

# The Evaluation of Competitive Adsorption on Selected Arsenic Adsorbents

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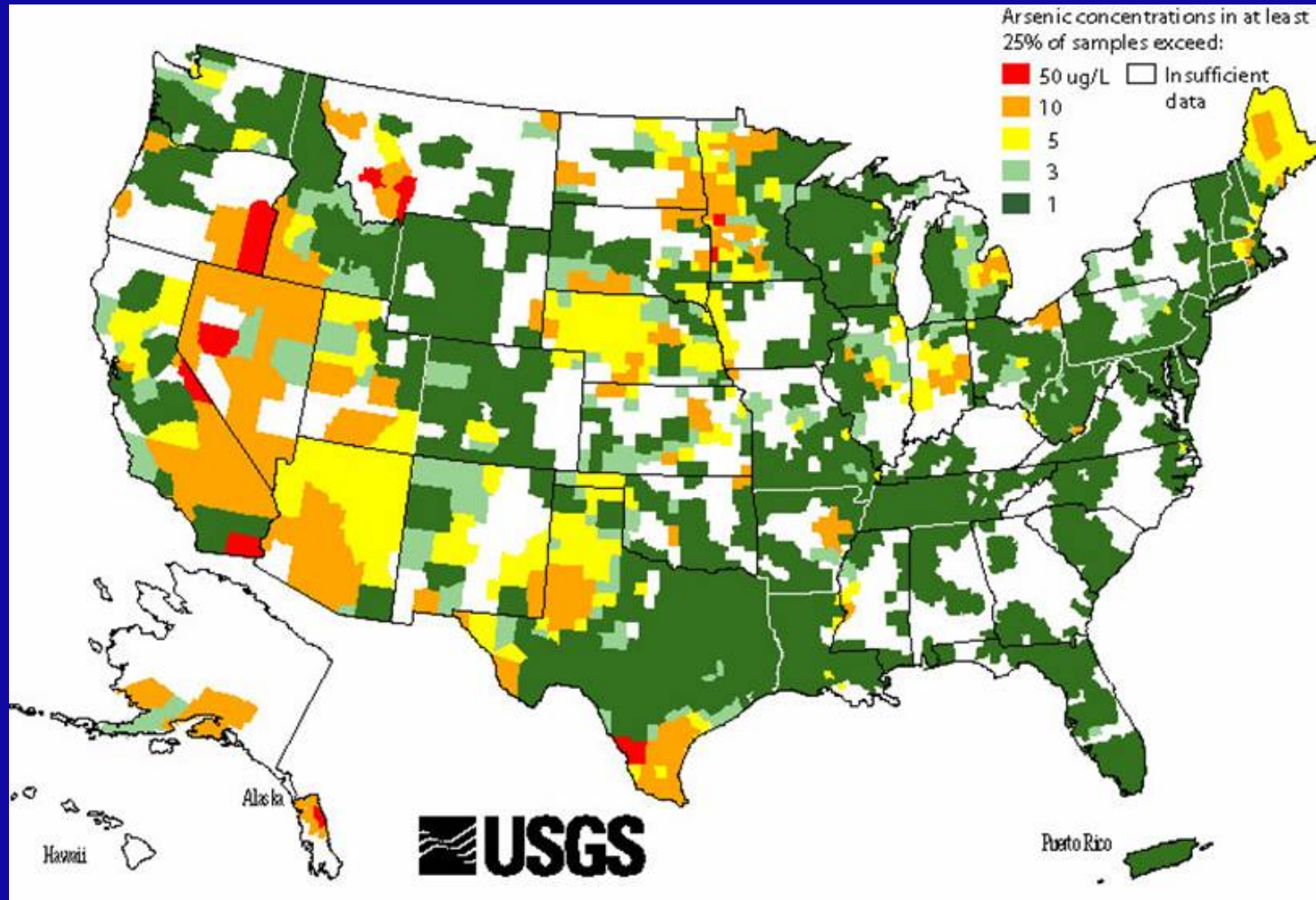
# Acknowledgements

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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



Background

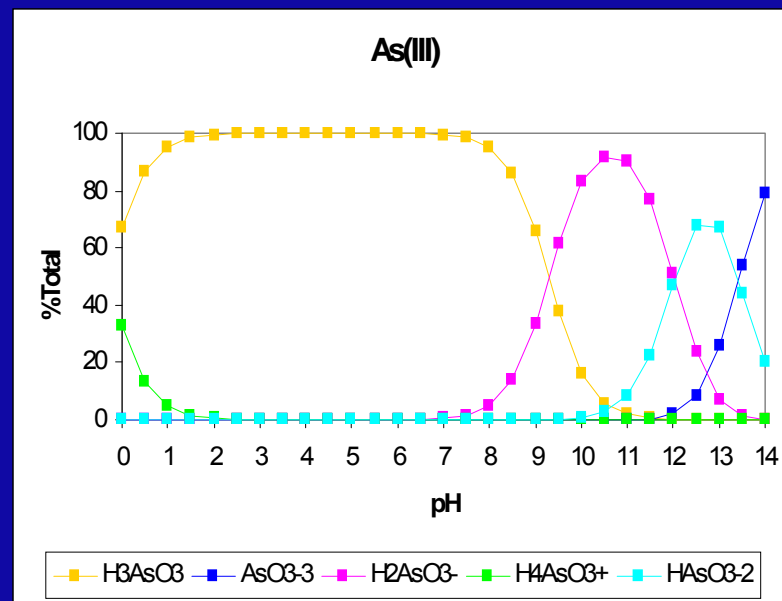
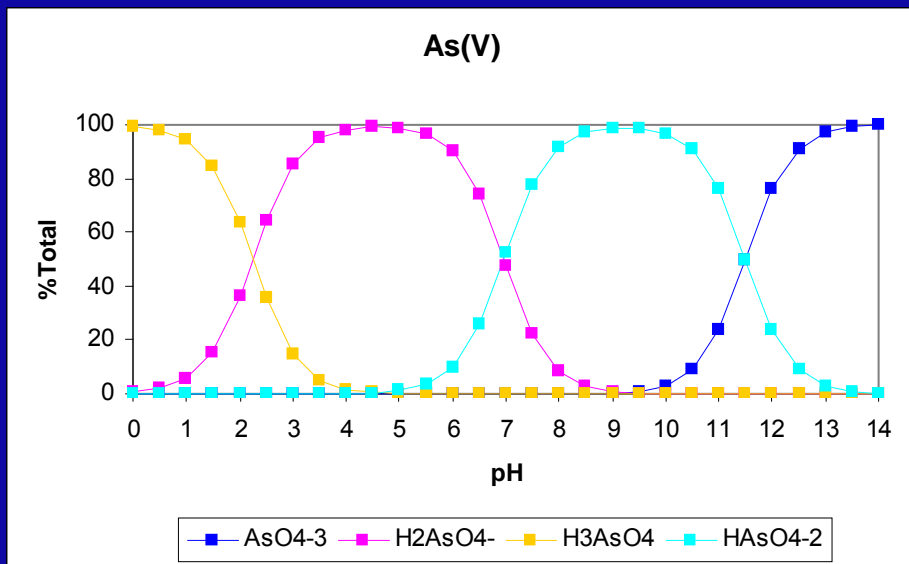
# Arsenic Occurrence and Speciation

- 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  $\text{H}_3\text{AsO}_3$  at  $\text{pH} < 9.3$
- As (V) – Arsenate, dominant in oxidized environment  
Dominant forms are  $\text{H}_2\text{AsO}_4^-$  at  $\text{pH} < 7$  and  $\text{HAsO}_4^{2-}$  at  $\text{pH} > 7$

# Arsenic Speciation Graphs



The pK<sub>a</sub> values for As(V) are 2.2, 7, and 11.5 and for As(III) 9.3, 12, and 13.4. T = 25 °C 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

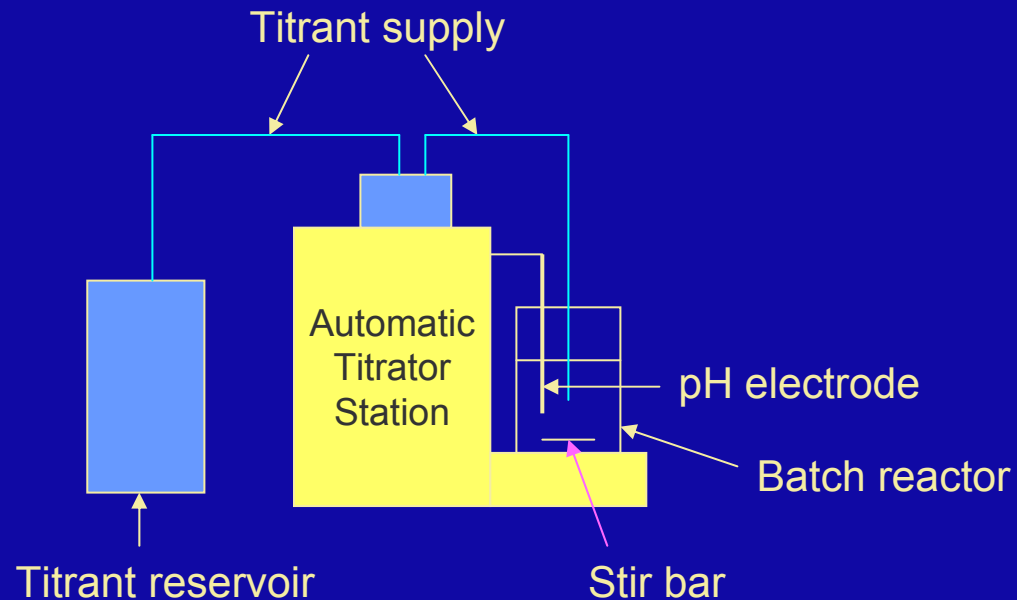
## **Anion Competition Study**

- 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):

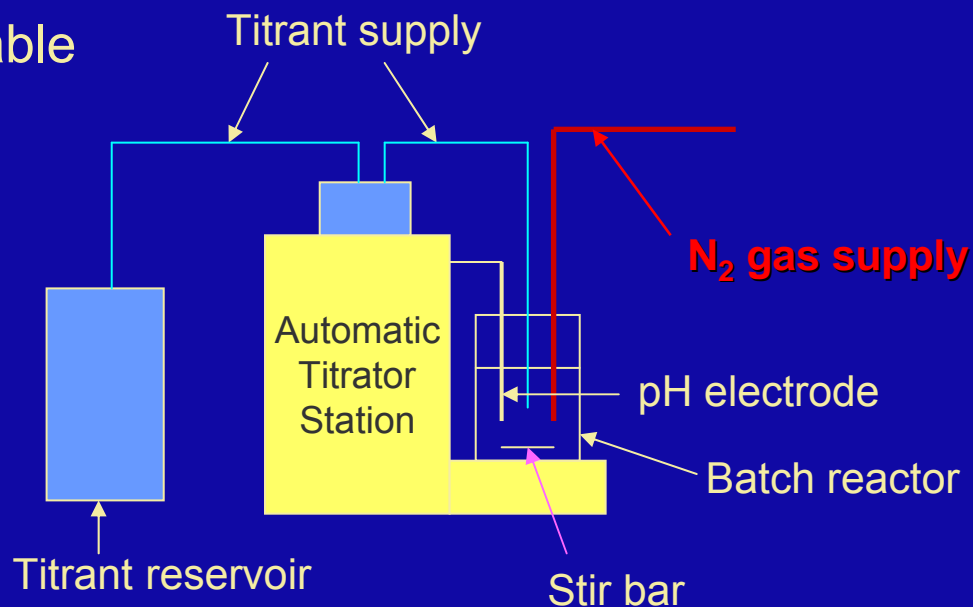
- Background alkalinity 50 mg CaCO<sub>3</sub> /L
- Background ionic strength 0.01M
- Arsenic as As(V) [0.15-2.0 mg/L]
- Adsorbents (powder or granular) [56-5556 mg/L]



# 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

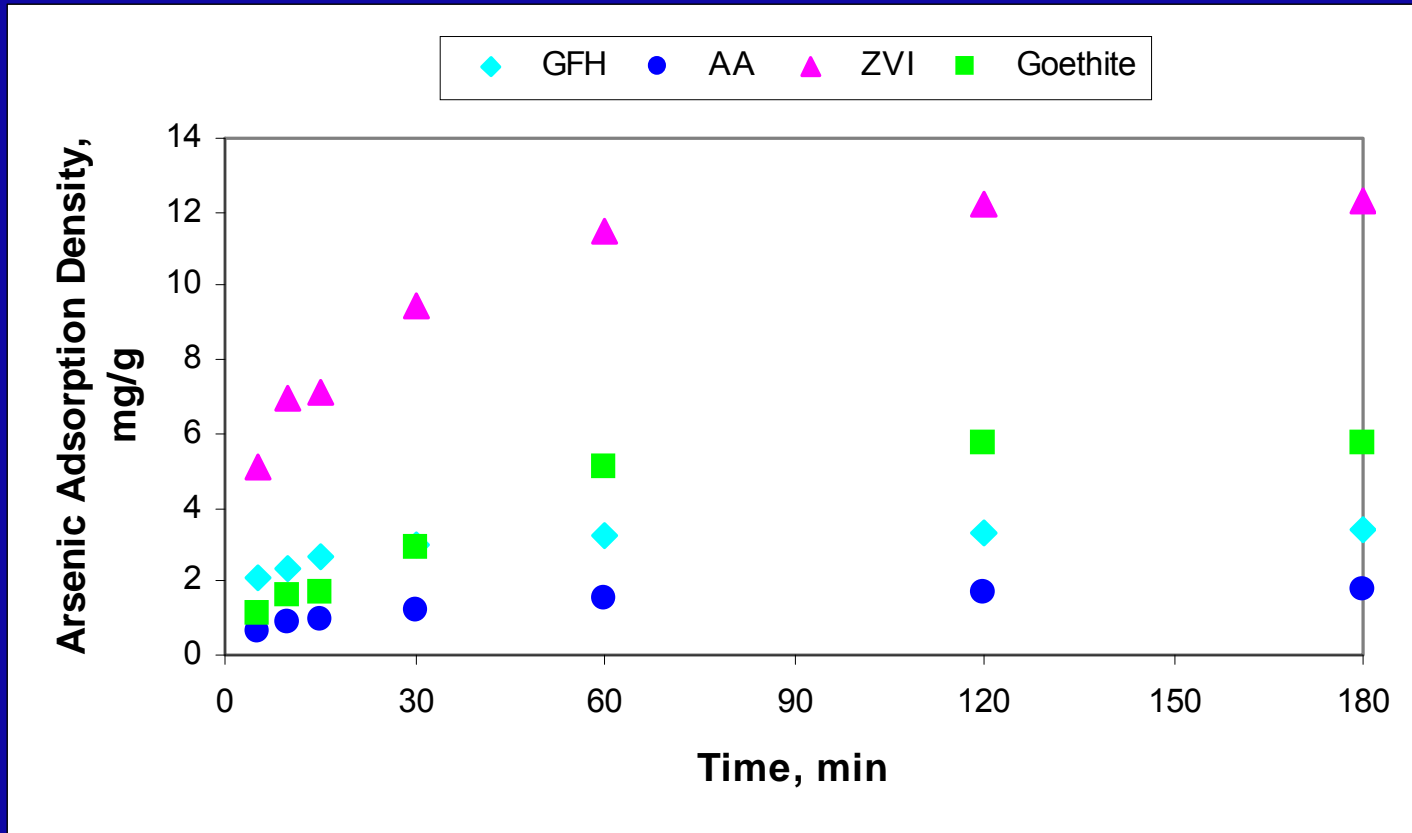
- Adsorbent Materials Tested
- Kinetic Study
- Isotherm Study
- Anion Competition Study
  - Preferential Anion Adsorption Series
  - Effect of Ionic Strength
  - Effect of Normalizing Anion Concentration Differences
- Treated Volume Example

# Adsorbent Materials Tested

#	Adsorbent Material	Grain Size, um (mesh)	Adsorption Density, ug/g	Arsenic Removal, %
1	Granular Ferric Hydroxide, <b>GFH</b>	<150	<b>2318</b>	<b>99</b>
2	Magnesium Oxide	<150	1329	55
3	Activated Alumina <b>AA</b>	(80 - 200)	<b>1669</b>	<b>96</b>
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 <b>ZVI</b>	<177	<b>799</b>	<b>98</b>
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)	<b>626</b>	<b>99</b>
15	DE coated with Hematite	<300	<b>1734</b>	<b>97</b>

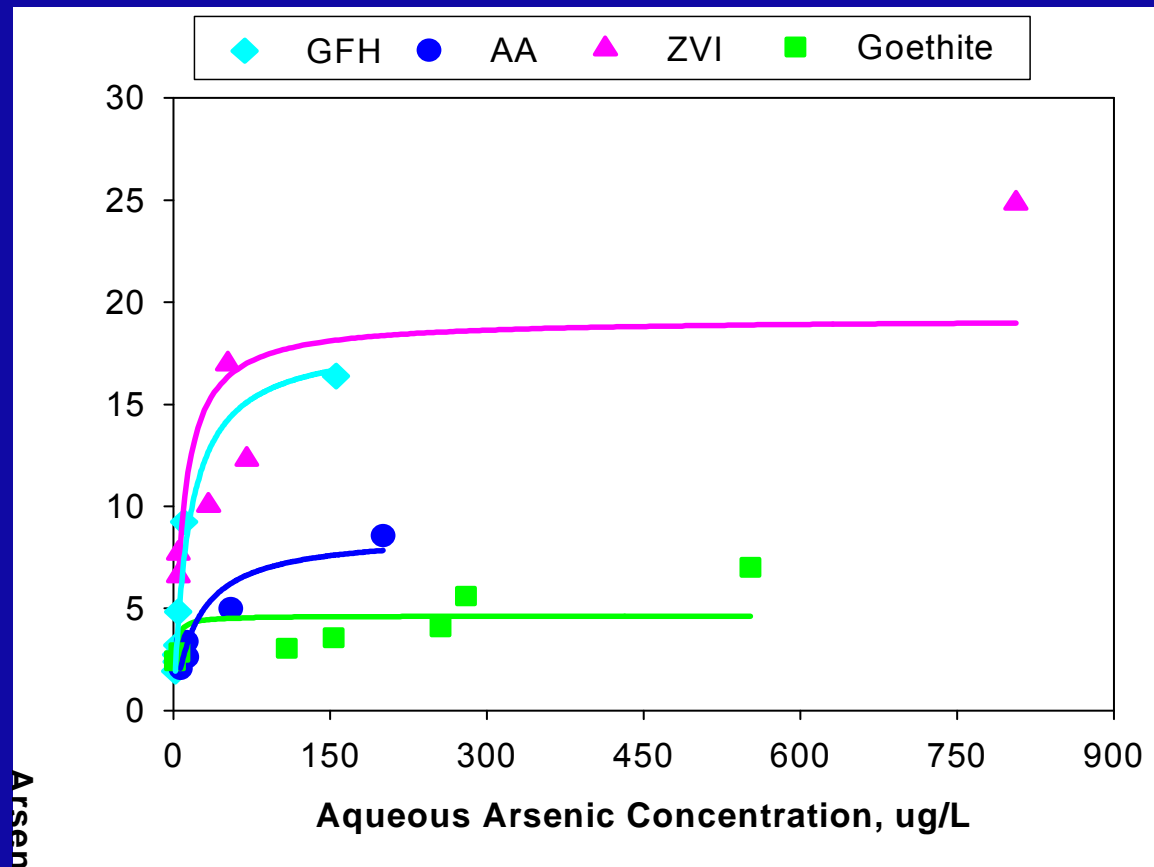
Results

# Kinetic Study



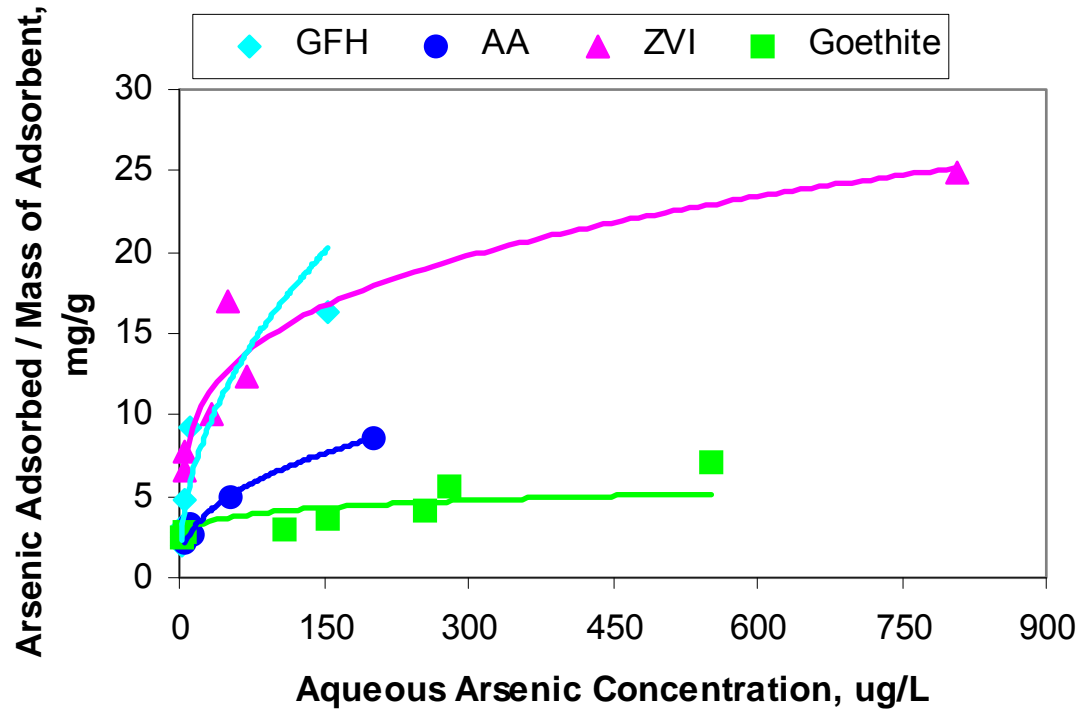
Results

# Langmuir Isotherms



Results

# Freundlich Isotherms



Results

# Isotherm Constants

## Langmuir Isotherm

Adsorbent	Nmax	b	R <sup>2</sup>
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 <sup>2</sup>
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 [H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> ]	1
Sulfate [SO <sub>4</sub> <sup>-2</sup> ]	250
Nitrate [NO <sub>3</sub> <sup>-</sup> ]	45
Ortho-silicate [Si(OH) <sub>4</sub> ]	50
Fluoride [F <sup>-</sup> ]	2
Bicarbonate [as CaCO <sub>3</sub> ]	250
Natural Organic Matter [as DOC]	4

# Design of Experiments

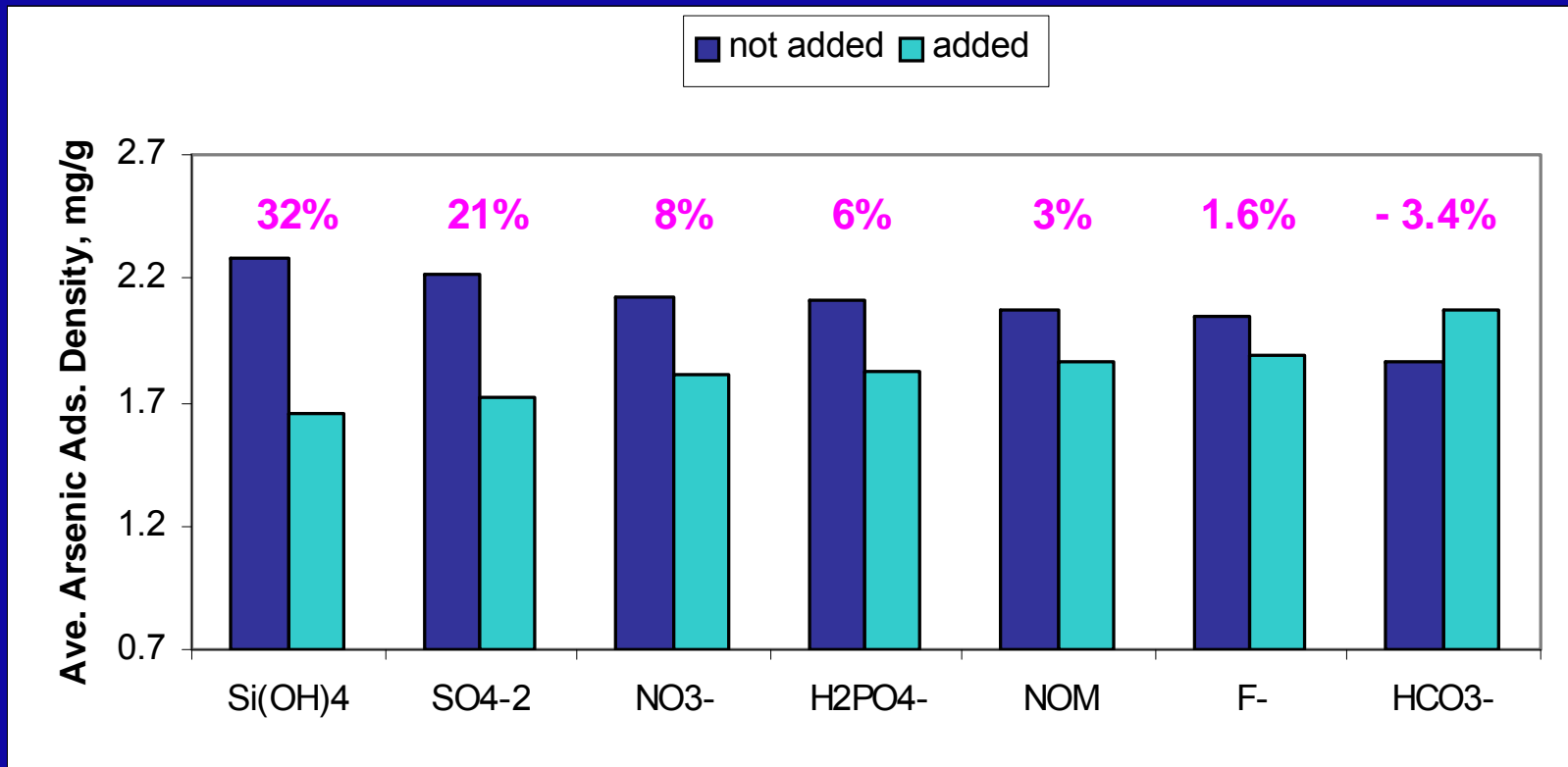
## Fractional factorial design of experiment and ANOVA test:

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



Results

# Enhancing Effect of Bicarbonate

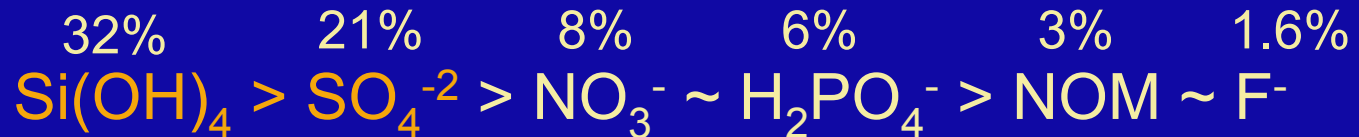
- Observed on Activated Alumina (AA)
- *Wijnja et al. (2000)* also observed carbonate enhancing effect (sulfate adsorption on AA at pH 6)
- The process was described with the following concurrent adsorption reactions:



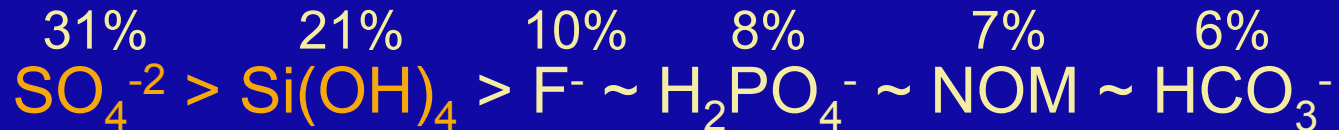
- Possible mechanism – generation of additional adsorption sites by extra protonated surface groups

# Preferential Anion Adsorption Series

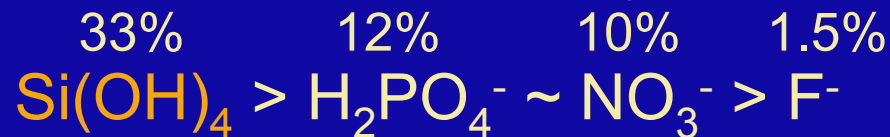
- **Activated Alumina** (7% error, 18% interactions):



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



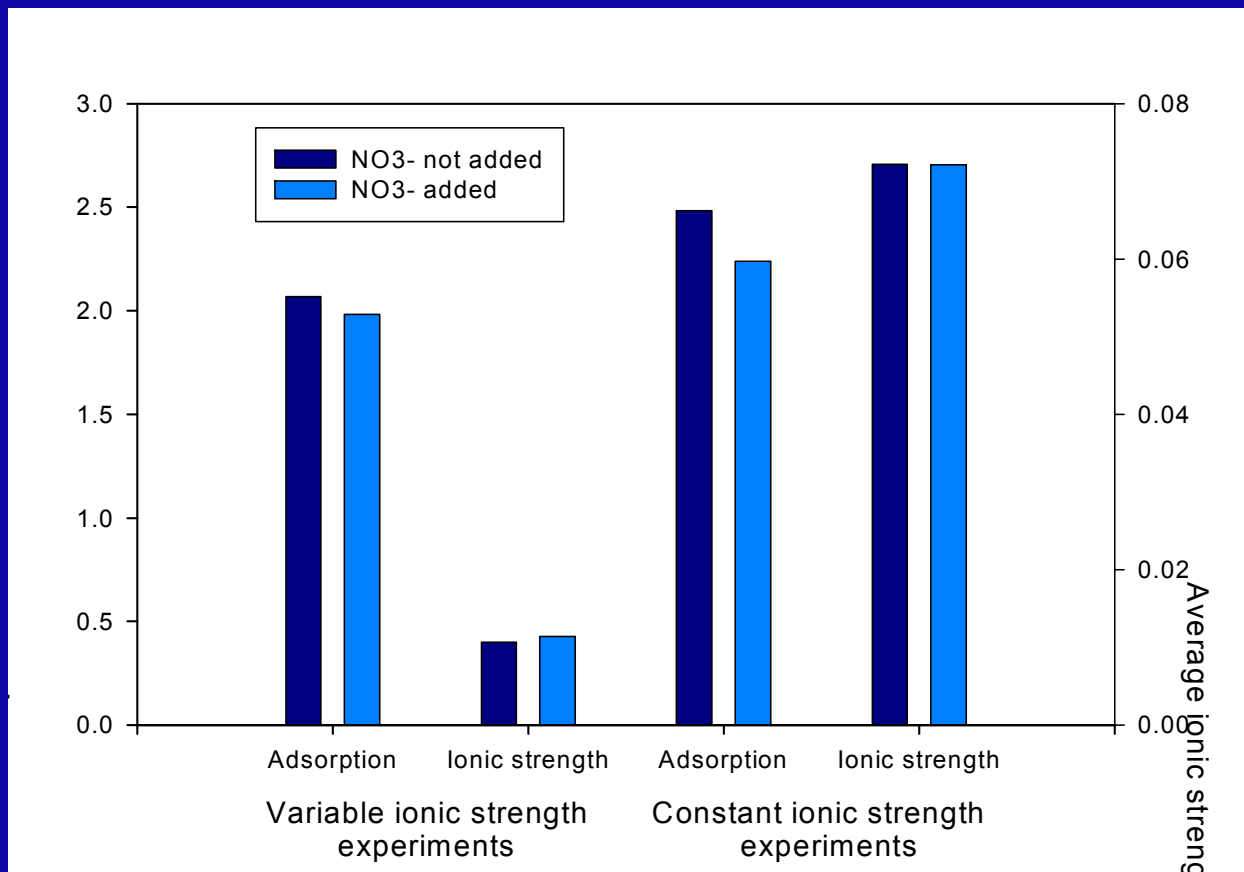
- **Goethite** (3% error, 30% interactions):



# Effect of Ionic Strength

- Experiments with no background ionic strength adjustment
- $I = 0.0001-0.0224\text{M}$  vs. previous  $0.075\text{M}$
- As  $I$  increased, the influence of:
  - $\text{SO}_4^{-2}$  increased on AA and GFH
  - $\text{Si(OH)}_4$  and  $\text{H}_2\text{PO}_4^-$  increased on goethite
  - $\text{NO}_3^-$  increased on AA and goethite

# Effect of Ionic Strength (cont'd)



Results



# 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  $0.034$ M)
- **Findings:**
  - 21%      15%      2.6%      0%
  - $\text{Si(OH)}_4 > \text{F}^- > \text{SO}_4^{-2} > \text{HCO}_3^-$
  - $\text{F}^-$  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)

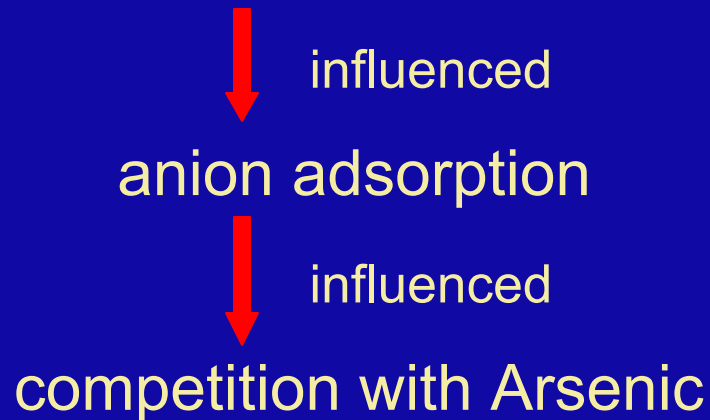
**Volume treated per g filter material** – assuming 50µg/L column influent arsenic concentration

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



## 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?