The Evaluation of Competitive Adsorption on Selected Arsenic Adsorbents

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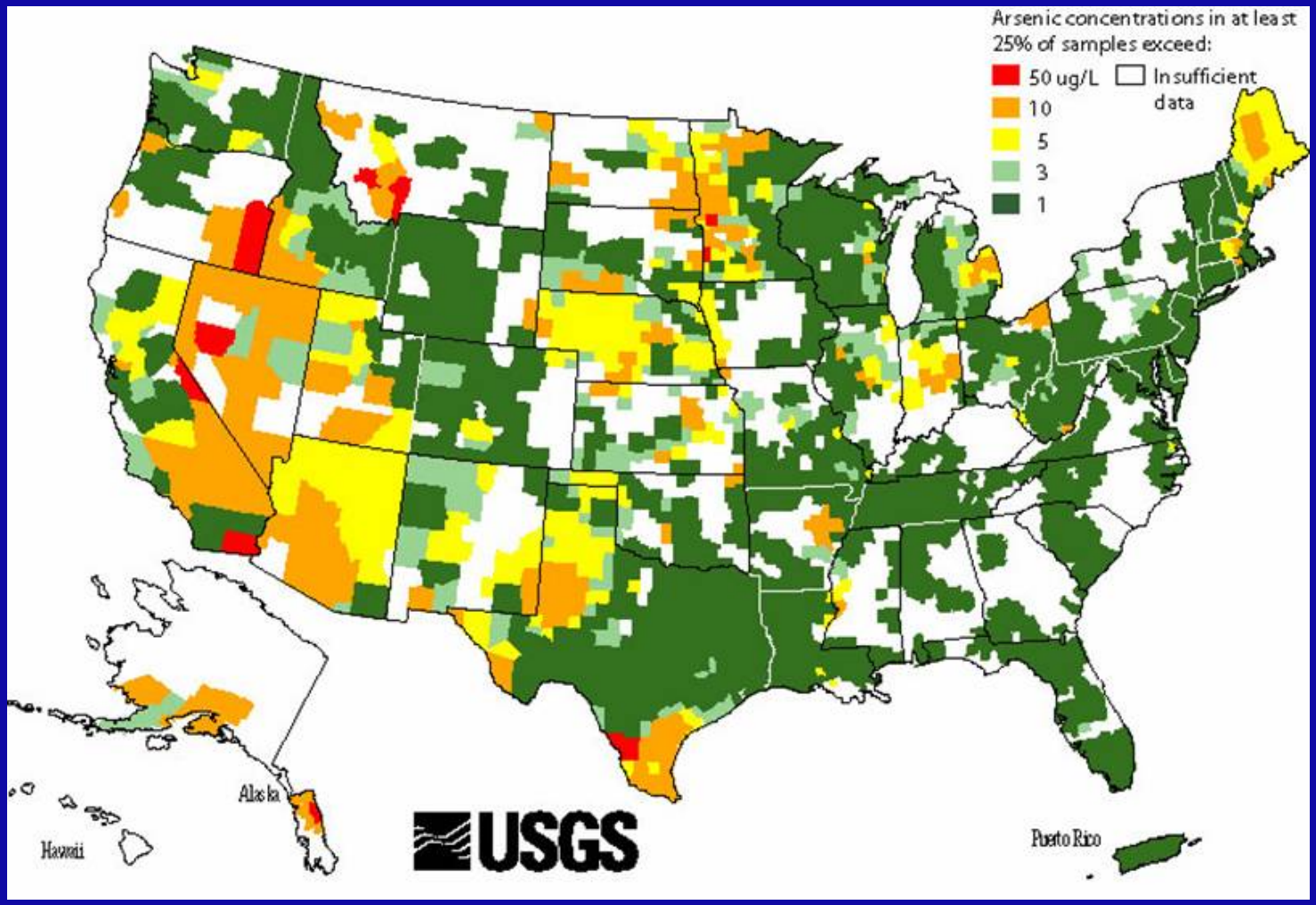
New Arsenic Rule

- Arsenic is a human carcinogen (EPA); long term exposure can cause e.g. cancer or heart disease
- New 10 µg/L Arsenic MCL (EPA)
- Effective from February 22, 2002; compliance deadline is January 23, 2006
- 4,000 public drinking water systems affected (97% small systems)
- ~13 million people affected
- Research – simple, cheap and efficient treatment technologies

Arsenic in Groundwater



Arsenic Occurrence and Speciation

- Naturally present in the environment (soil, rocks etc.)
- Mainly groundwater problem
- High Arsenic occurrence areas in the US:
  - Western states
  - Parts of the Midwest
  - New England

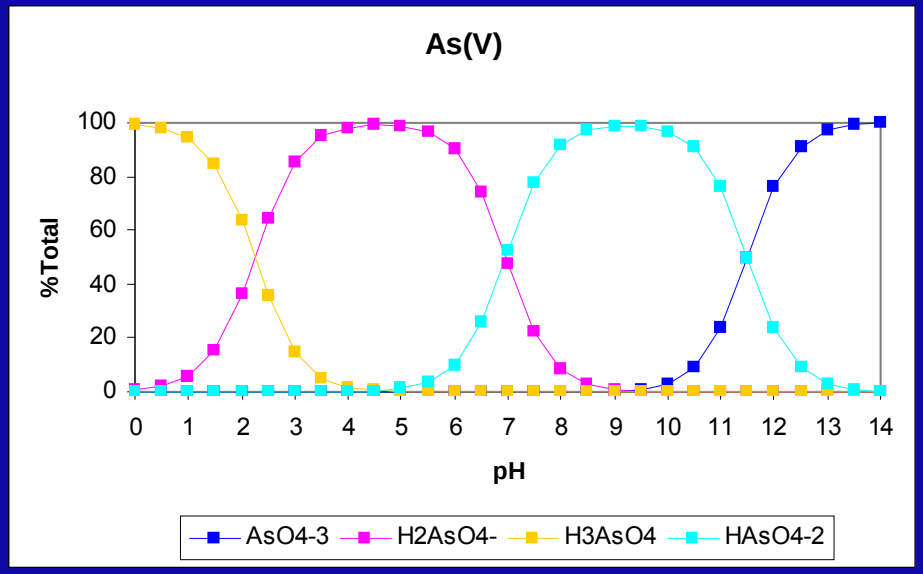
Speciation:

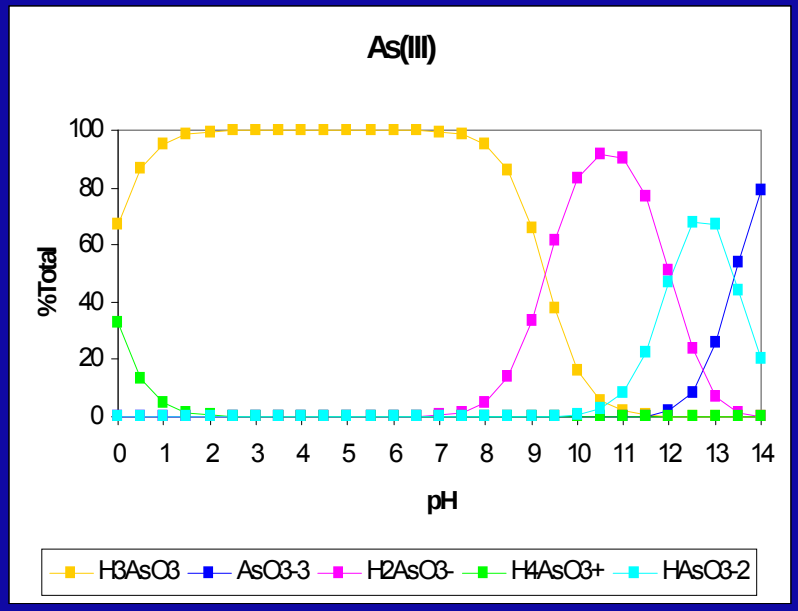
- As (III) – Arsenite, dominant in reduced environment

  Dominant form is H_3AsO_3 at pH < 9.3
- As (V) – Arsenate, dominant in oxidized environment

  Dominant forms are $H_2AsO_4^-$ at pH < 7 and $HAsO_4^{-2}$ at pH > 7

Arsenic Speciation Graphs





The pKa values for As(V) are 2.2, 7, and 11.5 and for As(III) 9.3, 12, and 13.4. T = 25 ºC and I = 0.000M.

Research Objectives

Preliminary Adsorbent Evaluation

- To test the arsenic removal efficiency of potential adsorbent materials
- To conduct kinetic and isotherm studies for selected adsorbents

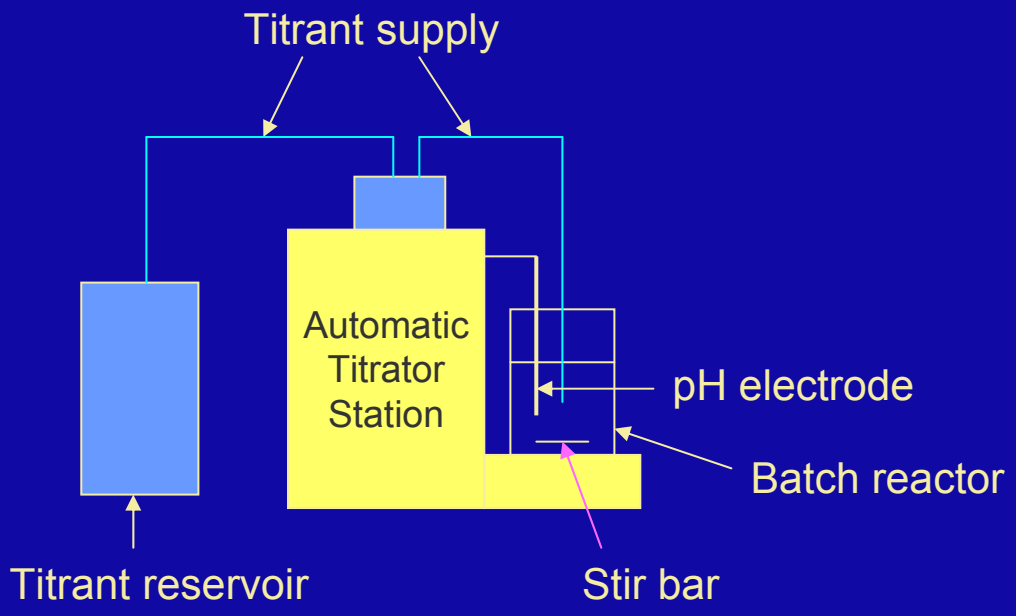
Anion Competition Study

- To evaluate the effect of competing anions on arsenic adsorption and establish a preferential anion removal series for the selected adsorbents

Experimental Approach

Experimental Apparatus:

- Constant temperature (22-23 °C) and pH (6)
- Time (2-3 hrs)



Experimental Approach (cont'd)

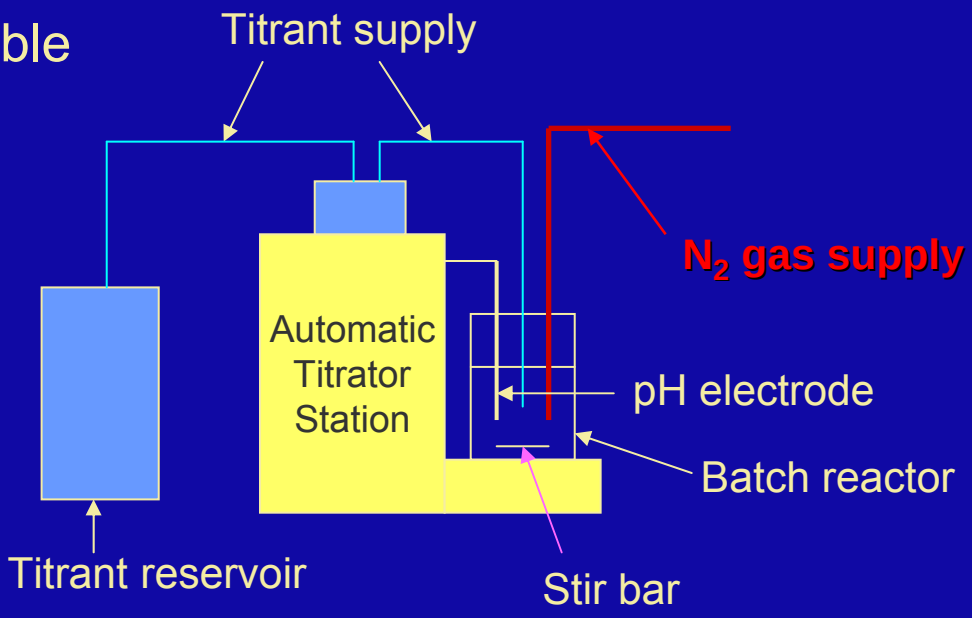
Typical solution composition (isotherm studies):

- Background alkalinity 50 mg $CaCO_3$ /L
- Background ionic strength 0.01M
- Arsenic as As(V) [0.15-2.0 mg/L]
- Adsorbents (powder or granular) [56-5556 mg/L]

Experimental Approach (cont'd)

Anion competition studies:

- Nitrogen gas constantly bubbled through solution
- Competing anions added
- No background alkalinity adjustment
- Ionic strength 0.075M or variable



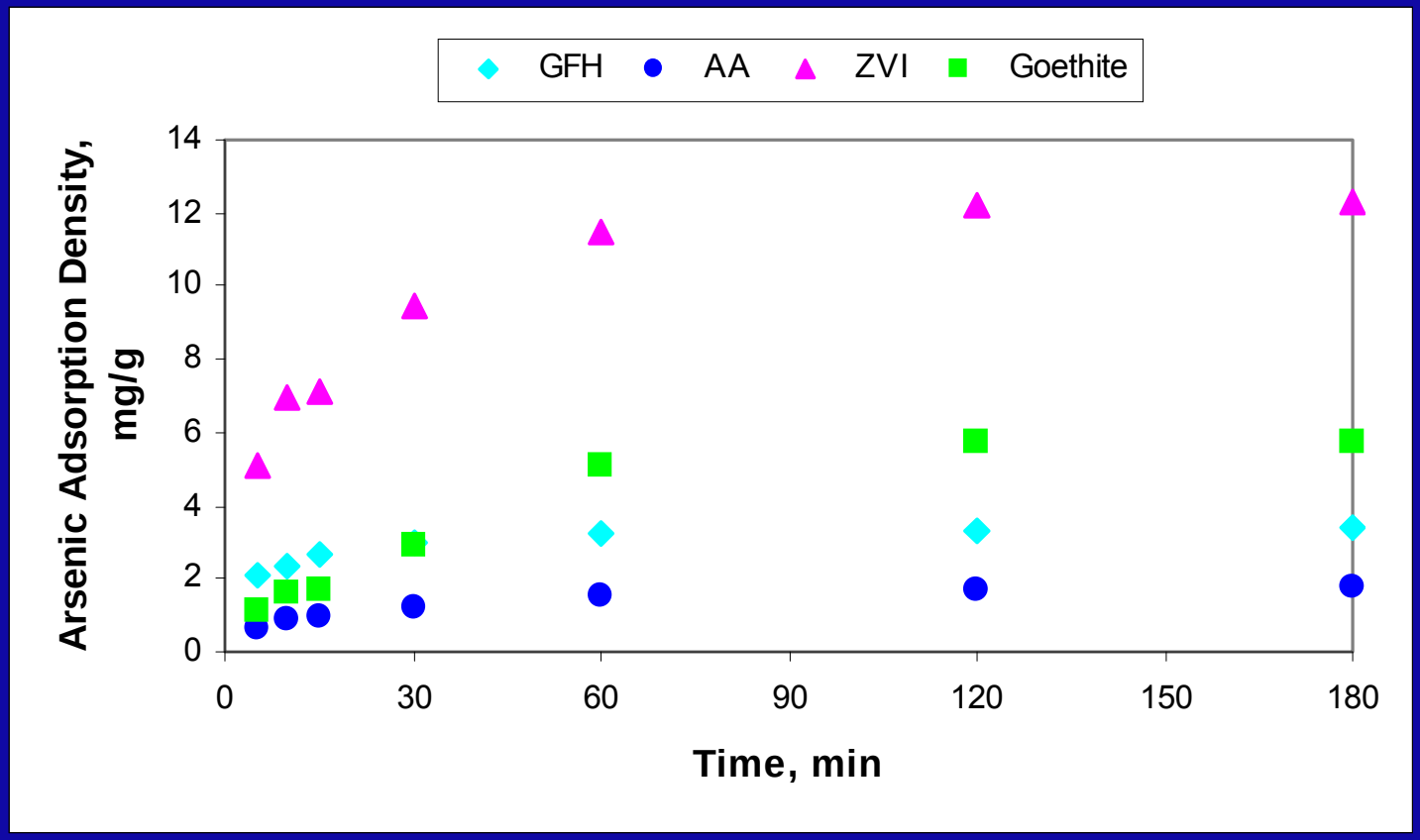
Results and Discussion Outline

- Adsorbent Materials Tested
- Kinetic Study
- Isotherm Study
- Anion Competition Study
  - Preferential Anion Adsorption Series
  - Effect of Ionic Strength
  - Effect of Normalizing Anion Concentration Differences
- Treated Volume Example

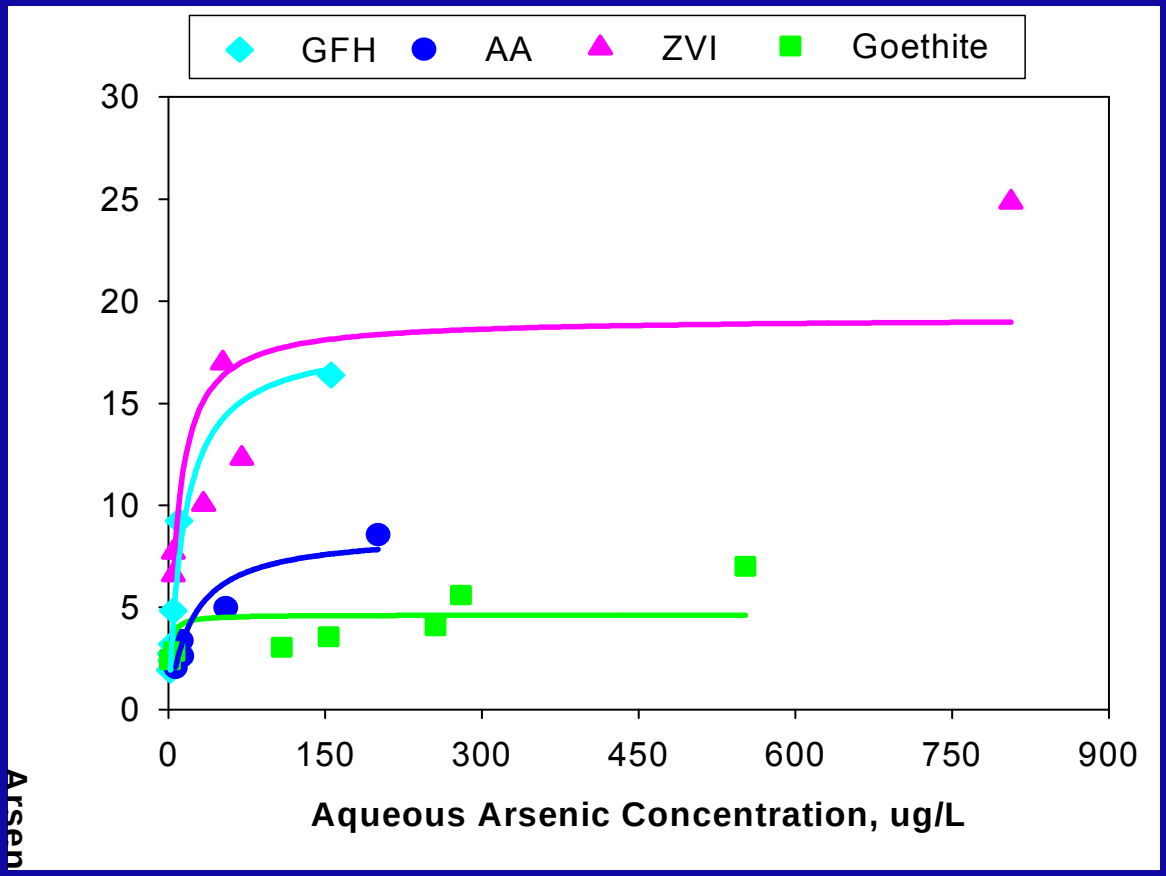
Adsorbent Materials Tested

#	Adsorbent Material	Grain Size, um (mesh)	Adsorption Density, ug/g	Arsenic Removal, %
1	Granular Ferric Hydroxide, GFH	<150	**2318**	**99**
2	Magnesium Oxide	<150	1329	55
3	Activated Alumina AA	(80 - 200)	**1669**	**96**
4	MN4 Celatom Diatomite (DE)	<150	6	24
5	AbsorbaKleen	<23	252	27
6	Carasol	250 - 700	157	17
7	Apatite (mineral)	<177	0	0
8	Zero-Valent Iron ZVI	<177	**799**	**98**
9	Bone Char	<177	56	8
10	Celite	<150	27	4
11	Fishbone	"filings"	17	3
12	Magnetite	<5	120	18
13	Hematite	<5	355	56
14	Goethite	(30 - 50)	**626**	**99**
15	DE coated with Hematite	<300	**1734**	**97**

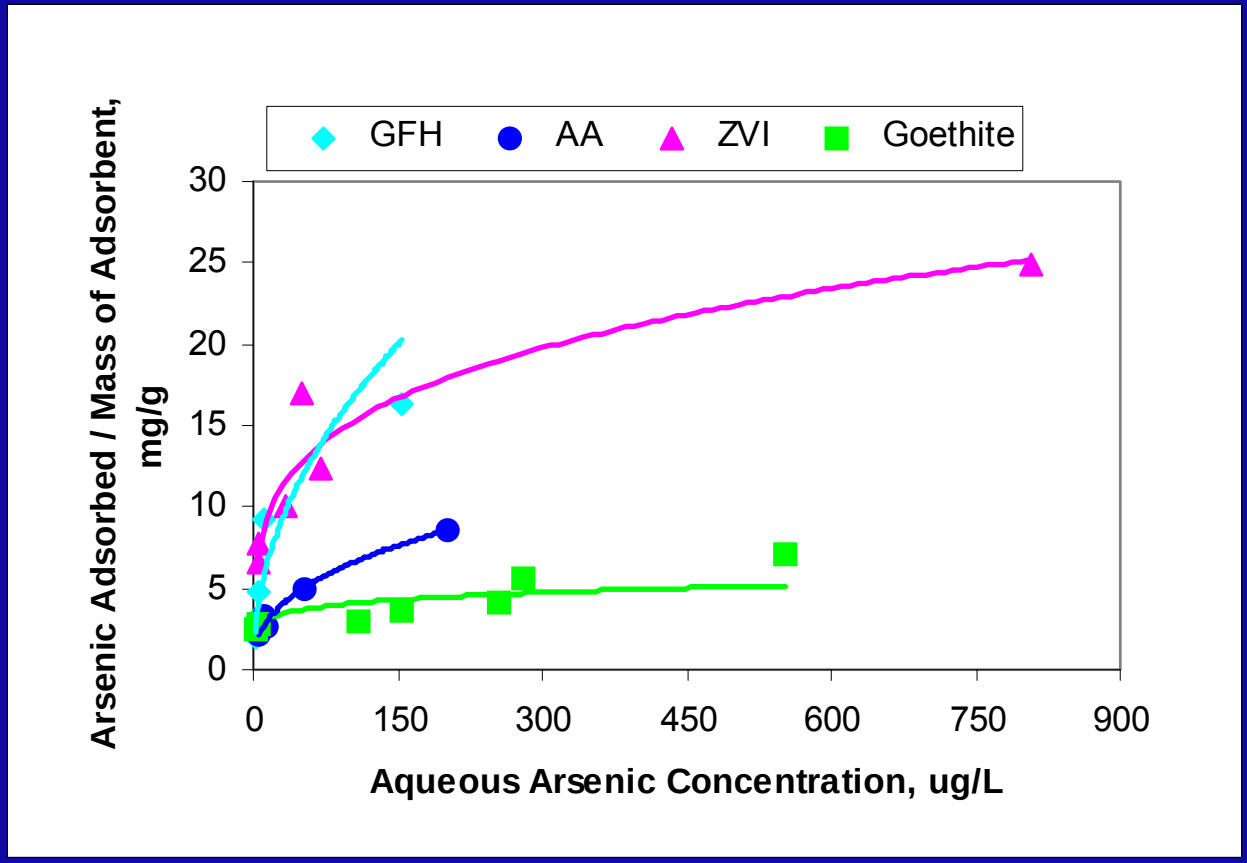
Kinetic Study



Langmuir Isotherms



Freundlich Isotherms



Isotherm Constants

Langmuir Isotherm

Adsorbent	Nmax	b	R^2
GFH	18.2485	0.0680	0.9853
AA	8.6863	0.0459	0.9527
ZVI	19.1832	0.1108	0.8255
Goethite	4.6325	0.7200	0.6814

Freundlich Isotherm

Adsorbent	K(F)	1/n	R^2
GFH	1.8173	0.4783	0.8703
AA	1.0326	0.3992	0.9614
ZVI	4.9148	0.2440	0.8994
Goethite	2.1218	0.1411	0.6814

Research Goals for the Anion Competition Study

- To determine which anions have significant influence on arsenic removal
- To rank the competing anions in a preferential adsorption series
- To compare anion competition between the 3 adsorbent materials tested (AA, GFH, and goethite)

Competing Anions Tested

Anion	Max. Concentration, mg/L
Phosphate [H2PO4-]	1
Sulfate [SO4-2]	250
Nitrate [NO3-]	45
Ortho-silicate [Si(OH)4]	50
Fluoride [F-]	2
Bicarbonate [as CaCO3]	250
Natural Organic Matter [as DOC]	4

Design of Experiments

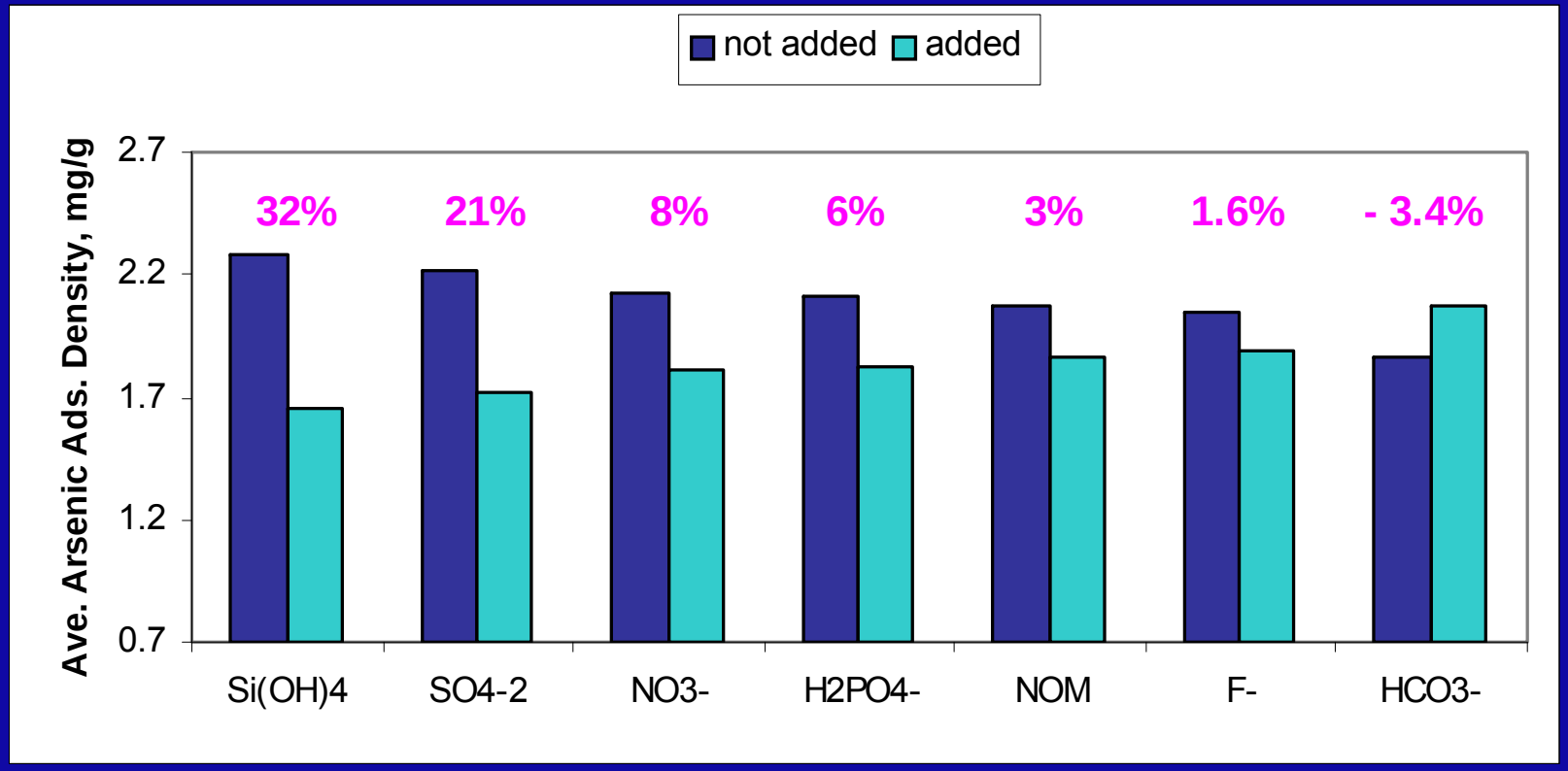
Fractional factorial design of experiment and ANOVA test:

The influence of each anion as %contribution to the total variation in arsenic adsorption is estimated. The experimental error or unexplained variation can be estimated as well.

- 7 factors – competing anions
- 2 levels for each factor – anion was not or was added
- L16 Orthogonal Array – 16 experiments (for each adsorbent)
- Experimental resolution – the effect of all main factors and groups of two-factor interactions was estimated

Anion Competition Factor Plot

On Activated Alumina



Enhancing Effect of Bicarbonate

- Observed on Activated Alumina (AA)
- Wijnja et al. (2000) also observed carbonate enhancing effect (sulfate adsorption on AA at pH 6)
- The process was described with the following concurrent adsorption reactions:

$$Al\text{-}OH + HCO_3^- \leftrightarrow Al\text{-}OCOO^- + H_2O$$

$$Al\text{-}OH + H^+ \leftrightarrow Al\text{-}OH_2^+$$

- Possible mechanism – generation of additional adsorption sites by extra protonated surface groups

Preferential Anion Adsorption Series

- **Activated Alumina** (7% error, 18% interactions):

  32% 21% 8% 6% 3% 1.6%

  $Si(OH)_4 > SO_4^{-2} > NO_3^- \sim H_2PO_4^- > NOM \sim F^-$

- **Granular Ferric Hydroxide** (3% error, 14% interactions):

  31% 21% 10% 8% 7% 6%

  $SO_4^{-2} > Si(OH)_4 > F^- \sim H_2PO_4^- \sim NOM \sim HCO_3^-$

- **Goethite** (3% error, 30% interactions):

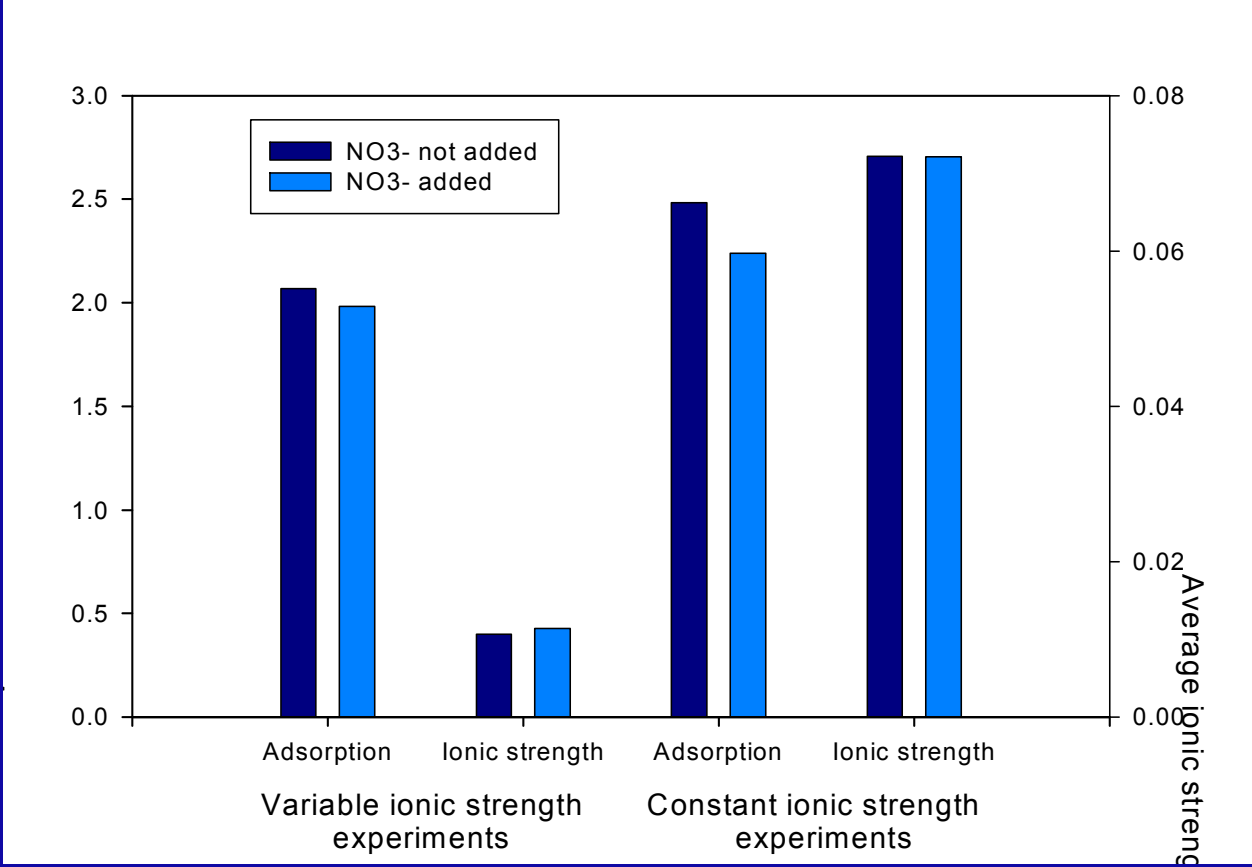
  33% 12% 10% 1.5%

  $Si(OH)_4 > H_2PO_4^- \sim NO_3^- > F^-$

Effect of Ionic Strength

- Experiments with no background ionic strength adjustment
- I = 0.0001-0.0224M vs. previous 0.075M
- As I increased, the influence of:
  - SO_4^{-2} increased on AA and GFH
  - $Si(OH)_4$ and $H_2PO_4^-$ increased on goethite
  - NO_3^- increased on AA and goethite

Effect of Ionic Strength (cont'd)



Effect of Normalizing Anion Concentration Differences

- Experiments with equal milliequivalent based anion concentrations (5.2 meq/L)
- Only conducted with AA
- I = 0.0105 to 0.0235 M (extremes: 0.0001 to 0.034M)
- **Findings:**

  21% 15% 2.6% 0%

  - $Si(OH)_4$ > F^- > SO_4^{-2} > HCO_3^-
  - F^- exhibited increased influence when present at higher concentrations (15% vs. 1.6% at lower conc.)

Estimated Treated Volume Differences Due to Anion Competition

Assumptions:

- Single column
- Constant influent Arsenic concentration
- Constant temperature and pH
- Equilibrium conditions
- Treatment till exhaustion of adsorbent material
- Adsorption based on both Freundlich and Langmuir isotherms

Estimated Treated Volume Differences Due to Anion Competition (cont'd)

Volume treated per g filter material – assuming 50µg/L column influent arsenic concentration

Isotherm Model	Adsorbent	No Anions Present	Anions Present*	
		Volume, L/g	Volume, L/g	Decrease in Vol., %
Freundlich	AA	98	60	**39**
	ZVI	256	n/a	n/a
	GFH	236	198	**16**
	goethite	74	61	**18**
Langmuir	AA	120	82	**31**
	ZVI	325	n/a	n/a
	GFH	282	244	**14**
	goethite	90	77	**14**

1 L/g = 119.8 gal/lb; pH = 6; T = 21-23 C; No anions: I = 0.01M; * I = 0.075M, max. realistic anion concentrations

Significant Findings

- Anions decreased arsenic adsorption on AA, GFH, and goethite
- Varying ionic strength and initial anion concentrations

↓ influenced

anion adsorption

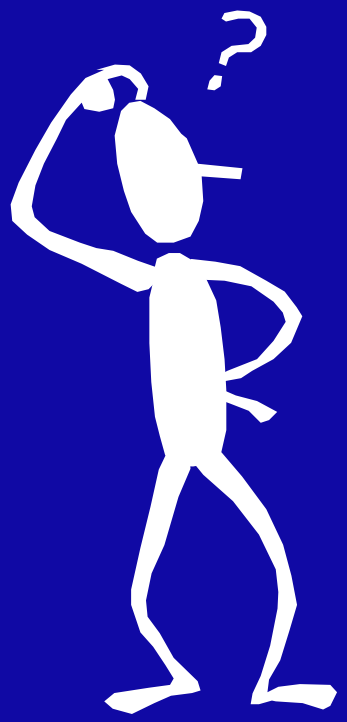
↓ influenced

competition with Arsenic

Significant Findings (cont'd)

- Preferential anion adsorption series were established for AA, GFH, and goethite
- **Silicate** competed with As for adsorption sites on all 3 adsorbents at pH 6 (!)
- **Sulfate** also competed (esp. on AA and GFH). Sulfate was influenced by the ionic strength conditions as well.
- **Bicarbonate** slightly enhanced As adsorption on AA
- **Fluoride** competed with As on AA when present at higher concentrations

Questions?



Orthogonal Array Experimental Design

Experiment	Anion, mg/L						
	H2PO4-	**SO4-2**	**NO3-**	**Si(OH)4**	**F-**	**HCO3-** (as CaCO3)	**NOM** (as DOC)
1	0	0	0	0	0	0	0
2	0	0	0	50	2	250	4
3	0	0	45	0	0	250	4
4	0	0	45	50	2	0	0
5	0	250	45	0	2	0	4
6	0	250	45	50	0	250	0
7	0	250	0	0	2	250	0
8	0	250	0	50	0	0	4
9	1	0	45	0	2	250	0
10	1	0	45	50	0	0	4
11	1	0	0	0	2	0	4
12	1	0	0	50	0	250	0
13	1	250	0	0	0	250	4
14	1	250	0	50	2	0	0
15	1	250	45	0	0	0	0
16	1	250	45	50	2	250	4

Recommendations for Future Research

- Evaluate anion competition at other pH values, e.g pH 7 or 8
- Further evaluate ZVI
- Further evaluate diatomaceous earth coated with hematite and other adsorbents, e.g. AA and various iron types
- Column studies – anion competition under continuous-flow conditions?