# *Assessing Arsenic Removal By Zero Valent Iron Under Various Water Quality and Precoat Filtration Conditions*

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Funding Provided by the US EPA

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# Project Objectives

BENCH STUDY, Task I

- Assess arsenic removal by zero valent iron under various water quality conditions to determine optimum conditions for arsenic adsorption and the minimization of iron dissolution

PILOT STUDY, Task II

- Develop a ZVI amended precoat filtration strategy for the removal of arsenic from drinking water while minimizing iron dissolution

# Outline

- Background
- Adsorption Processes
- Experimental Approach
- Results and Conclusions

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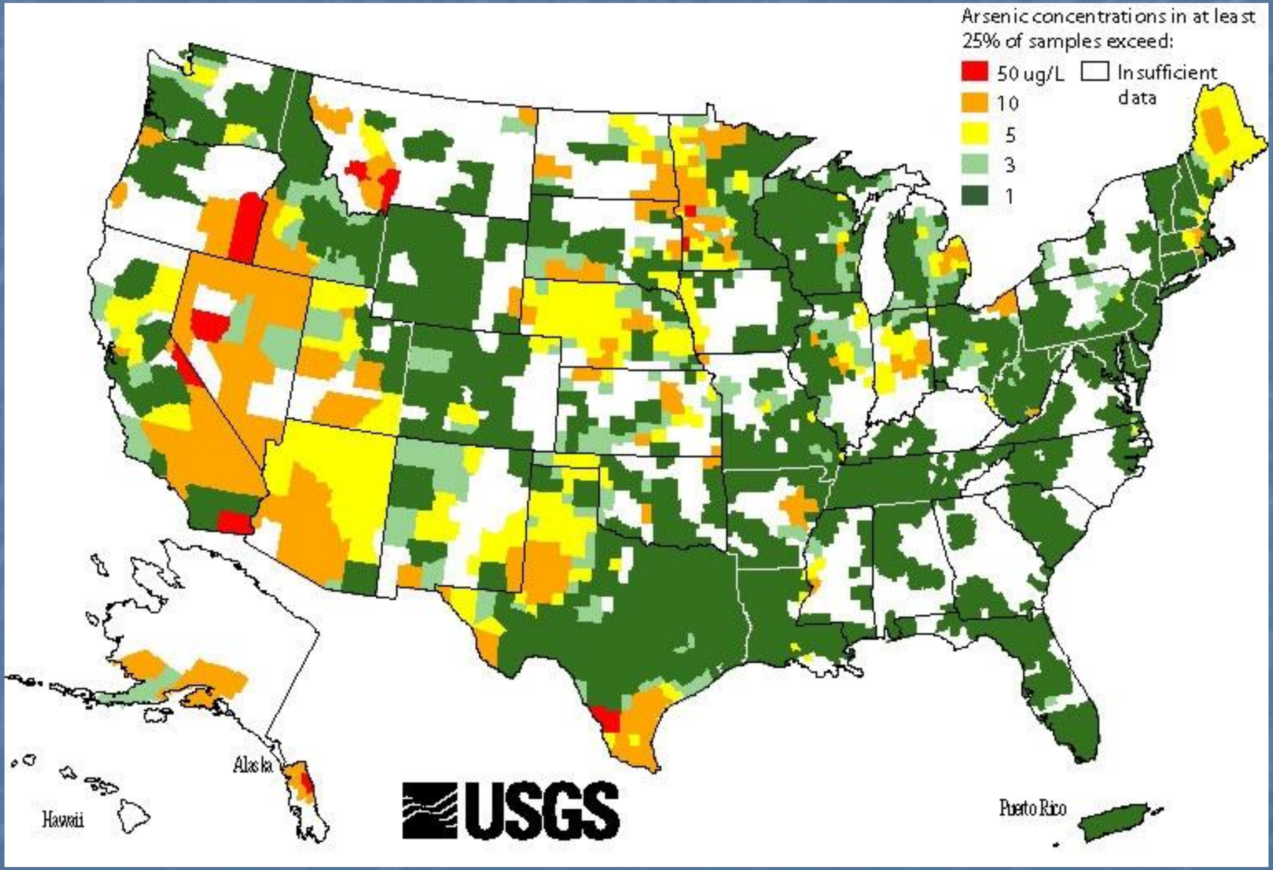
# Background

- Arsenic is a class A human carcinogen
- Arsenic concentrations in public drinking water supplies is regulated by the USEPA
- MCL was reduced from 0.05mg/L to 0.01mg/L in 2001 with compliance by 2006

# US Arsenic Distribution



# Effect on Water Systems

- EPA estimates annual national costs to be $181 million
- Harder on smaller systems
- Need for technologies that are inexpensive, efficient, easy to implement and operate

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# Best Available Technologies for As Removal (USEPA 2003)

- Ion exchange
- Activated alumina
- Oxidation / filtration
- Reverse osmosis
- Enhanced coagulation and flocculation
- Enhanced lime softening

# Some Adsorbents

- Iron oxide coated sand
- Iron Hydroxides and Oxides
  - Geothite
  - Granular ferric hydroxide
- Lanthanum oxide
- Zeolite
- Zero-Valent Iron

# Zero Valent Iron

- High adsorption capacity
- Relatively fast removal kinetics
- Inexpensive
- Efficient over wide range of pH
- Simple

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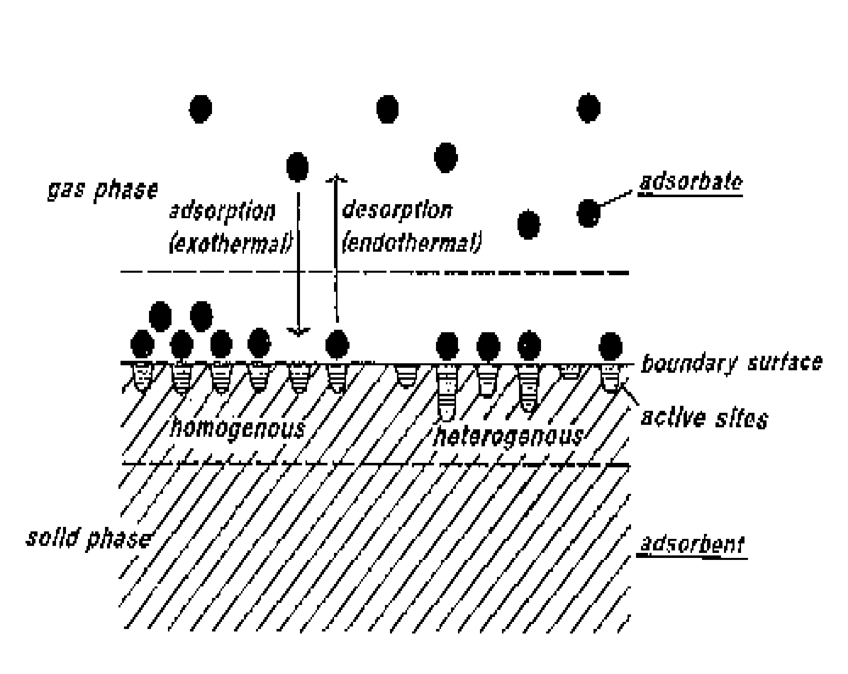
# Adsorption Processes

- Physical Adsorption
- Exchange Adsorption
- Chemical Adsorption




Source: activated-carbon.com

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# Assessing Factors Influencing Arsenic Removal

## BENCH STUDY

## Experimental Design:

- 24 Treatments
- 4 levels for pH
- 3 levels for Oxidant
- 2 levels for sulfate

| Trial | pH | Oxidant | Sulfate |
|---|---|---|---|
| 1 | 5 | $N_2$ | + |
| 2 | | | - |
| 3 | | $O_2$ | + |
| 4 | | | - |
| 5 | | $Cl_2$ | + |
| 6 | | | - |
| 7 | 6 | $N_2$ | + |
| 8 | | | - |
| 9 | | $O_2$ | + |
| 10 | | | - |
| 11 | | $Cl_2$ | + |
| 12 | | | - |
| 13 | 7 | $N_2$ | + |
| 14 | | | - |
| 15 | | $O_2$ | + |
| 16 | | | - |
| 17 | | $Cl_2$ | + |
| 18 | | | - |
| 19 | 8 | $N_2$ | + |
| 20 | | | - |
| 21 | | $O_2$ | + |
| 22 | | | - |
| 23 | | $Cl_2$ | + |
| 24 | | | - |

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# Bench Study Experimental set up


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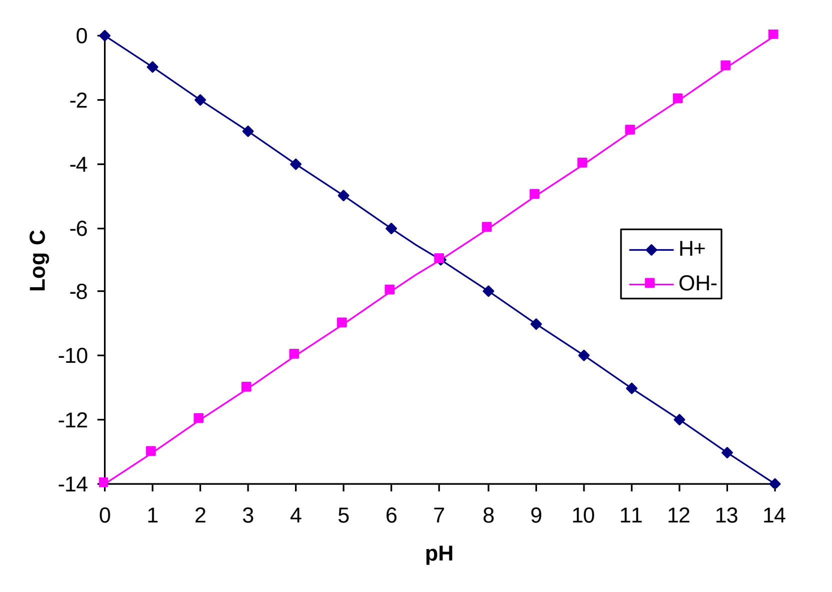
# Calculating pH

- pH = -Log ($H^+$)

$H_2O \leftarrow\rightarrow H^+ + OH^-$

- $K_W = (H^+)(OH^-) = 10^{-14}$
  @ 25˚C




$Fe(OH)_3(s) + 3H^+ \leftarrow\rightarrow Fe^{3+} + 3H_2O$

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# Calculating Redox Condition

# pe = -Log ($e^-$)

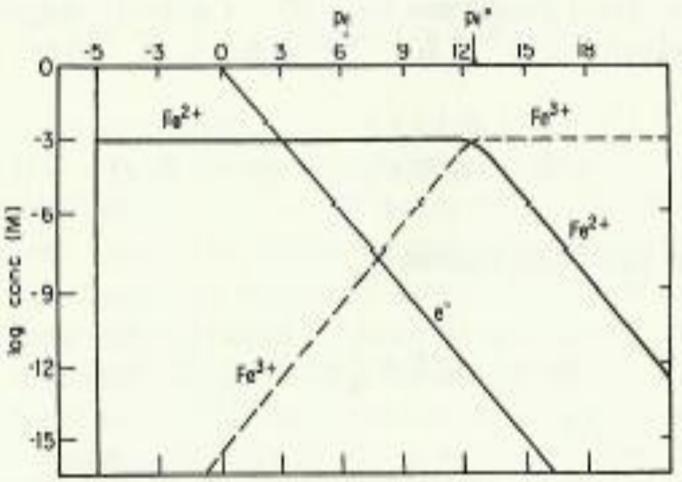
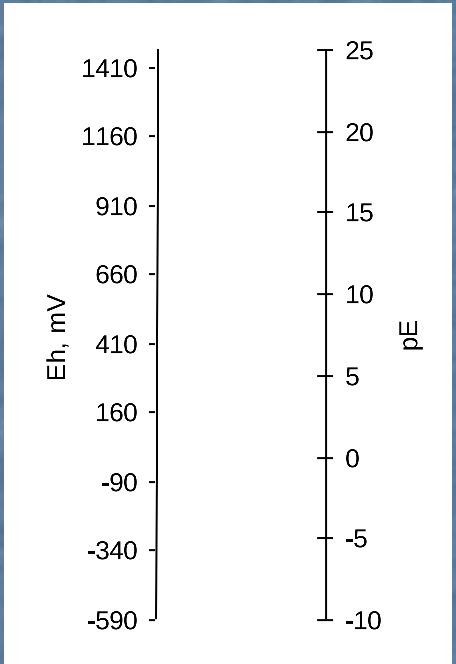



**Figure 8.1.** Redox equilibrium $Fe^{3+}$, $Fe^{2+}$. Equilibrium distribution of a $10^{-3}$ M solution of aqueous iron as a function of pe (acid solution).




Source: Stumm and Morgan, 1996

$Fe^{2+} = Fe^{3+} + e^-$

Eh = 2.3RT/F*pe

Eh = 0.059pe

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# Oxidation Reduction (Redox) Reactions

- Oxidation = a chemical donates an electron

  $Fe^{2+} = Fe^{3+} + e^-$

- Reduction = a chemical accepts an electron

  $\frac{1}{4} O_2 + e^- + H^+ = \frac{1}{2} H_2O$

- Redox reaction

  $4Fe^{2+} + 4H^+ + O_2 = 4Fe^{3+} + 2H_2O$

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# Measuring Redox Condition Oxidation Reduction Potential (ORP) measured as Eh

- ORP is the voltage measured between a redox (Pt) electrode and a reference electrode
- Under reducing conditions potentials are negative

$E_h = 0.059pe$

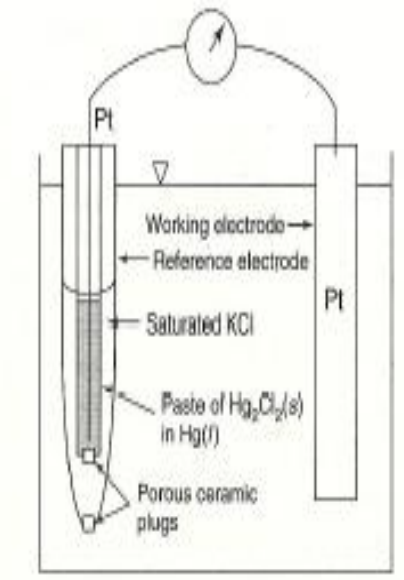
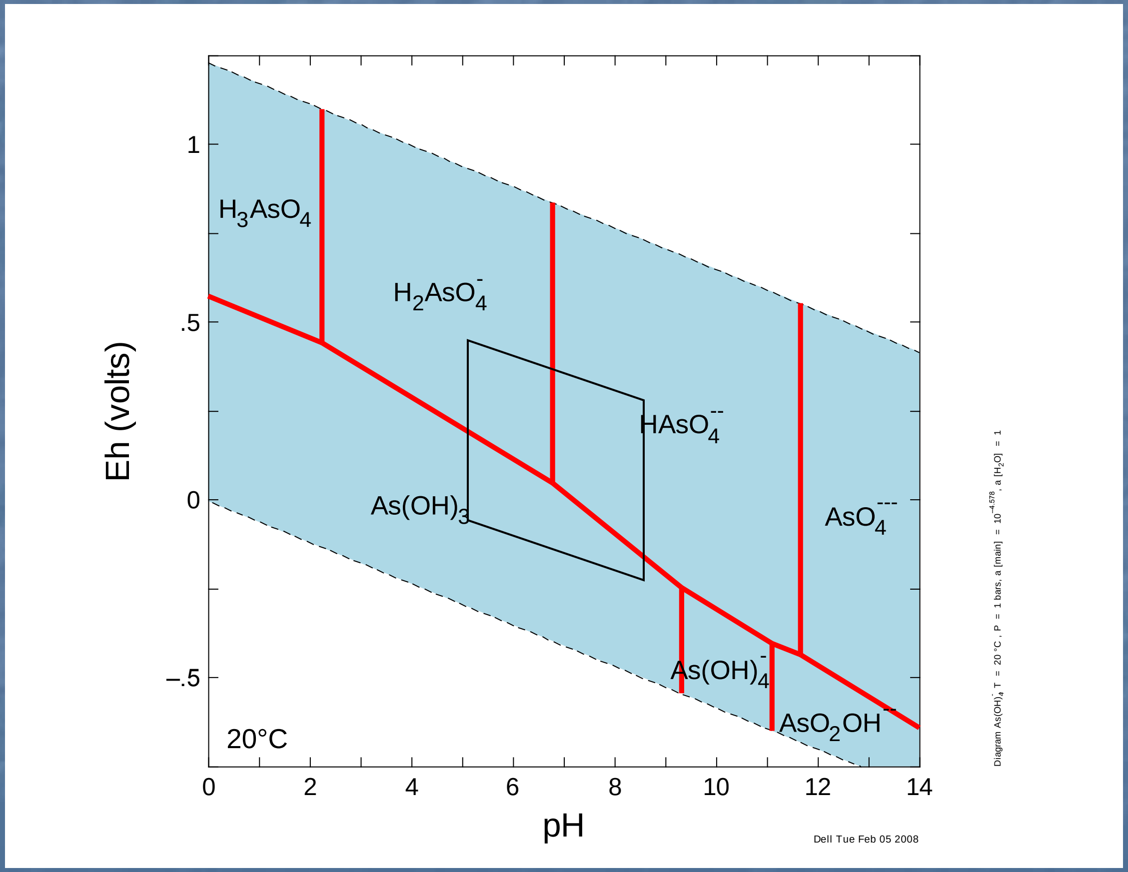



**Figure 9.19** A calomel reference electrode (on left) connected to a platinum working electrode for the measurement of solution $E_H$. If the Pt electrode is selectively responsive to the $H^+/H_2(g)$ couple, and if solution is bubbled with $H_2(g)$ at a known partial pressure, the reading on the voltmeter can be related to the pH of the solution.

Source: Benjamin, 2002

# Putting it all together

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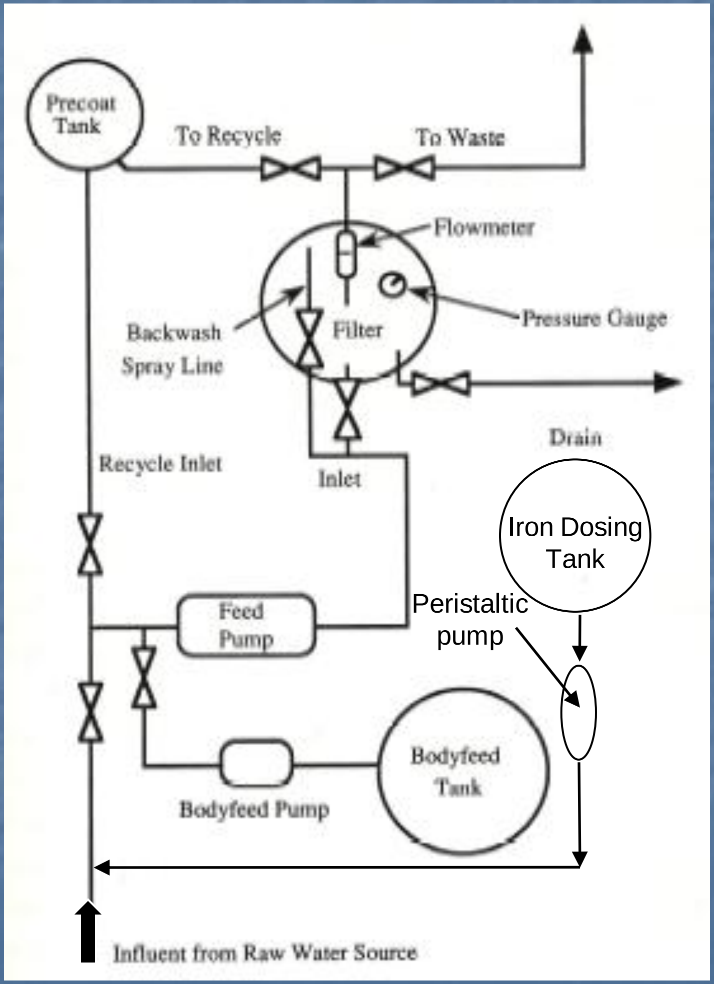
# Presence/Absence $SO_4$

- May play a role in arsenic removals
- Not clear in the literature

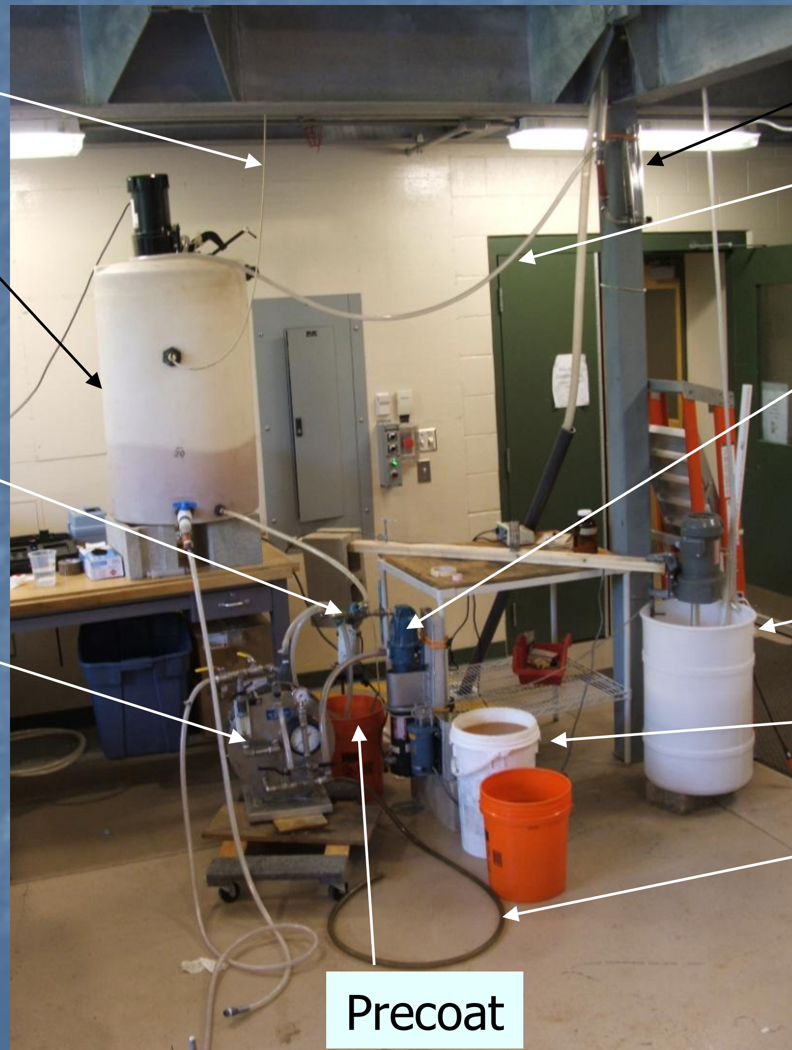
# Pilot Study Experimental Design

| Trial | Oxidant | Contact Time, minutes |
|---|---|---|
| 1 | $Cl_2$ | 22 |
| 2 | $O_2$ | 22 |
| 3 | $Cl_2$ | 2 |
| 4 | $O_2$ | 2 |

# Precoat filtration



# Precoat filtration



Iron Dosing
Reactor
Valves
DE Filter
Flow Meter
Influent
Pump
Body Feed
Residuals
Drain
Precoat

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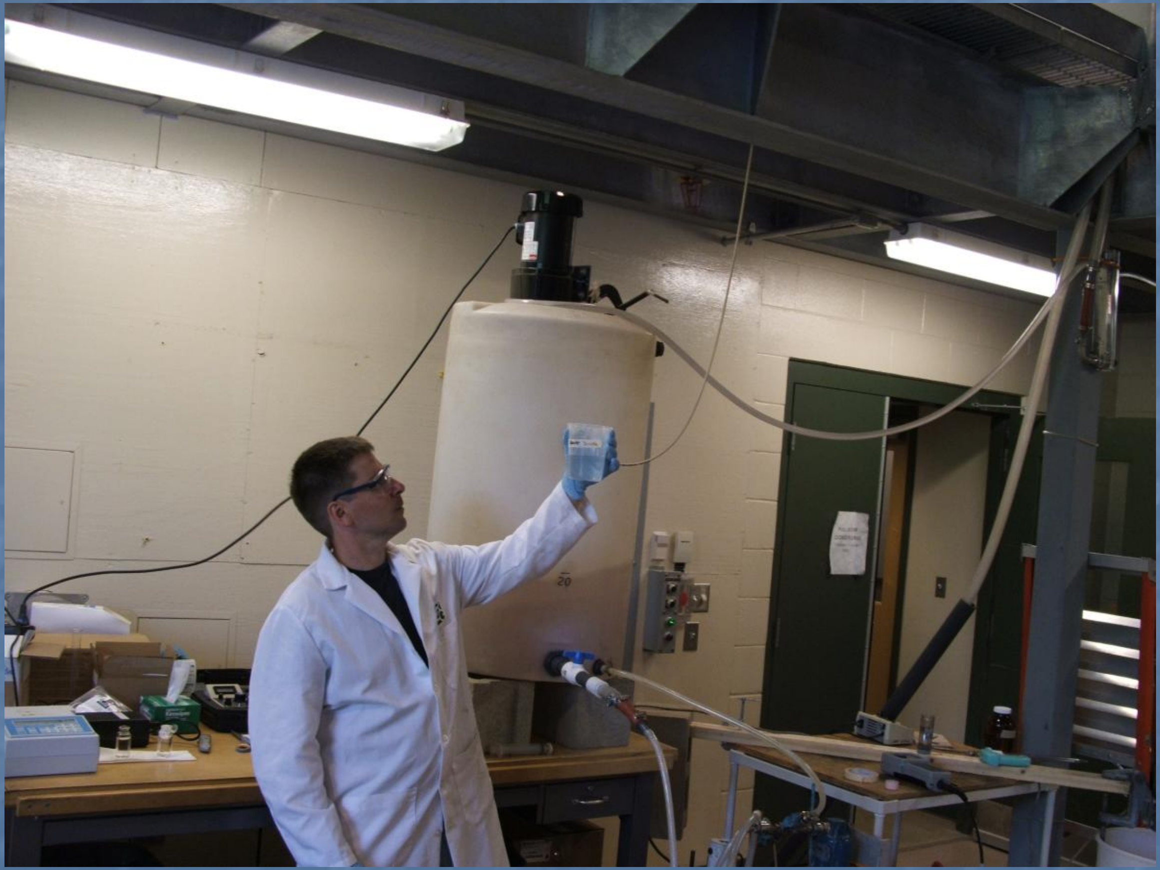
# Results



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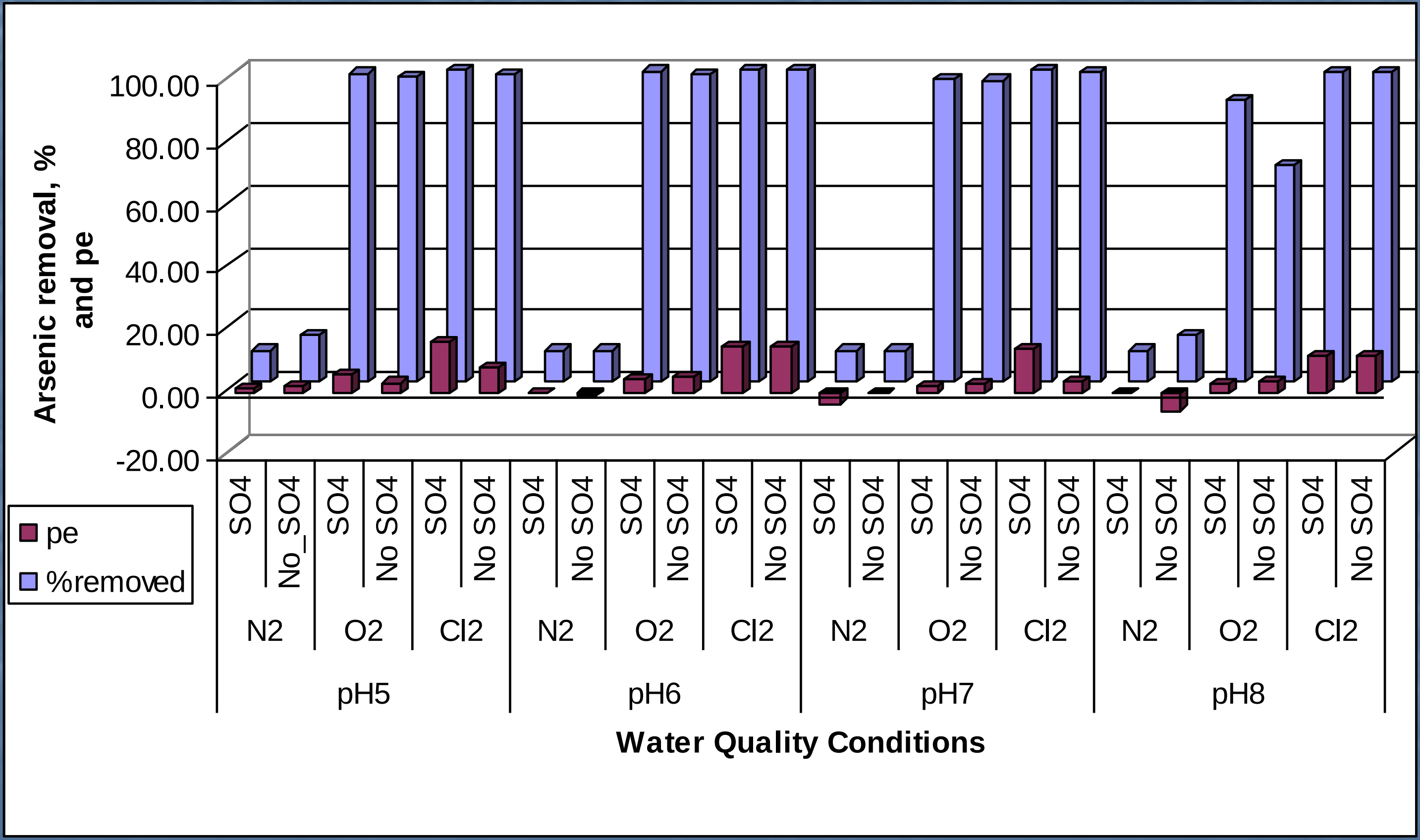
# Assessing Factors Influencing Arsenic Removal

## BENCH STUDY, Task I

Assessing arsenic removal by ZVI under various water quality conditions to determine optimum conditions for arsenic adsorption and the minimization of iron dissolution

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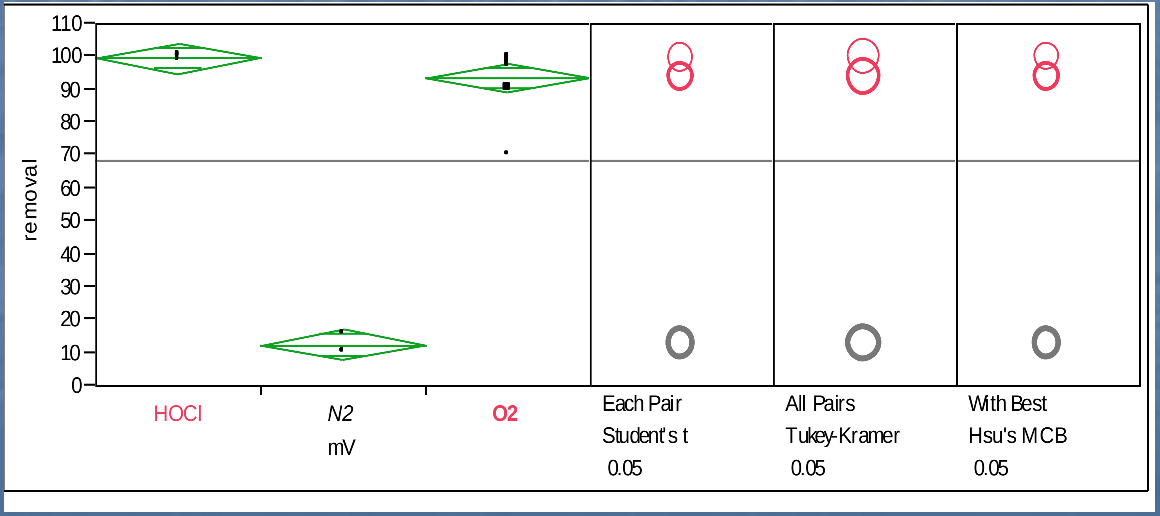
# Assessing Factors Influencing Arsenic Removal

| Main Factors and Interactions | F Ratio | p | % contribution |
|---|---|---|---|
| pH | 3.4473 | 0.0881 | 0.14 |
| Oxidant | 866.9455 | <.0001 | 97.88 |
| pH*Oxidant | 6.2259 | 0.014 | 0.59 |
| SO4 | 0.3914 | 0.5433 | -0.03 |
| pH*SO4 | 1.5678 | 0.2344 | 0.03 |
| Oxidant*SO4 | 1.6087 | 0.2405 | 0.07 |
| pH*Oxidant*SO4 | 1.2392 | 0.3242 | 0.03 |

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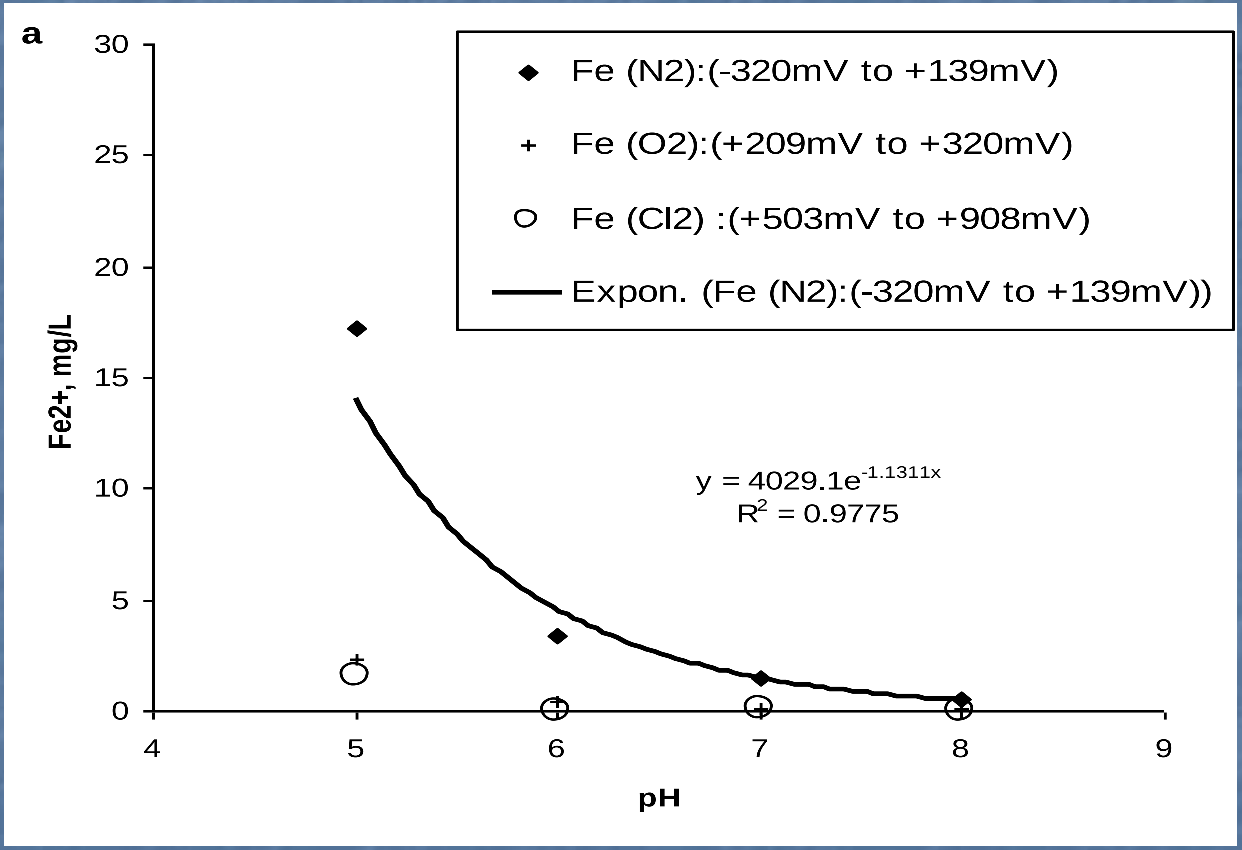
# Assessing Iron Solubility, Task I

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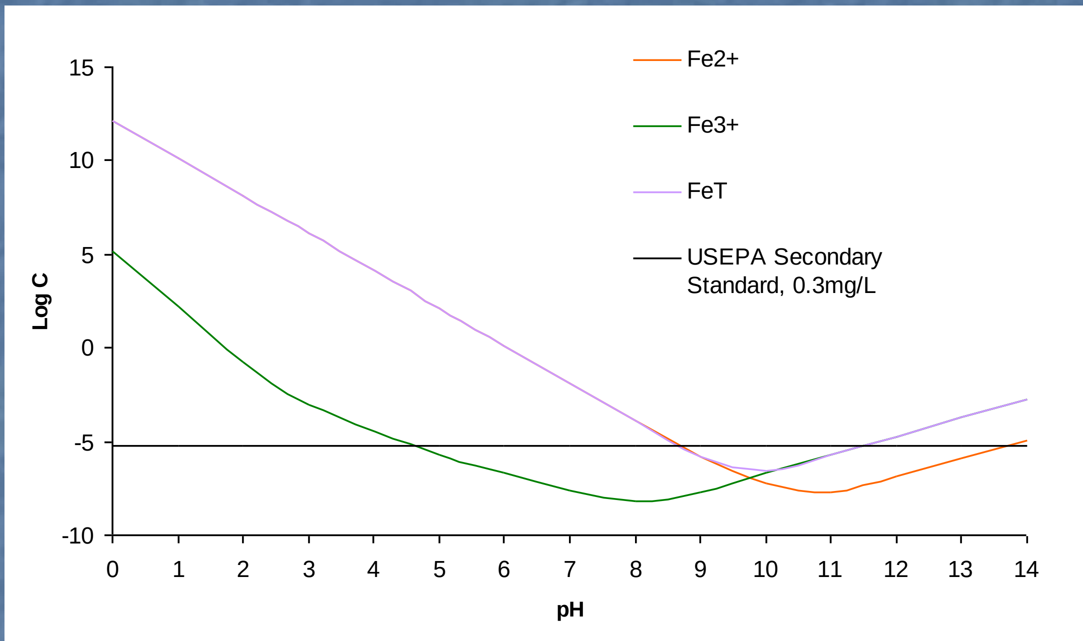
# Assessing Factors Influencing Arsenic Removal

## Calculated pH of minimum iron solubility




Solubility of iron as a function of pH. Includes Fe2+ and Fe3+ complexes of Cl- and OH- in equilibrium with $Fe(OH)_2$ and $Fe(OH)_3$.

## Kinetics of $Fe^{2+}$ oxidation at pH values

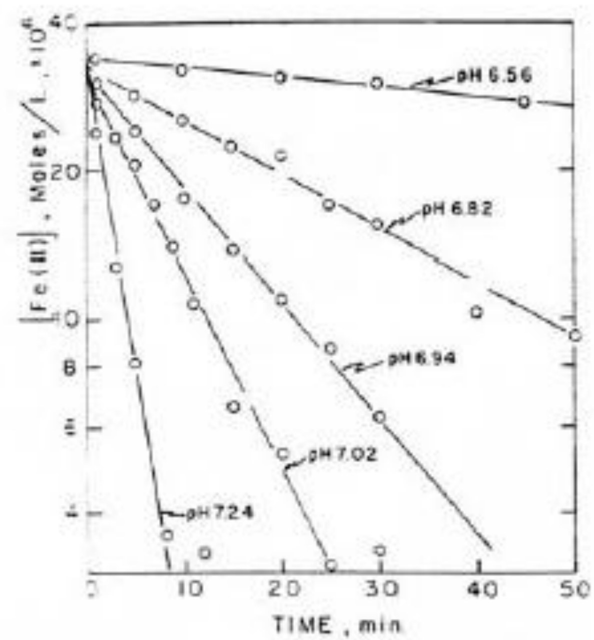



**Figure 1.** Oxygenation rate of ferrous iron is proportional to Fe(II) and is strongly influenced by pH

20.5 ° C. $P_O$ = const.

Source: Stumm and Lee, 1961

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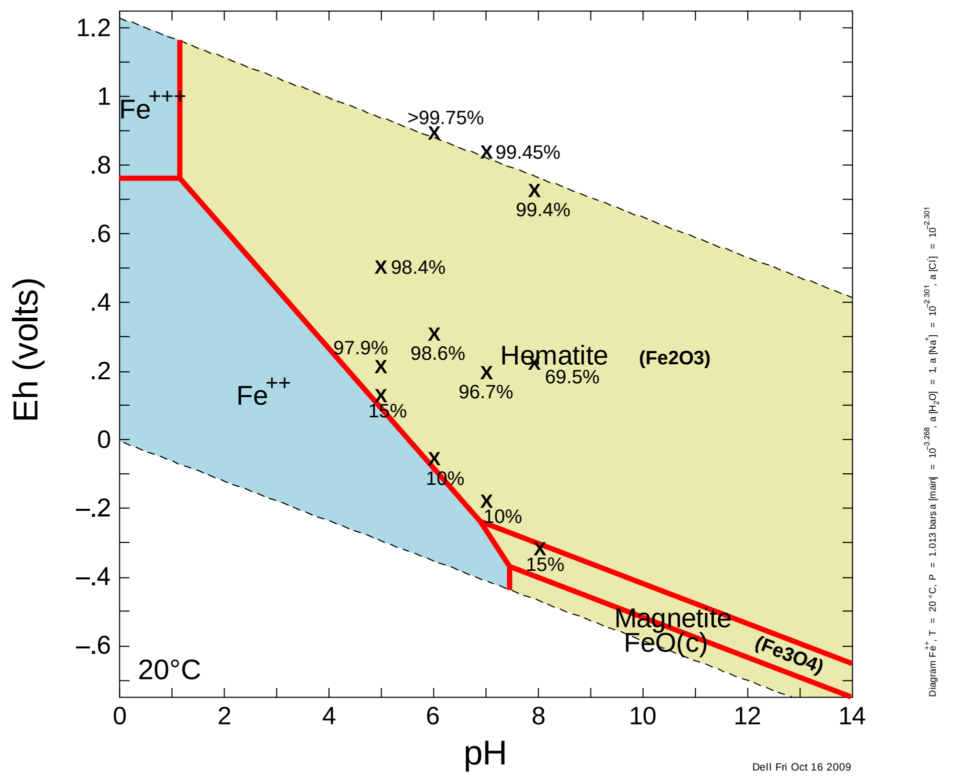
# Predominance Diagram for Iron




*Does not include As or $SO_4$*

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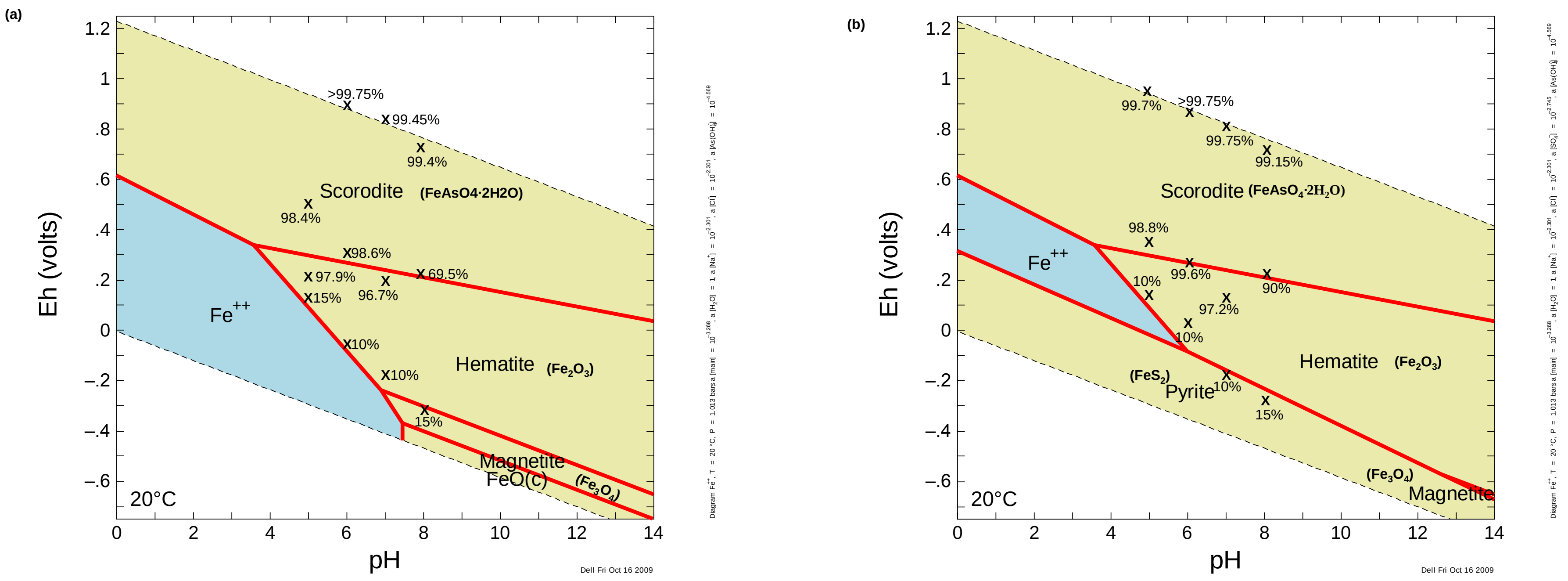
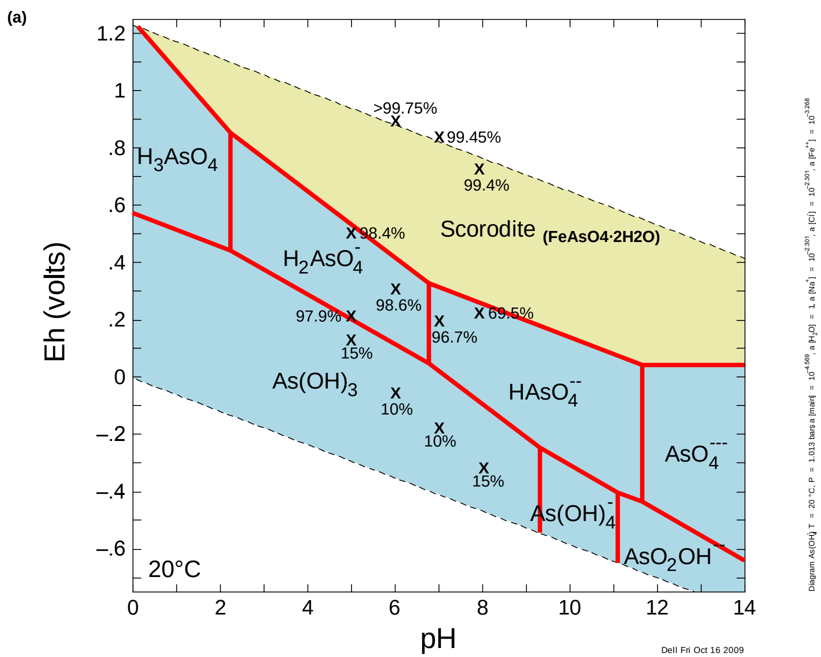
# Predominance Diagram for Iron

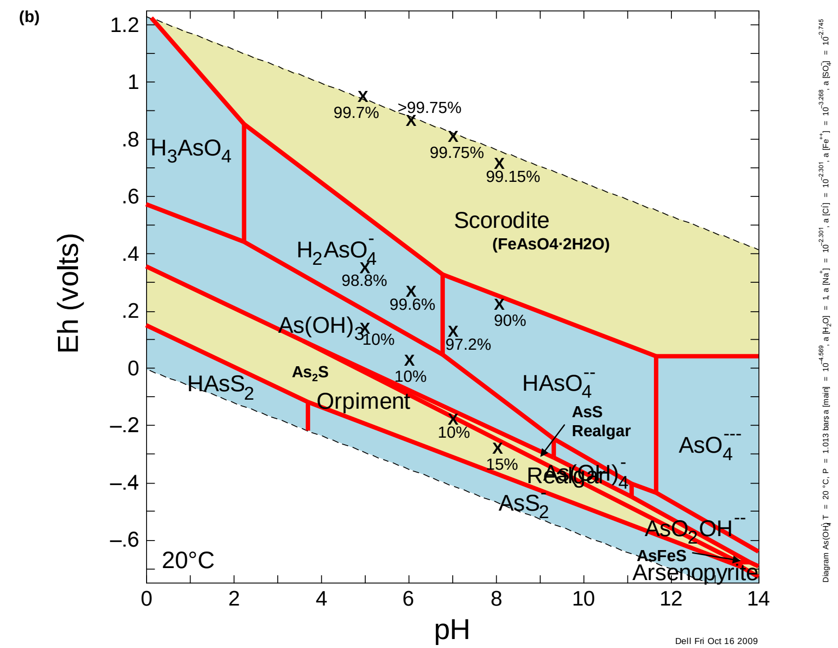



Without $SO_4$

With $SO_4$

# Predominance Diagram for Arsenic




Without $SO_4$

With $SO_4$

# Take Home Message

- ORP is very important to arsenic removal by ZVI
- pH is not very important from 5-8 if sufficient time allowed for ZVI pretreatment and contact time
- It appears that the optimal pH to minimize iron dissolution from ZVI is 7

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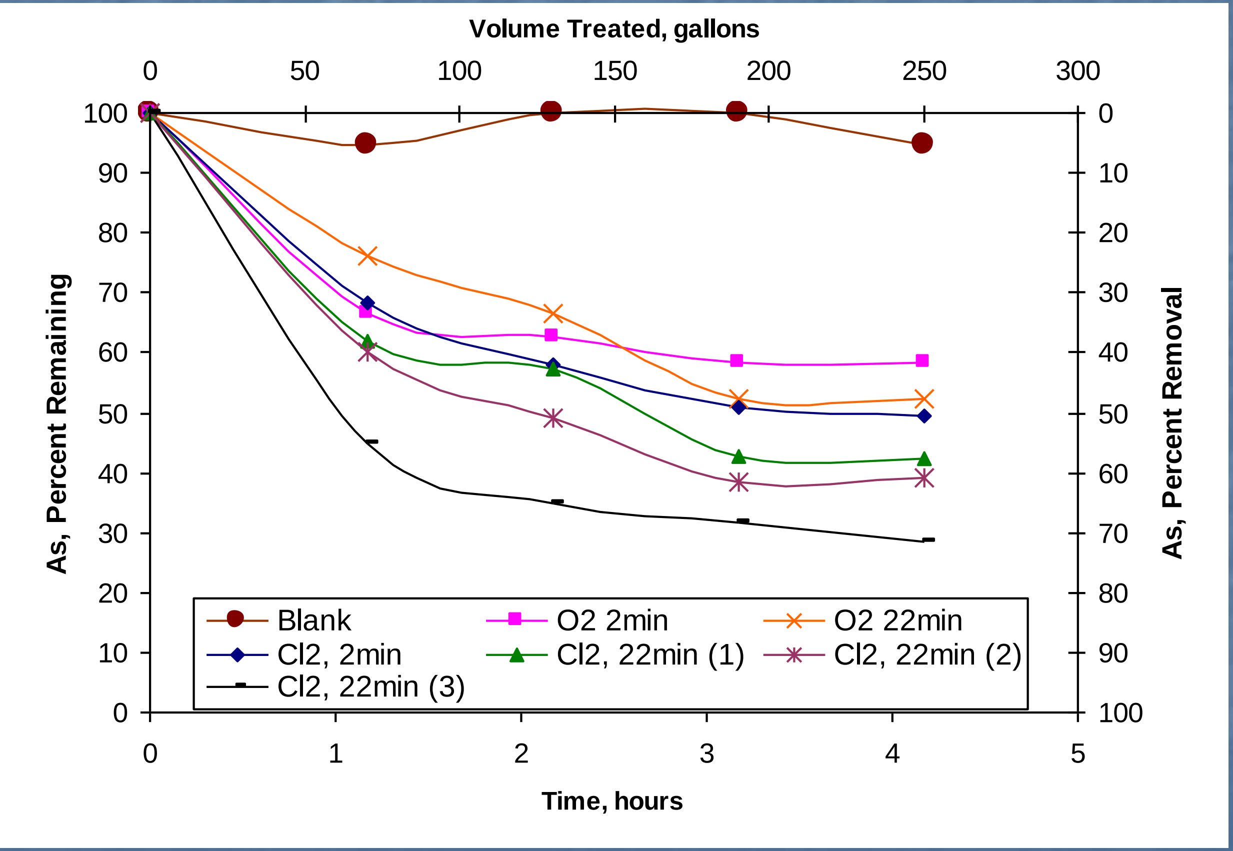
# Arsenic Removals by ZVI amended precoat filtration Task II





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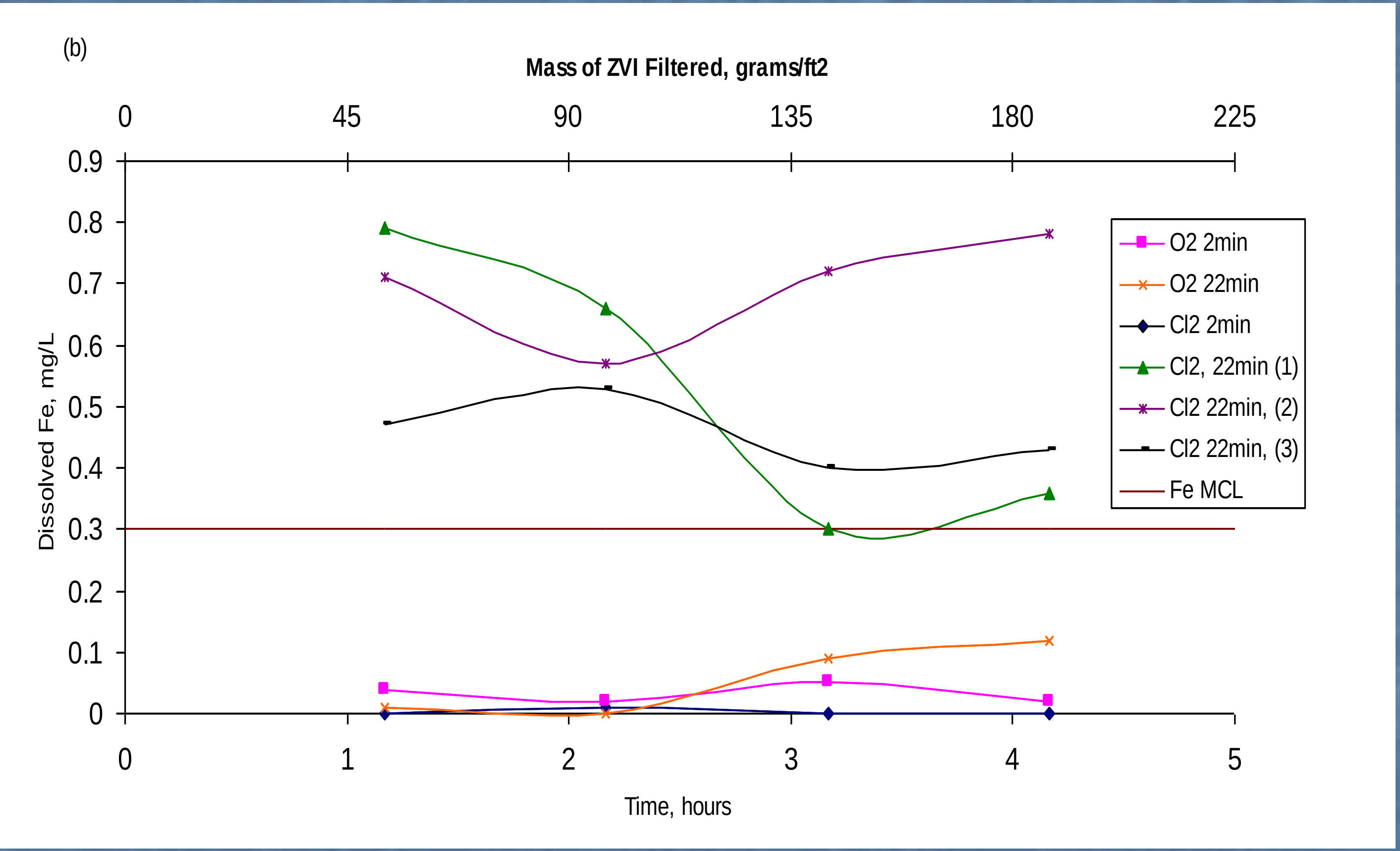
## Dissolved Iron Concentrations
## Task II





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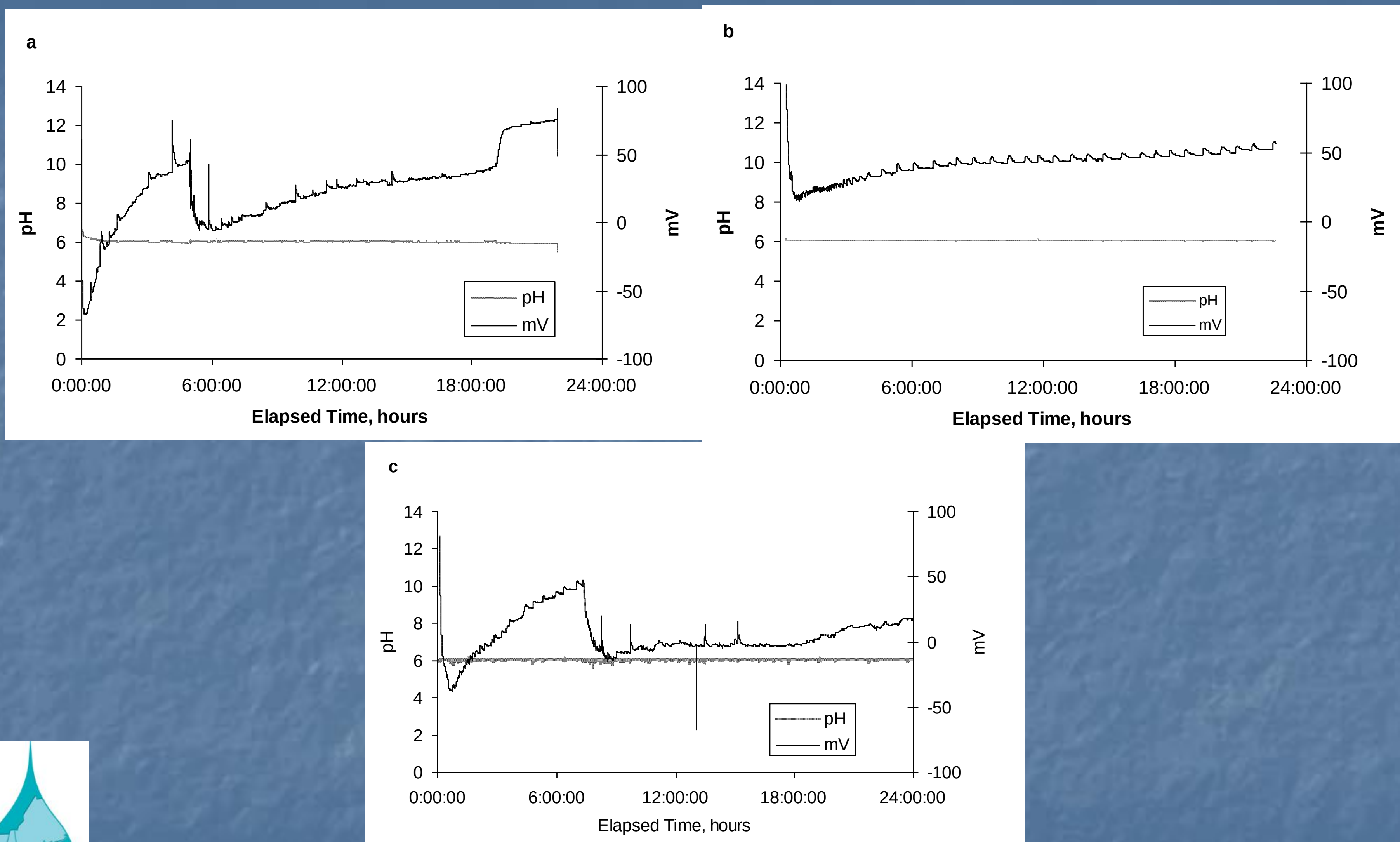
# Assessing the Applicability of ZVI Amended Precoat Filtration for Arsenic Removal




Water quality conditions during ZVI pretreatment period. ZVI=9.6mg/L, NaCl=0.005M, air flow rate=3L/min. **a**: $O_2$, 2 min; **b:** $Cl_2$, 2 min; **c:** $O_2$, 22 min.

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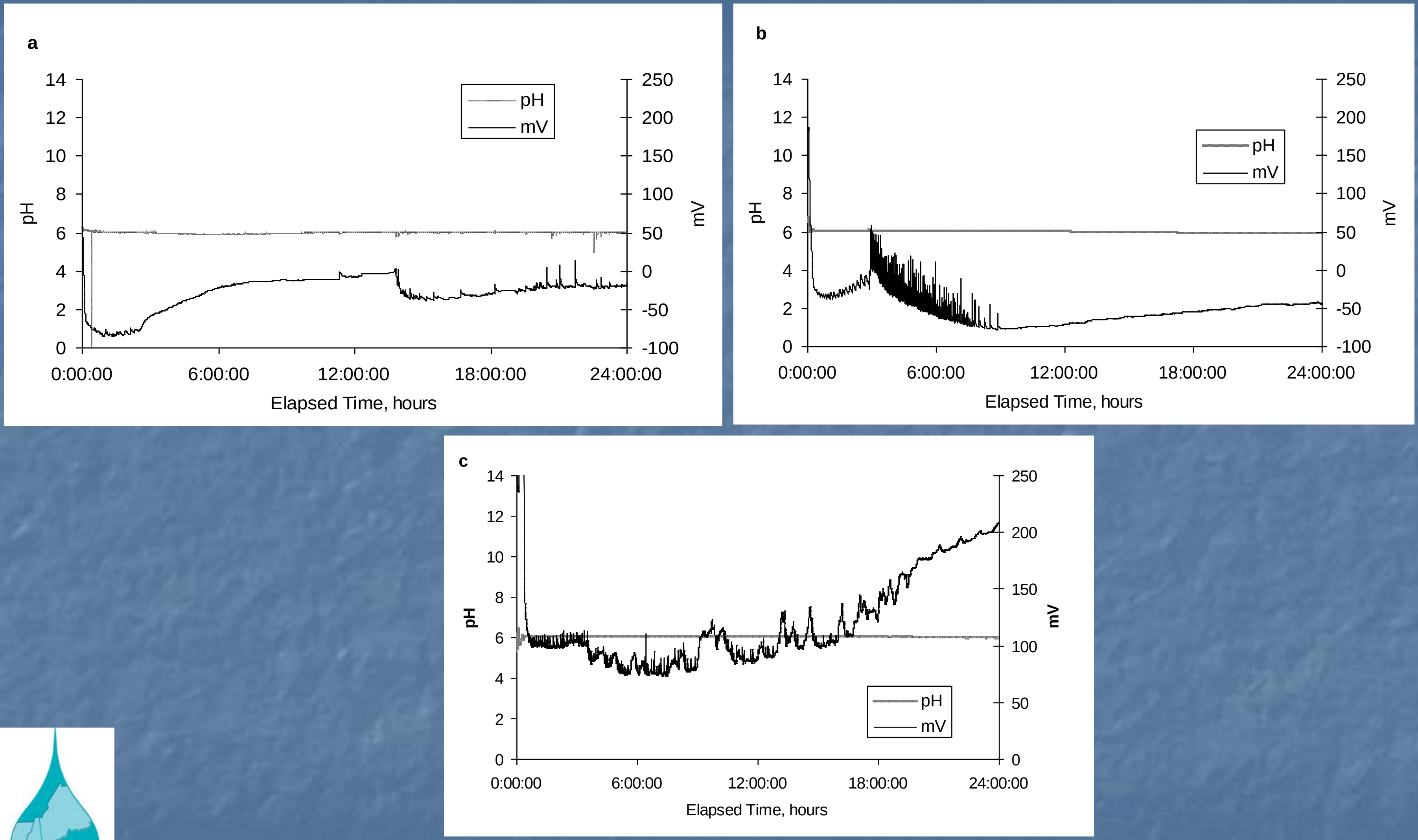
# Assessing the Applicability of ZVI Amended Precoat Filtration for Arsenic Removal




Water quality conditions during ZVI pretreatment period. ZVI=9.6mg/L, NaCl=0.005M.. **a**: $Cl^{-}_{2}$, 22 min (1), air flow=3L/M. **b**: $Cl_2$, 22min, air flow=3L/min (2). **c**: $Cl_2$, 22min (3), air flow=8L/min.

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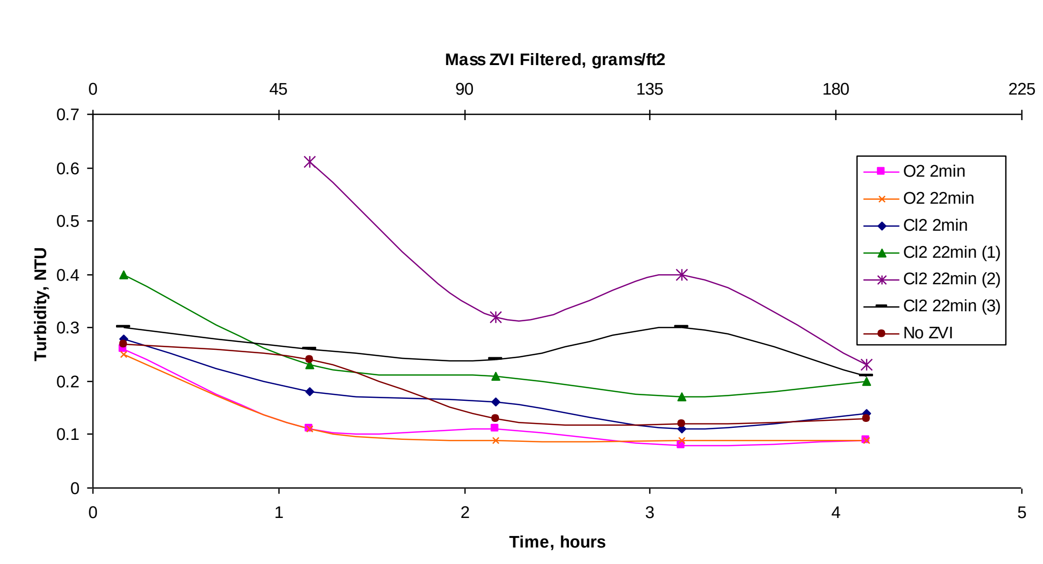
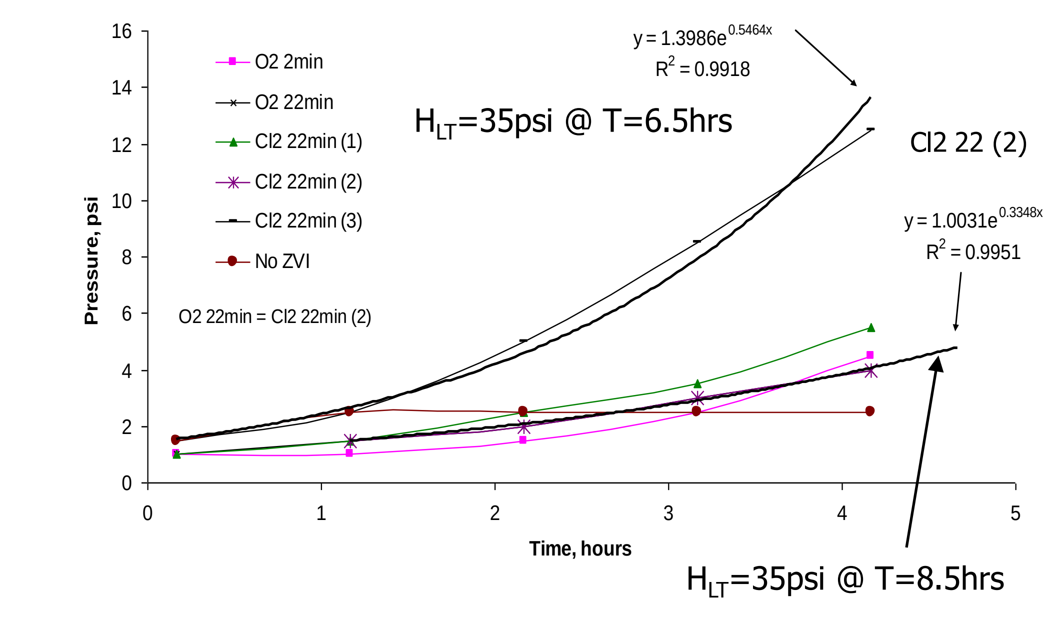
# Influence of ZVI A Addition on Precoat Filtration Operating Parameters




Turbidity

Pressure



# Take Home Message

- ZVI amended precoat filtration is an effective treatment for the removal of arsenic
- The pH and ORP of the ZVI pretreatment are important considerations because of the possibility of iron dissolution: pH7
- Body feed rate may need to be adjusted to minimize head loss development

# Conclusions

- Oxidation reduction potential (ORP) exerts a strong influence on arsenic removals by ZVI, with high removals occurring at elevated ORP values
- The influence exerted by pH on arsenic removals by ZVI is drastically reduced at pH values 5-8 if sufficient pretreatment time is allowed for the creation of sorption sites
- ZVI amended precoat filtration is an effective treatment for the removal of arsenic but close attention needs to be paid to conditions as they relate to iron dissolution
- The pH and ORP of the ZVI pretreatment are important considerations because of the possibility of iron dissolution: need tighter controls
- When using pretreated ZVI to amend precoat filtration for the removal of arsenic, body feed rate may need to be adjusted to minimize head loss development

# Questions?

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**EPA weight-of-evidence classification for carcinogenicity**

| Group | Description |
|---|---|
| **A** | Human carcinogen |
| **B1** | Probable human carcinogen, limited human data available |
| **B2** | Probable human carcinogen, sufficient evidence in animals and inadequate or no evidence in humans |
| **C** | Possible human carcinogen |
| **D** | Not classifiable as to human carcinogenicity |
| **E** | Evidence of noncarcinogenicity for humans |

*Source: Hazardous Waste Management, LeGrega*

# Recommendations for Future Research

- Investigate the influence of different ZVI pretreatment pH and ORP values on the removal of arsenic and dissolution of iron.
- Investigate the influence of different ZVI pretreatment oxidants on the removal of arsenic and dissolution of iron.
- Investigate the influence of different source water pH values on the removal of arsenic and dissolution of iron.
- Investigate the influence to ZVI pretreatment time on the removal of arsenic and dissolution of iron.

| | ZVI1 mg/kg | ZVI2 (mg/kg) | AVERAGE | STANDARD DEVIATION |
|---|---|---|---|---|
| **Ag 328.068** | 0.95 | 0.91 | 0.93 | 0.03 |
| **Al 308.215** | 178.78 | 299.18 | 238.98 | 85.14 |
| **As 193.696** | 40.68 | 45.54 | 43.11 | 3.44 |
| **Ba 455.403** | 25.47 | 40.17 | 32.82 | 10.39 |
| **Be 313.107** | BDL | BDL | | |
| **Ca 317.933** | 434.42 | 654.13 | 544.28 | 155.35 |
| **Cd 226.502** | 51.30 | 60.04 | 55.67 | 6.18 |
| **Co 228.615** | 29.87 | 34.47 | 32.17 | 3.25 |
| **Cr 267.716** | 706.38 | 766.24 | 736.31 | 42.33 |
| **Cu 324.754** | 1641.83 | 1972.05 | 1806.94 | 233.50 |
| **Fe 259.837** | **917682.00** | **1255302.50** | 1086492.25 | 238733.75 |
| **K 766.491** | 38.91 | 63.10 | 51.00 | 17.10 |
| **Mg 279.800** | 217.46 | 263.90 | 240.68 | 32.84 |
| **Mn 257.610** | 3539.13 | 4972.68 | 4255.90 | 1013.67 |
| **Na 588.995** | | | 0.00 | |
| **Ni 231.604** | 289.86 | 307.50 | 298.68 | 12.47 |
| **Pb 220.353** | 29.09 | 41.95 | 35.52 | 9.09 |
| **S 181.972** | 521.63 | 520.57 | 521.10 | 0.74 |
| **Sb 206.834** | 26.14 | 27.79 | 26.96 | 1.16 |
| **Se 196.026** | BDL | BDL | | |
| **Tl 190.794** | BDL | BDL | | |
| **V 292.401** | 130.06 | 149.14 | 139.60 | 13.49 |
| **Zn 213.857** | 99.66 | 118.48 | 109.07 | 13.31 |
| **Total Mass** | 925683.62 | 1265640.33 | | |
| **Percentage** | 0.93 | 1.27 | 109.57 | |

# UNH Water Treatment Technology

Microtrac Inc. 10.4.6

20082VI-1

MT6057, File S1796

10/08/2008 08:53

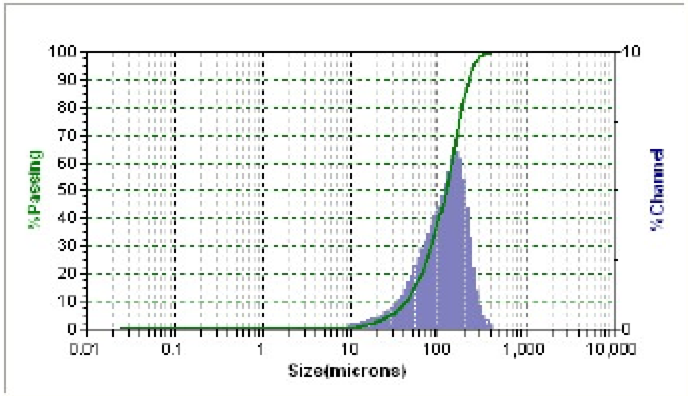
DB Rec: 4

S3000/S3500

S3501

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Distribution: | Volume | Run Time: | 30 Sec | Fluid: | WATER | | |
| Progression: | Geom 8 Root | Run Num: | Avg of 3 | Fluid Ref. Index: | 1.333 | Loading Factor: | 0.0714 |
| Up Edge(um): | 1408 | Particle: | IRON FILLINGS | Above Residual: | 0 | Transmission: | 0.954 |
| Low Edge(um): | 0.0215 | Transparency: | Absorbing | Below Residual: | 0 | RMS Residual: | 0.051% |
| Residuals: | Disabled | Part. Ref. Index: | N/A | | | Flow: | 40 % |
| Num. Channels: | 128 | Part. Shape: | Irregular | Cell ID: | 0236 | Usonic Power: | N/A |
| Analysis Mode: | S3000/3500 | | | Multi-Run Delay: | 0 Min. | Usonic Time: | N/A |
| Filter: | Enabled | DB Record: | 4 | Recalc Status: | Original | Serial Num: | S3501 |
| Analysis Gain: | Default(3) | Database: | C:\Program Files\Microtrac FLEX 10.4.6\Databases\UHH Water Treatment Technology | | | | |

| Data Item | Value | Size(um) | %Tile | %Tile | Size(um) | Dia(um) | Vol% | Width |
|---|---|---|---|---|---|---|---|---|
| MV(um): | 128.3 | | | 10.00 | 43.28 | 123.1 | 100.0 | 143.00 |
| MN(um): | 18.80 | | | 20.00 | 64.48 | | | |
| MA(um): | 81.31 | | | 30.00 | 83.81 | | | |
| CS: | 7.40E-02 | | | 40.00 | 103.4 | | | |
| SD: | 71.62 | | | 50.00 | 123.1 | | | |
| | | | | 60.00 | 142.8 | | | |
| Mz: | 126.4 | | | 70.00 | 163.8 | UDef Name | UDef Data | |
| σi: | 69.76 | | | 80.00 | 188.0 | | | |
| Ski: | 0.1149 | | | 90.00 | 222.4 | | | |
| Kg: | 0.810 | | | 95.00 | 263.2 | | | |

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Warnings: NONE

| Size(um) | %Chan | % Pass | Size(um) | %Chan | % Pass | Size(um) | %Chan | % Pass | Size(um) | %Chan | % Pass |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1408 | 0.00 | 100.00 | 74.00 | 3.18 | 24.92 | 3.89 | 0.00 | 0.00 | 0.2040 | 0.00 | 0.00 |
| 1291 | 0.00 | 100.00 | 67.86 | 2.89 | 21.74 | 3.57 | 0.00 | 0.00 | 0.1870 | 0.00 | 0.00 |
| 1184 | 0.00 | 100.00 | 62.23 | 2.59 | 18.85 | 3.27 | 0.00 | 0.00 | 0.1720 | 0.00 | 0.00 |
| 1086 | 0.00 | 100.00 | 57.06 | 2.28 | 16.26 | 2.999 | 0.00 | 0.00 | 0.1580 | 0.00 | 0.00 |
| 995.6 | 0.00 | 100.00 | 52.33 | 1.98 | 13.98 | 2.750 | 0.00 | 0.00 | 0.1450 | 0.00 | 0.00 |
| 913.0 | 0.00 | 100.00 | 47.98 | 1.71 | 12.00 | 2.522 | 0.00 | 0.00 | 0.1330 | 0.00 | 0.00 |
| 837.2 | 0.00 | 100.00 | 44.00 | 1.45 | 10.29 | 2.312 | 0.00 | 0.00 | 0.1220 | 0.00 | 0.00 |
| 767.7 | 0.00 | 100.00 | 40.35 | 1.23 | 8.84 | 2.121 | 0.00 | 0.00 | 0.1110 | 0.00 | 0.00 |
| 704.0 | 0.00 | 100.00 | 37.00 | 1.05 | 7.61 | 1.945 | 0.00 | 0.00 | 0.1020 | 0.00 | 0.00 |
| 645.6 | 0.00 | 100.00 | 33.93 | 0.90 | 6.56 | 1.783 | 0.00 | 0.00 | 0.0940 | 0.00 | 0.00 |
| 592.0 | 0.00 | 100.00 | 31.11 | 0.78 | 5.66 | 1.635 | 0.00 | 0.00 | 0.0860 | 0.00 | 0.00 |
| 542.9 | 0.00 | 100.00 | 28.53 | 0.67 | 4.88 | 1.499 | 0.00 | 0.00 | 0.0790 | 0.00 | 0.00 |
| 497.8 | 0.00 | 100.00 | 26.16 | 0.59 | 4.21 | 1.375 | 0.00 | 0.00 | 0.0720 | 0.00 | 0.00 |
| 456.5 | 0.00 | 100.00 | 23.99 | 0.53 | 3.62 | 1.261 | 0.00 | 0.00 | 0.0660 | 0.00 | 0.00 |
| 418.6 | 0.17 | 100.00 | 22.00 | 0.47 | 3.09 | 1.156 | 0.00 | 0.00 | 0.0610 | 0.00 | 0.00 |
| 383.9 | 0.33 | 99.83 | 20.17 | 0.41 | 2.62 | 1.060 | 0.00 | 0.00 | 0.0560 | 0.00 | 0.00 |
| 352.0 | 0.51 | 99.50 | 18.50 | 0.37 | 2.21 | 0.972 | 0.00 | 0.00 | 0.0510 | 0.00 | 0.00 |
| 322.8 | 0.85 | 98.99 | 16.96 | 0.33 | 1.84 | 0.892 | 0.00 | 0.00 | 0.0470 | 0.00 | 0.00 |
| 296.0 | 1.41 | 98.14 | 15.56 | 0.30 | 1.51 | 0.818 | 0.00 | 0.00 | 0.0430 | 0.00 | 0.00 |
| 271.4 | 2.21 | 96.73 | 14.27 | 0.27 | 1.21 | 0.750 | 0.00 | 0.00 | 0.0390 | 0.00 | 0.00 |
| 248.9 | 3.28 | 94.52 | 13.08 | 0.24 | 0.94 | 0.688 | 0.00 | 0.00 | 0.0360 | 0.00 | 0.00 |
| 228.2 | 4.36 | 91.24 | 12.00 | 0.22 | 0.70 | 0.630 | 0.00 | 0.00 | 0.0330 | 0.00 | 0.00 |
| 209.3 | 5.43 | 86.88 | 11.00 | 0.21 | 0.48 | 0.578 | 0.00 | 0.00 | 0.0300 | 0.00 | 0.00 |
| 191.9 | 6.12 | 81.45 | 10.09 | 0.16 | 0.27 | 0.530 | 0.00 | 0.00 | 0.02790 | 0.00 | 0.00 |
| 176.0 | 6.40 | 75.33 | 9.25 | 0.08 | 0.11 | 0.486 | 0.00 | 0.00 | 0.02550 | 0.00 | 0.00 |
| 161.4 | 6.39 | 68.93 | 8.48 | 0.03 | 0.03 | 0.446 | 0.00 | 0.00 | 0.02340 | 0.00 | 0.00 |
| 148.0 | 6.10 | 62.54 | 7.78 | 0.00 | 0.00 | 0.409 | 0.00 | 0.00 | | | |
| 135.7 | 5.72 | 56.44 | 7.13 | 0.00 | 0.00 | 0.375 | 0.00 | 0.00 | | | |
| 124.5 | 5.25 | 50.72 | 6.54 | 0.00 | 0.00 | 0.344 | 0.00 | 0.00 | | | |
| 114.1 | 4.81 | 45.47 | 6.00 | 0.00 | 0.00 | 0.315 | 0.00 | 0.00 | | | |
| 104.7 | 4.42 | 40.66 | 5.50 | 0.00 | 0.00 | 0.2890 | 0.00 | 0.00 | | | |
| 95.96 | 4.08 | 36.24 | 5.04 | 0.00 | 0.00 | 0.2650 | 0.00 | 0.00 | | | |
| 88.00 | 3.77 | 32.16 | 4.62 | 0.00 | 0.00 | 0.2430 | 0.00 | 0.00 | | | |
| 80.70 | 3.47 | 28.39 | 4.24 | 0.00 | 0.00 | 0.2230 | 0.00 | 0.00 | | | |