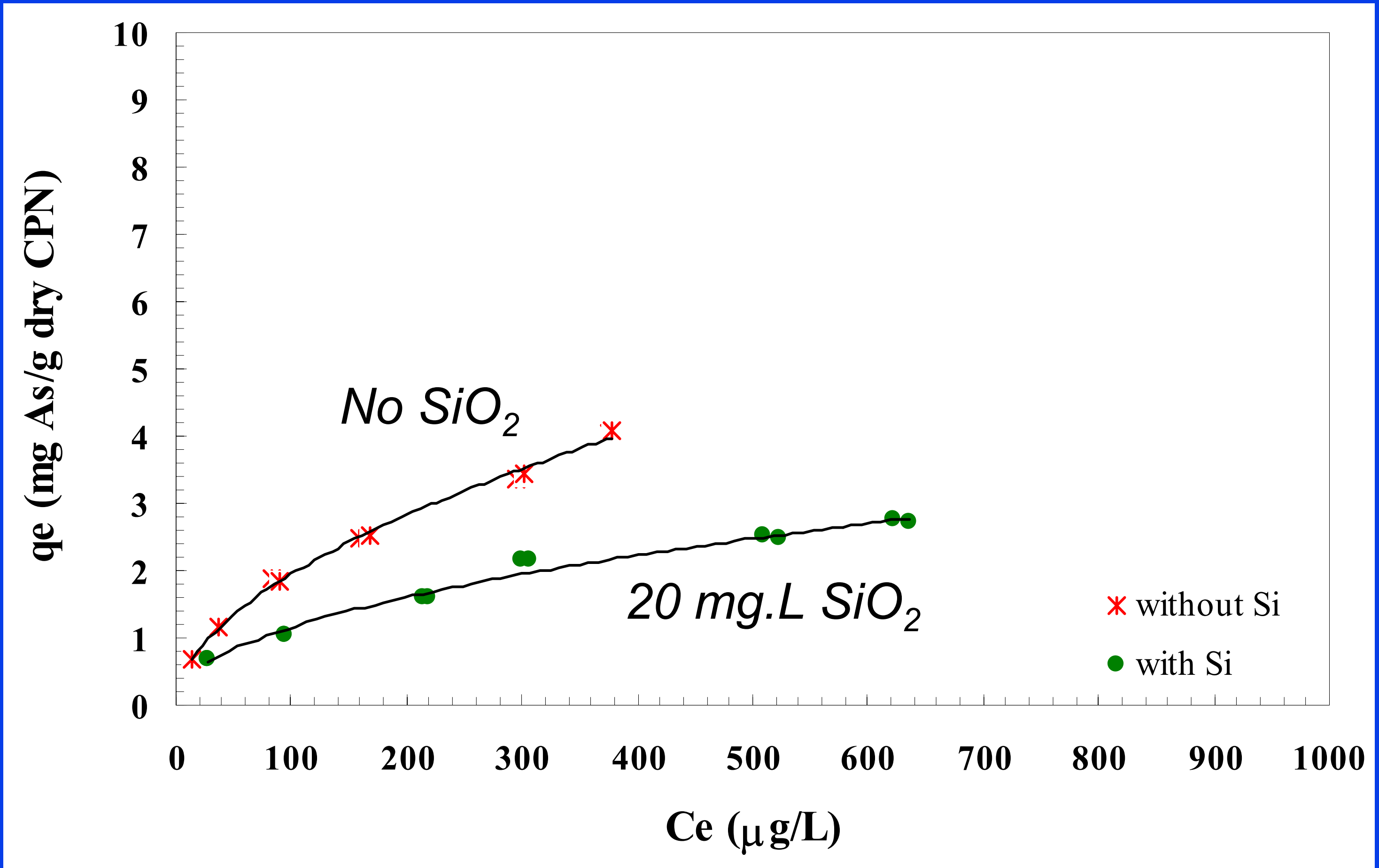
Effect of pH on As(V) adsorption onto CPN in challenge water in the absence of silica

Effect of pH on As(III) Adsorption (without Si)



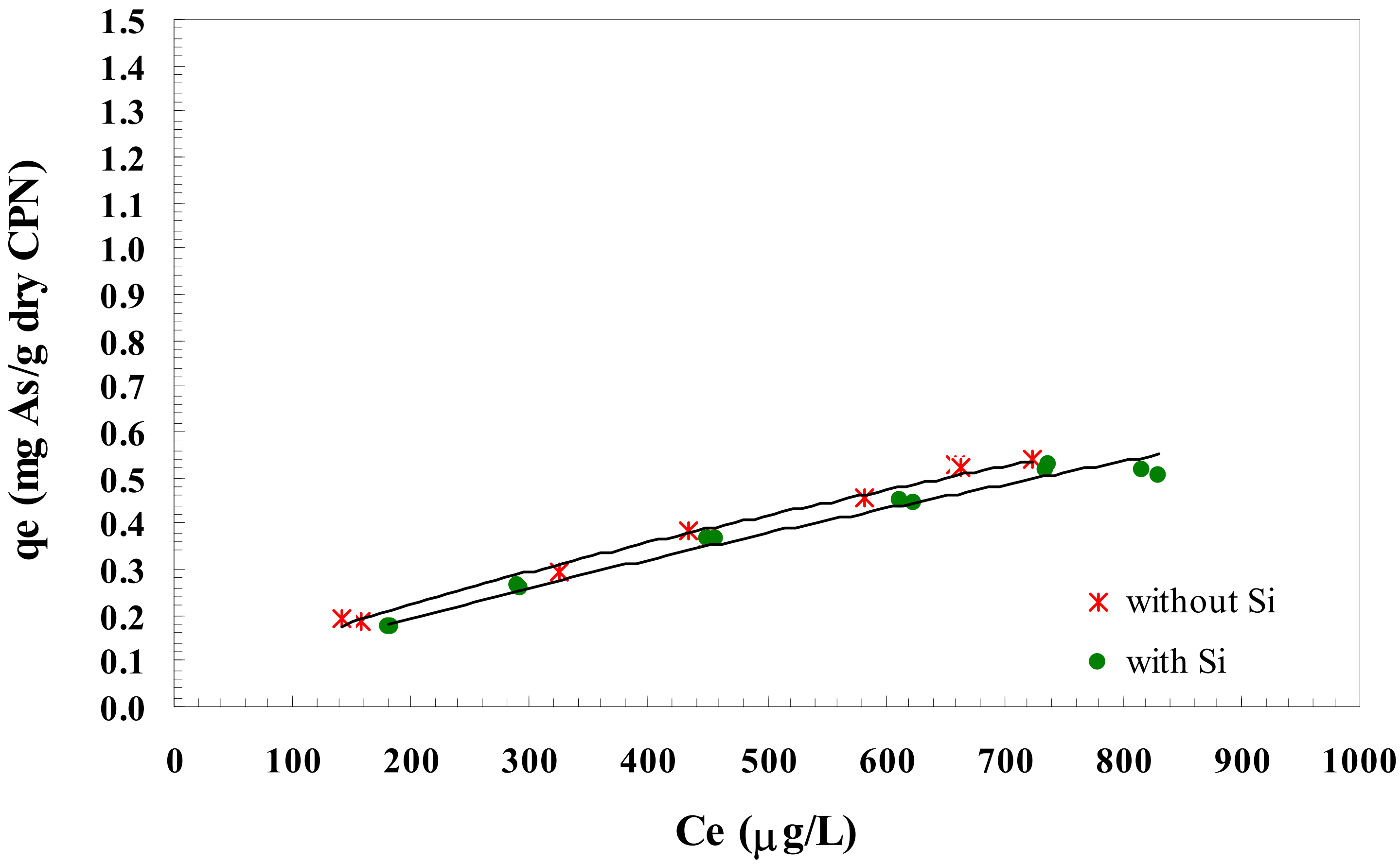
Effect of pH on As(III) adsorption onto CPN in challenge water in the absence of silica

Effect of Silica on As(V) Adsorption at pH=8.4±0.2



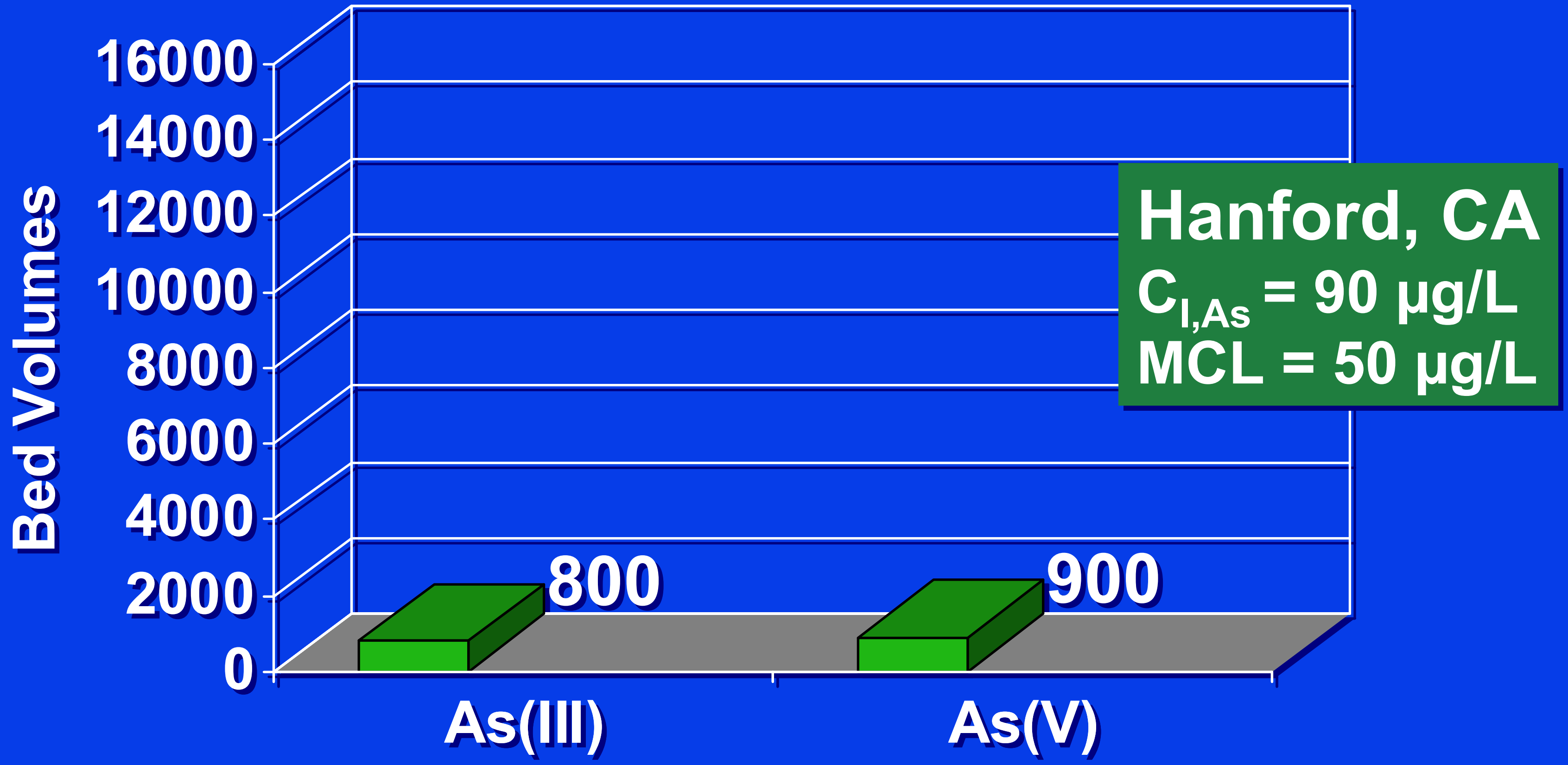
Effect of silica on As(V) adsorption onto CPN in challenge water at pH = 8.4+/-0.2

Effect of Silica on As(III) Adsorption at pH=7.0±0.2

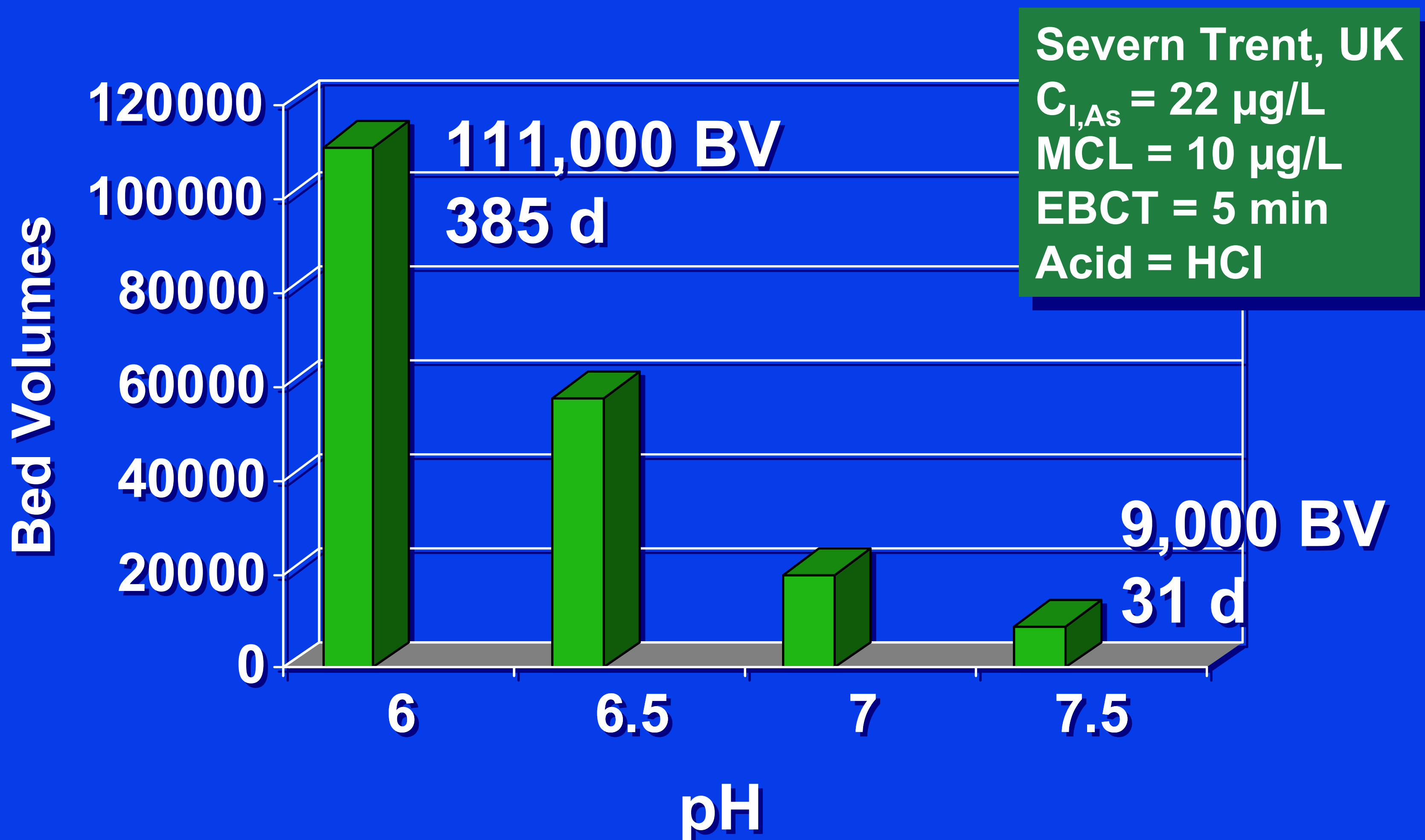


Effect of silica on As(III) adsorption onto CPN in challenge water at pH = 7.0+/-0.2

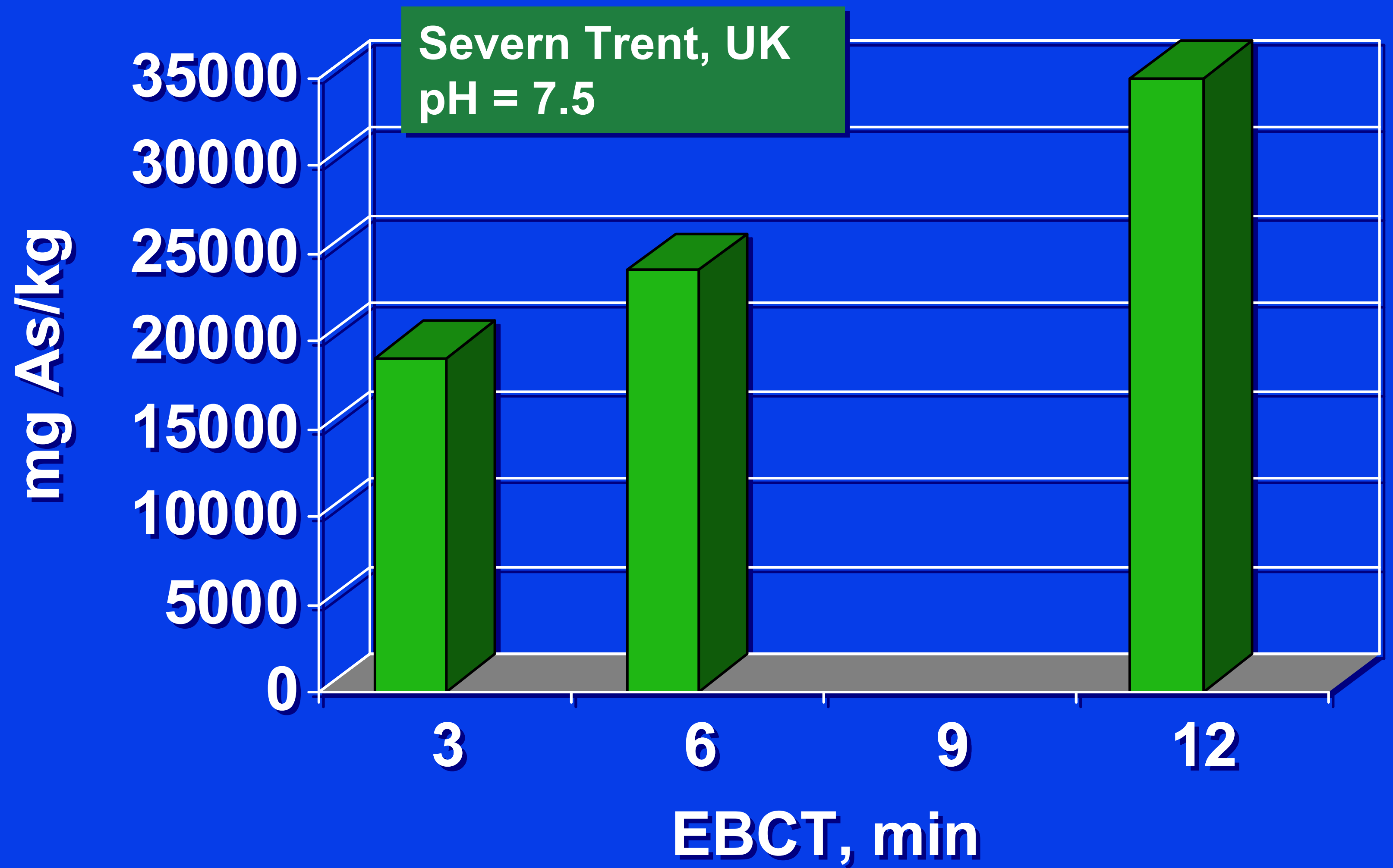
As(III) vs As(V) at pH 8.7



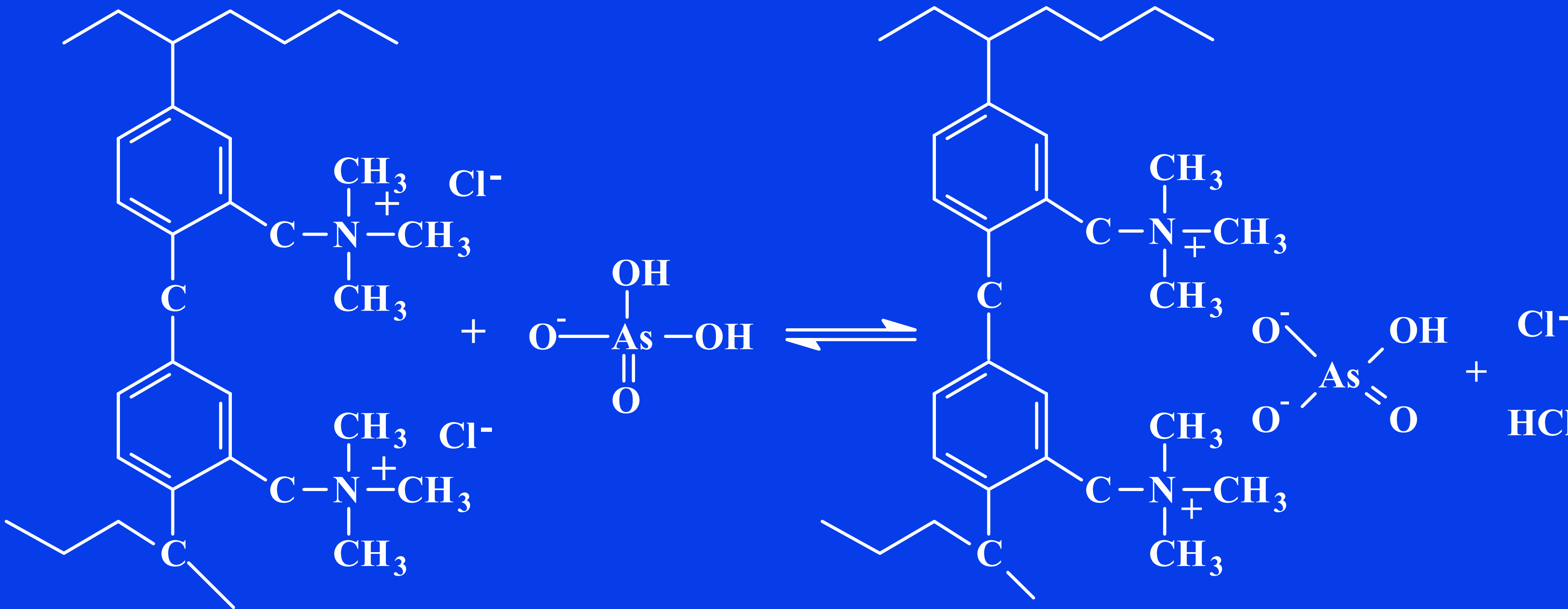
AAI—As(V) Capacity vs pH



AAl—As(V) Capacity vs EBCT

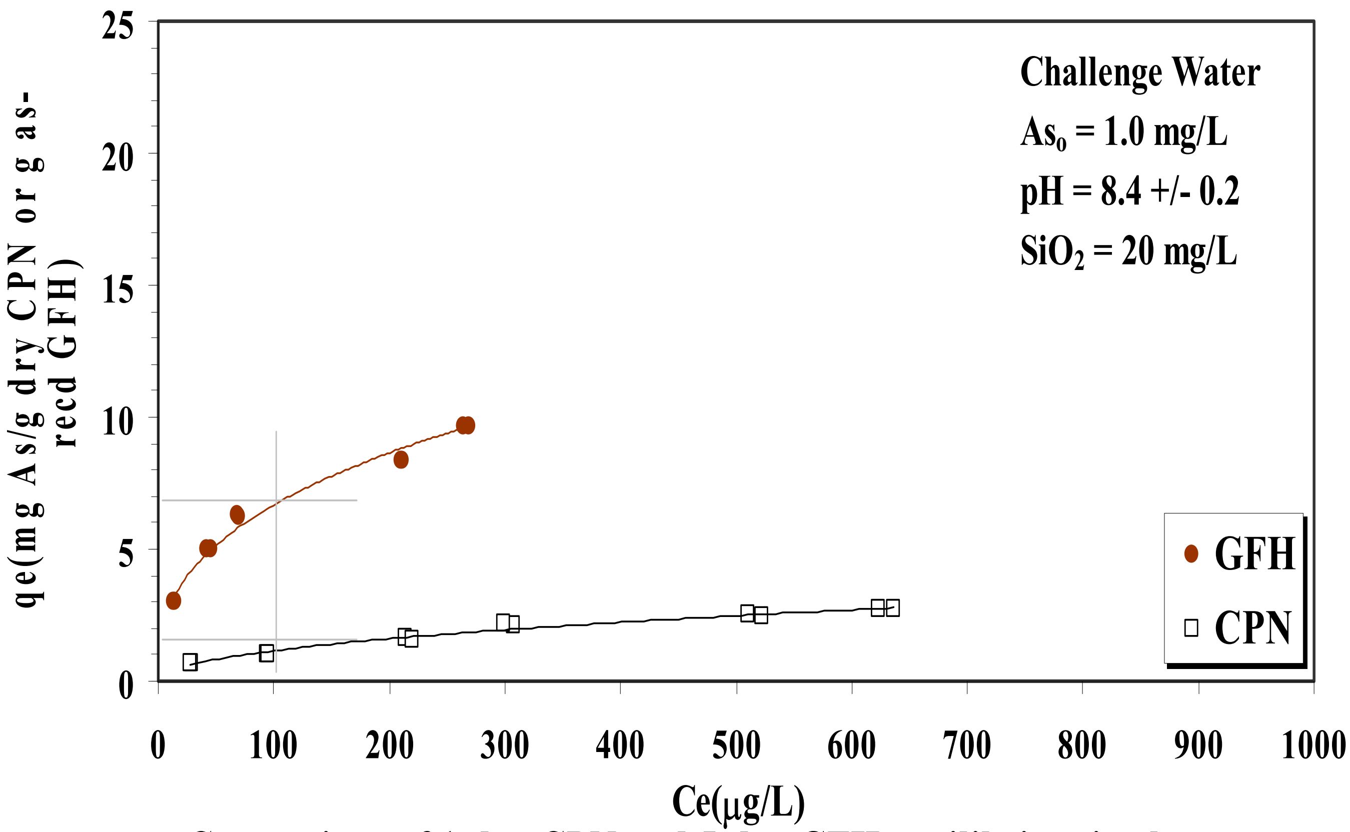


Arsenic Ion Exchange



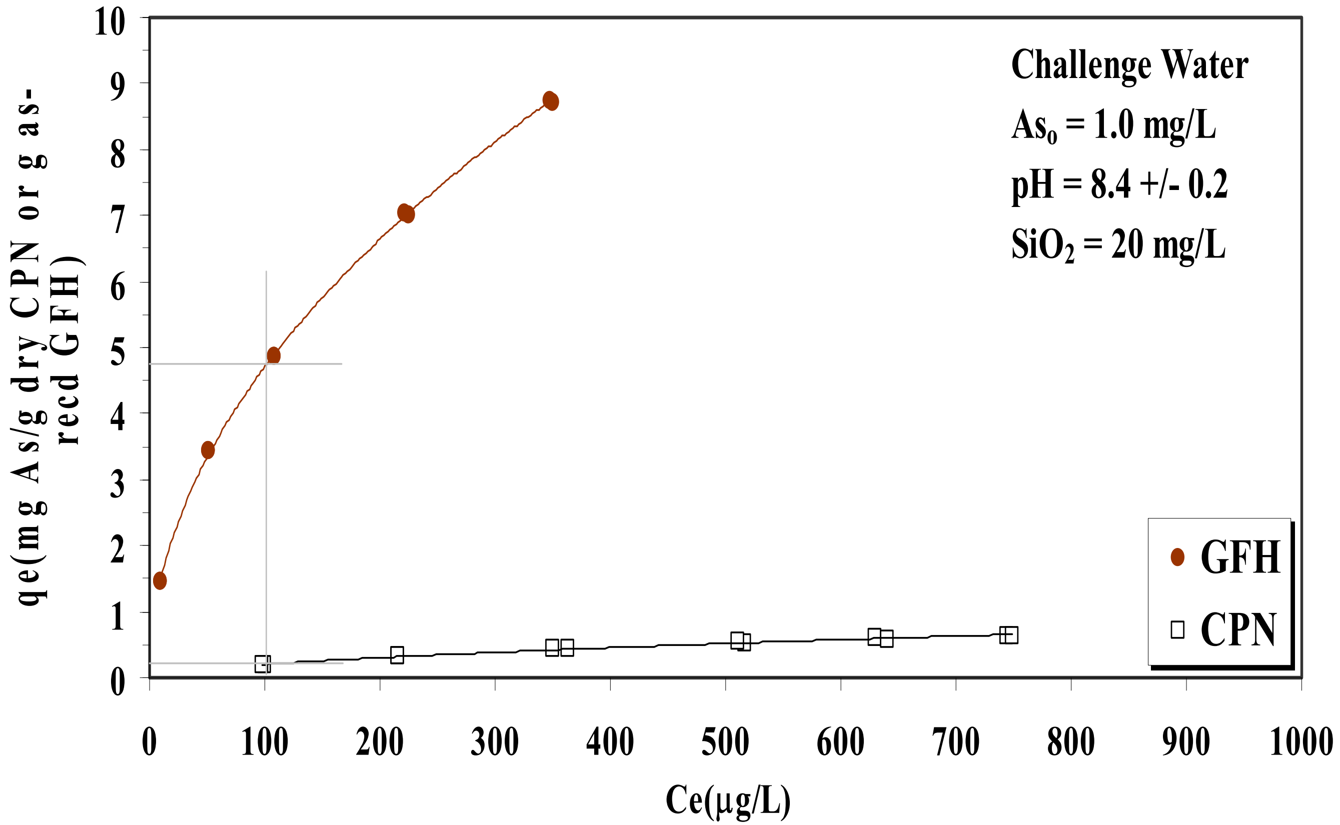
$$2\ RCl + H_2AsO_4^{\ -} = R_2HAsO_4 + HCl + Cl^-$$

GFH vs CPN Alumina, pH 8.4, As(V)



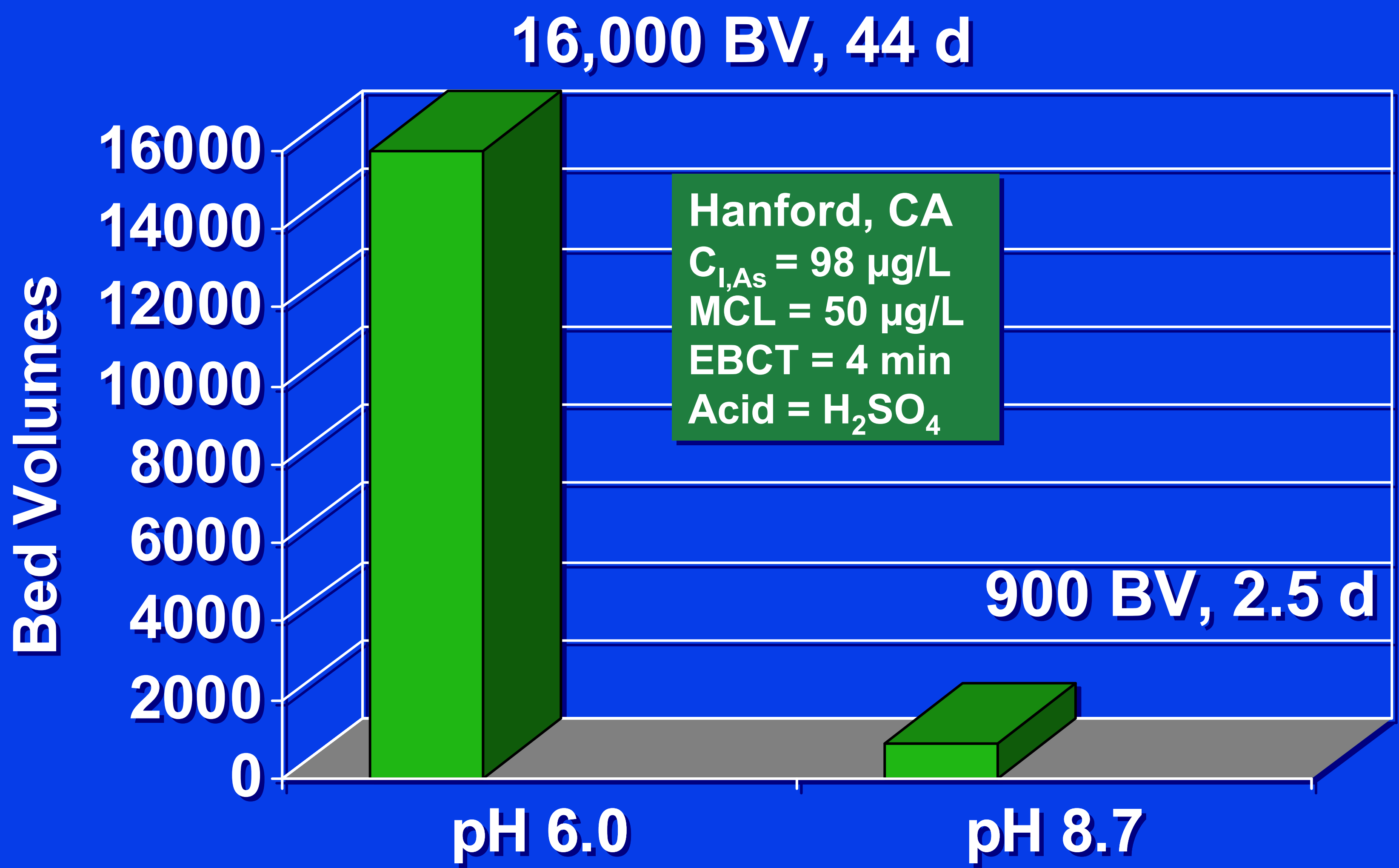
Comparison of 1-day CPN and 5-day GFH equilibrium isotherms, As(V), challenge water, pH = 8.4 +/- 0.2, with silica

GFH vs CPN Alumina, pH 8.4, As(III)

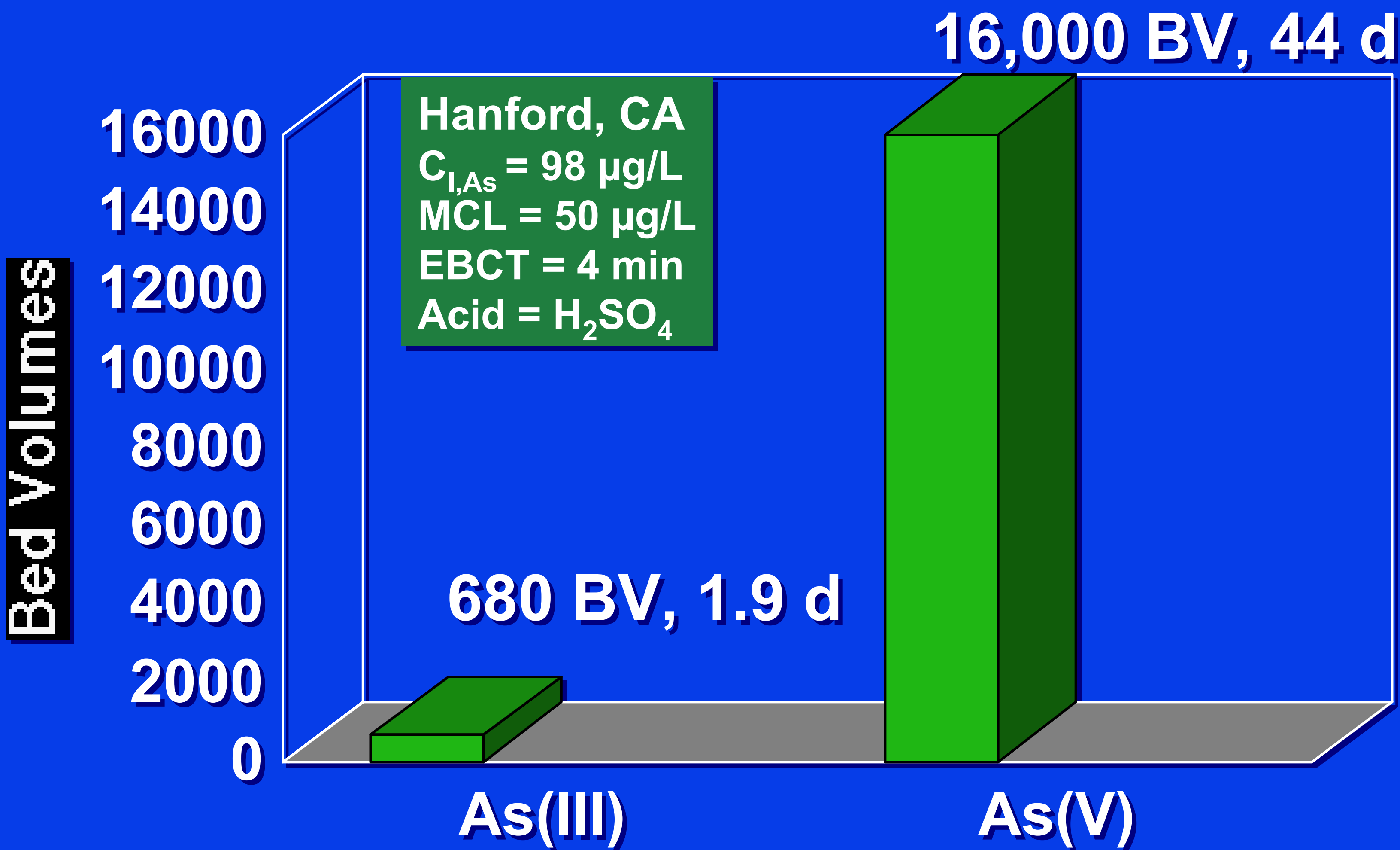


Comparison of 1-day CPN and GFH equilibrium isotherms, As(III), challenge water, pH = 8.4 +/- 0.2, with silica

Effect of pH on As(V)Run Length



As(III) vs As(V) at pH 6.0



Effect of pH on GFH Performance