Arsenic Treatment Update

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MDEQ - Water Bureau

16th Groundwater Conference
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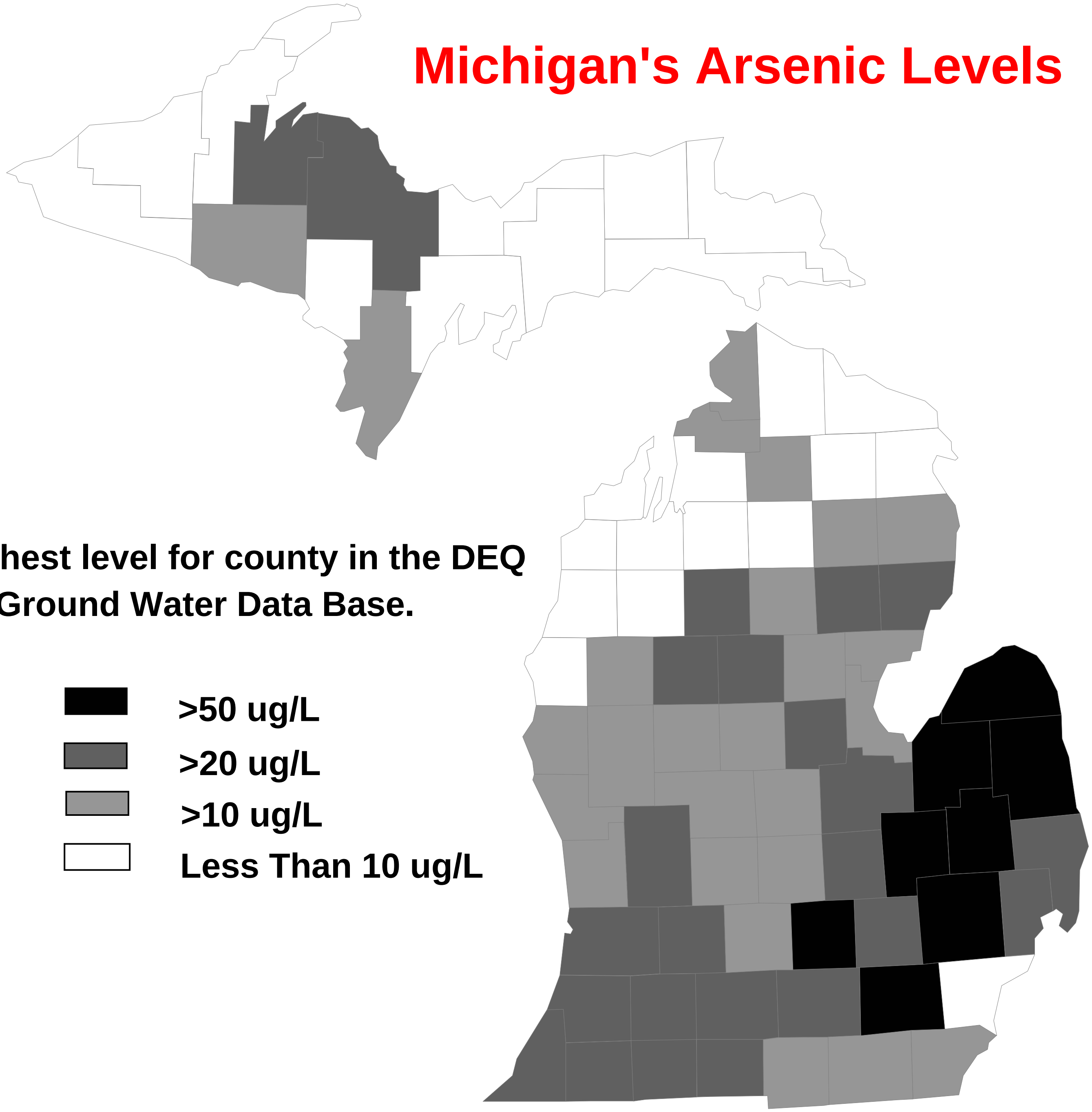
Arsenic Occurrence

- Naturally occurring element
- Found throughout the United States
- Weathers from rocks and soils
- Primarily found in ground waters

- MCL lowered from 50 to 10 ppb on Jan 23, 2006 for Community and Nontransient Noncommunity supplies

Michigan's Arsenic Levels



Highest level for county in the DEQ Ground Water Data Base.

Arsenic Chemistry

- Arsenic has two primary valence states:

As (III)	As +3	Arsenite
As (V)	As +5	Arsenate

- Arsenic occurrence by valence state
  - *Surface waters* - predominately As (V)
  - *Ground waters* - usually found as As (III)
    - concentrations of As (V)
    - combination of As (III) and As (V)

Arsenic Chemistry

What is the significance of arsenic speciation?

As (V) more effectively removed than As (III) by most treatment technologies

- As (III) is neutral at natural pH levels (6-9)
- As (V) is negatively charged at natural pH levels

•The negative surface charges facilitate removal by adsorption, anion exchange and co-precipitative processes

As III Oxidation

Effective

- **Free Chlorine**
- **Potassium Permanganate**
- **Ozone**
- **Solid Oxidizing Media (MnO_2 solids)**

Ineffective

- **Chloramines**
- **Chlorine Dioxide**
- **UV Radiation**
- **Aeration**

Arsenic treatment options

- Conventional iron removal
- Modified iron removal
- Anion exchange
- Membranes (nano or RO)
- Adsorptive media
  - -Iron
  - -Alumina
  - -Titanium

As Removal by Iron Removal

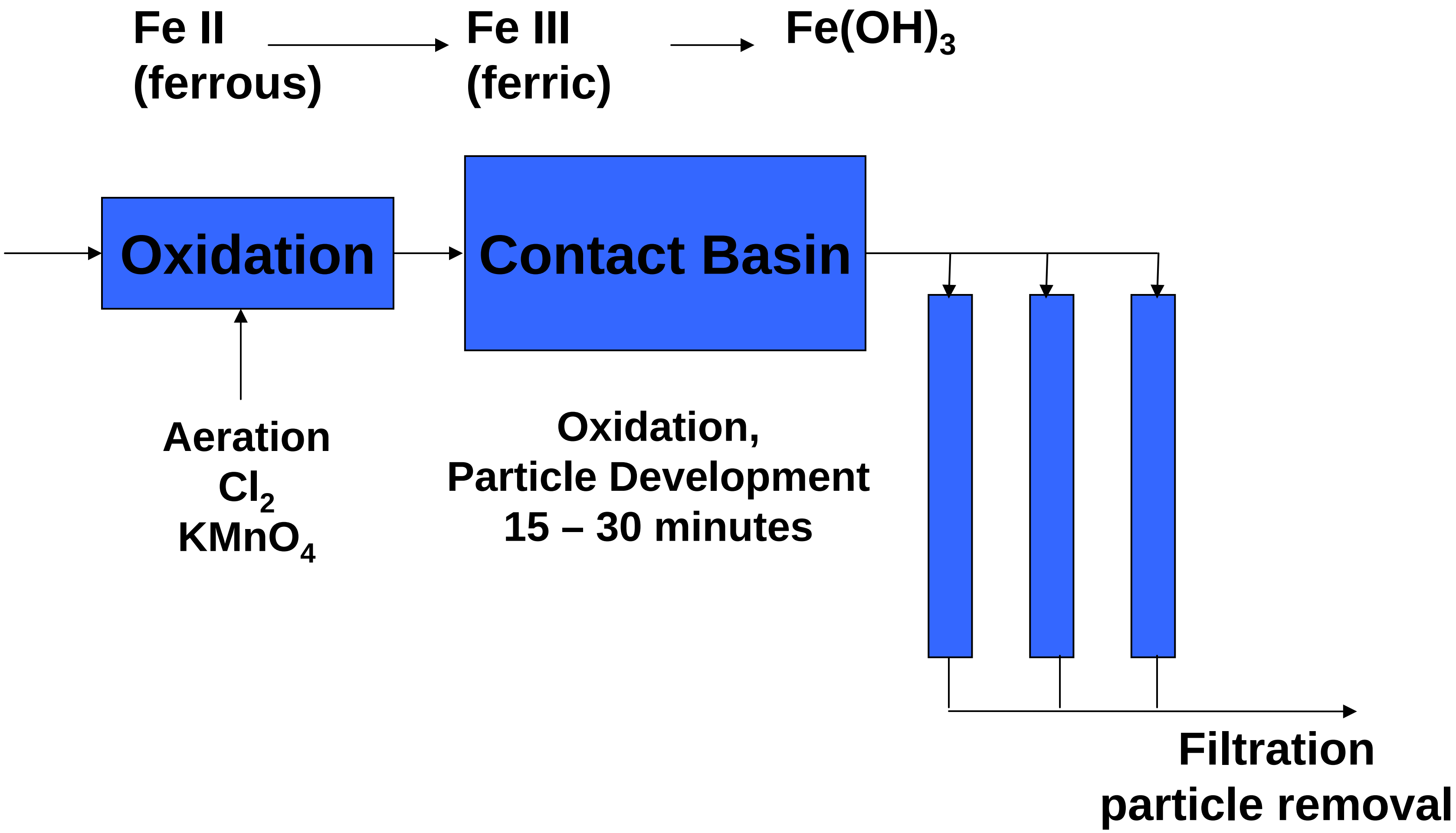
Removal of 1 mg/L of iron

achieves

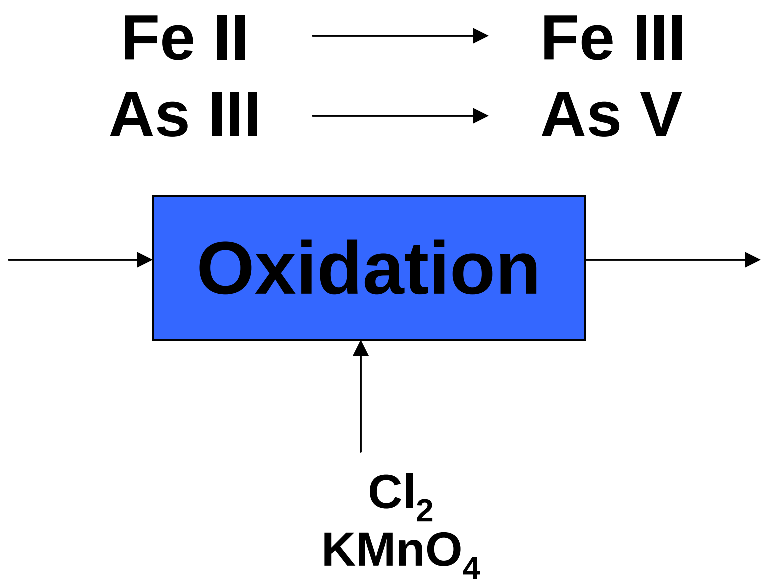
removal of 50 ug/L arsenic
(0ptimized conditions and As[V])

Can add iron before treatment process to make As removal more efficient

Iron Removal Basics



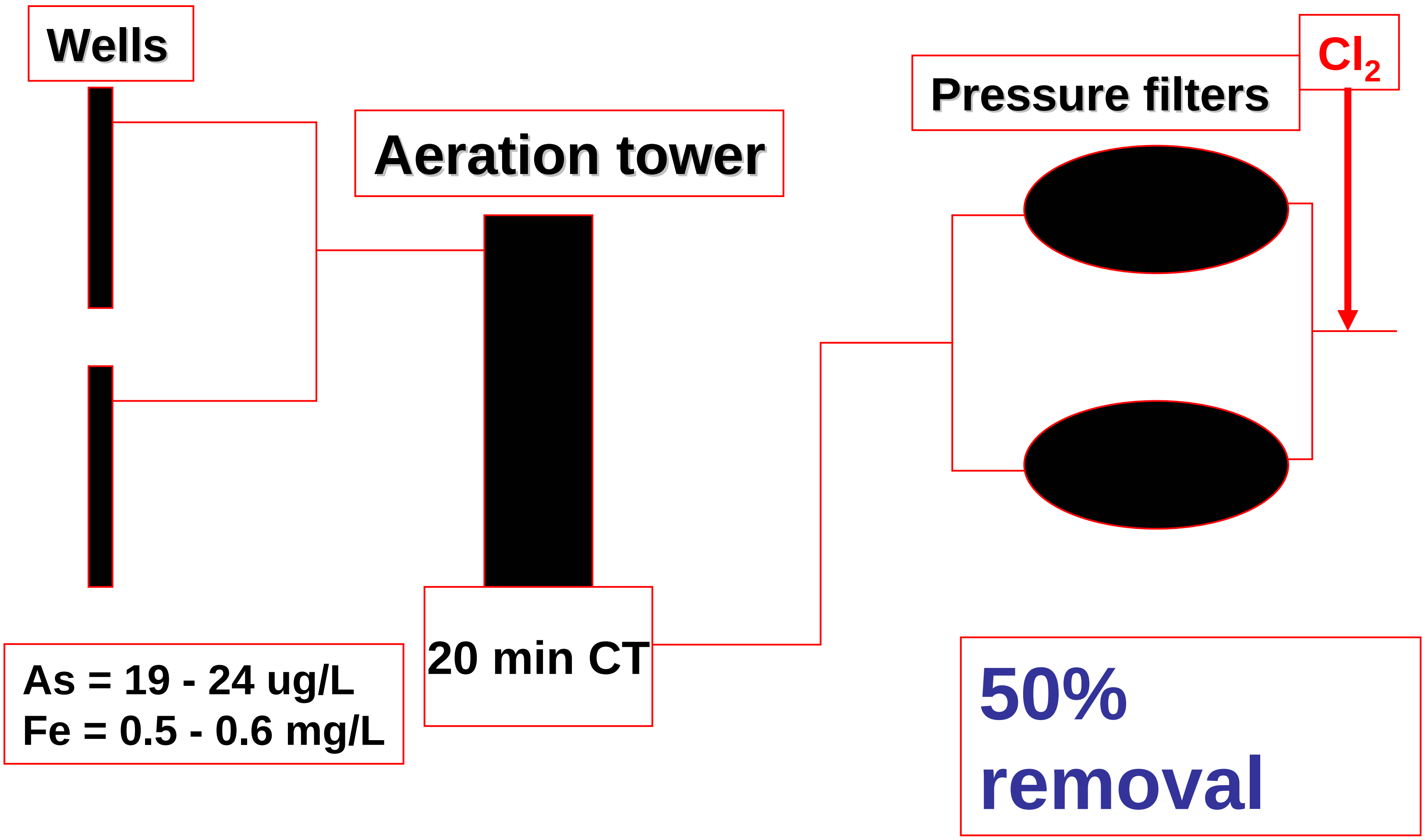
Iron and Arsenic Removal



Note: Aeration will not oxidize As III to As V

Oxidation- Point of Application

Case Study - Michigan



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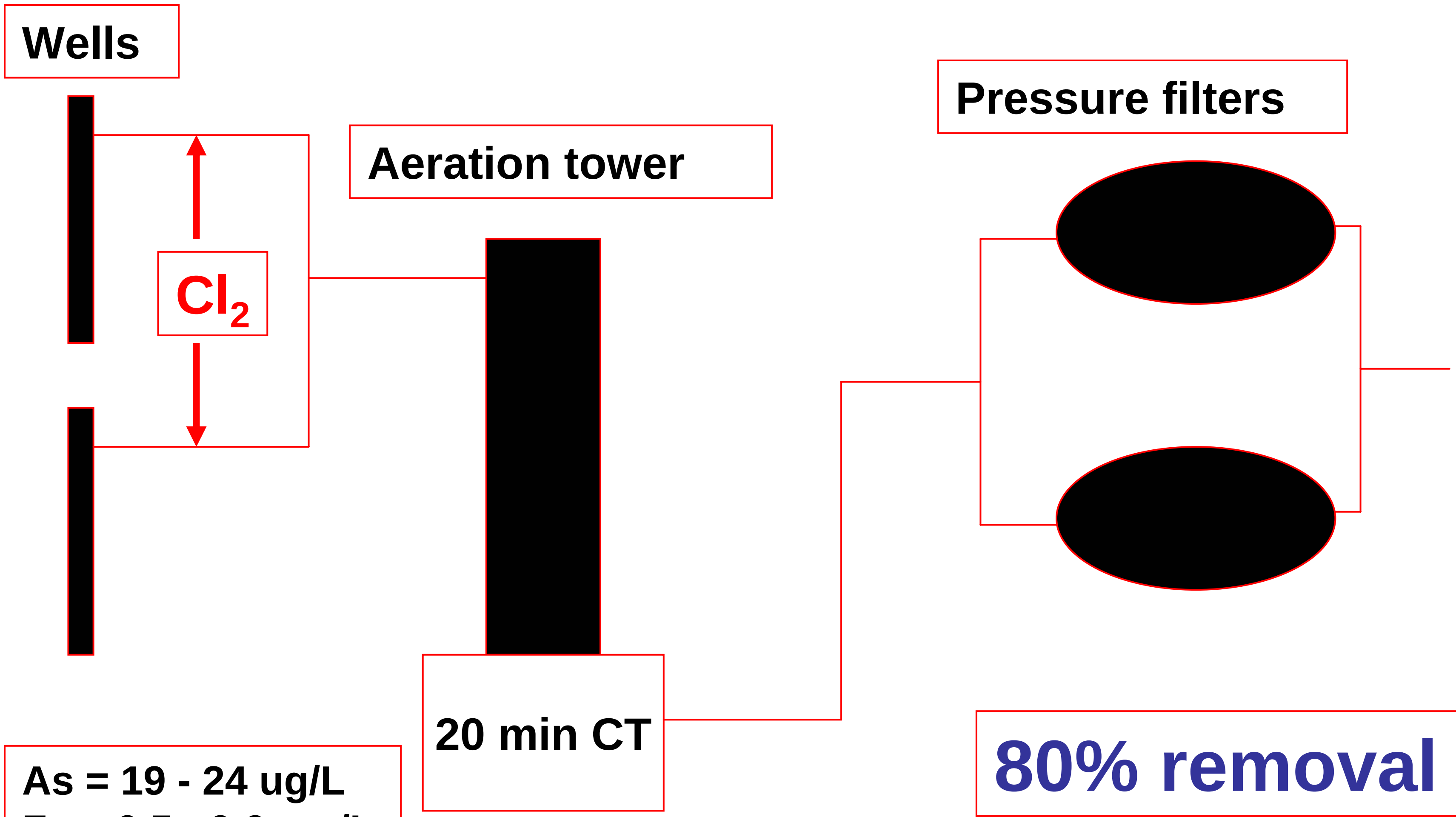


As = 19 - 24 ug/L
Fe = 0.5 - 0.6 mg/L

80% removal

Modified Iron removal

- Uses an oxidizer to convert ferrous iron to ferric plus As(III) to As(V), then filter the Fe & As out
- The media acts as both a filter and oxidizer
- High catalytic activity accelerates conversion of Fe and As resulting in higher loading rates
- Basically an oxidation, precipitation, filtration process
- Filtration rates range from 4 -10 gpm/ft^2
- Continuous oxidation is a must!

Modified Iron removal (con't)

Medias are MnO_2 based media

- Potassium permanganate - Mn greensand
- Layne Northern – Layne Ox
- Artesian of Pioneer – Maris Media
- Peerless, Inc – Triple XIP (greensand, anthracite)
- Iversand Greensand Plus

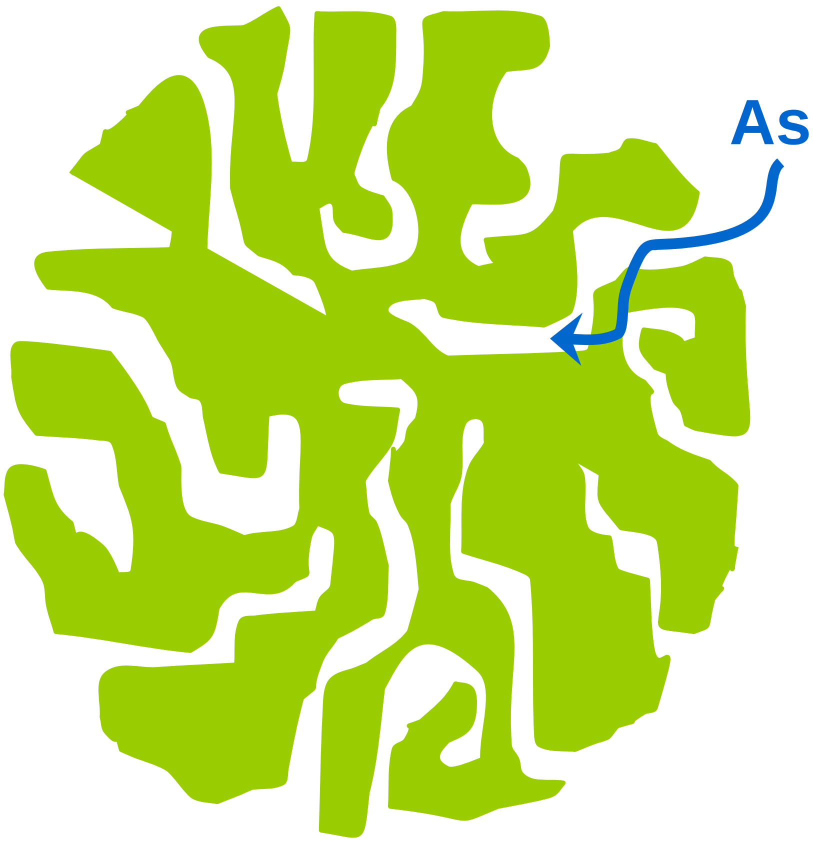
- Kinetico – Macrolite (ceramic)

Adsorption medias-Intro

- A**d**sorption is contaminant removal from water by attachment onto the surface of a porous solid (pie in the face)

- A**b**sorption is contaminant removal by dissolution/reaction in another phase (eating a pie)

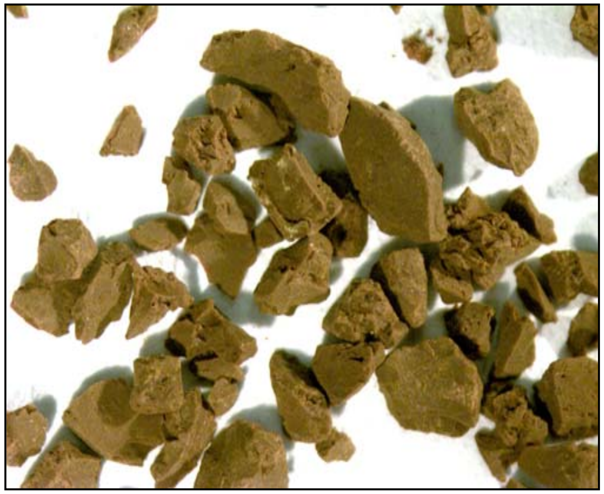
Accessible Area of Granular Media



> 99% of surface for removal is internal

Examples of Adsorbent Media

ADI G2



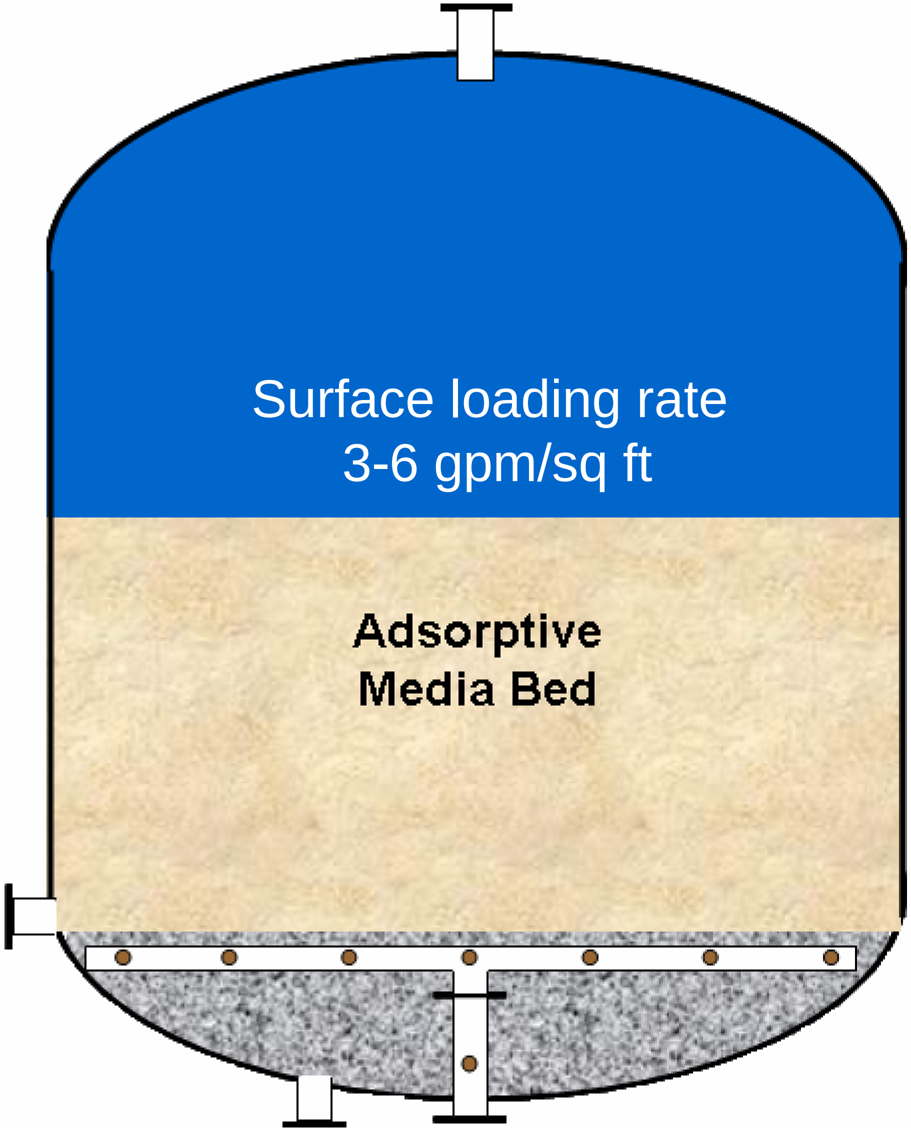
Bayoxide E33

Activated alumina

Adsorptive Media Pressure Tank

<u>EBCT</u>
3-10 mins

Volume of media / flow

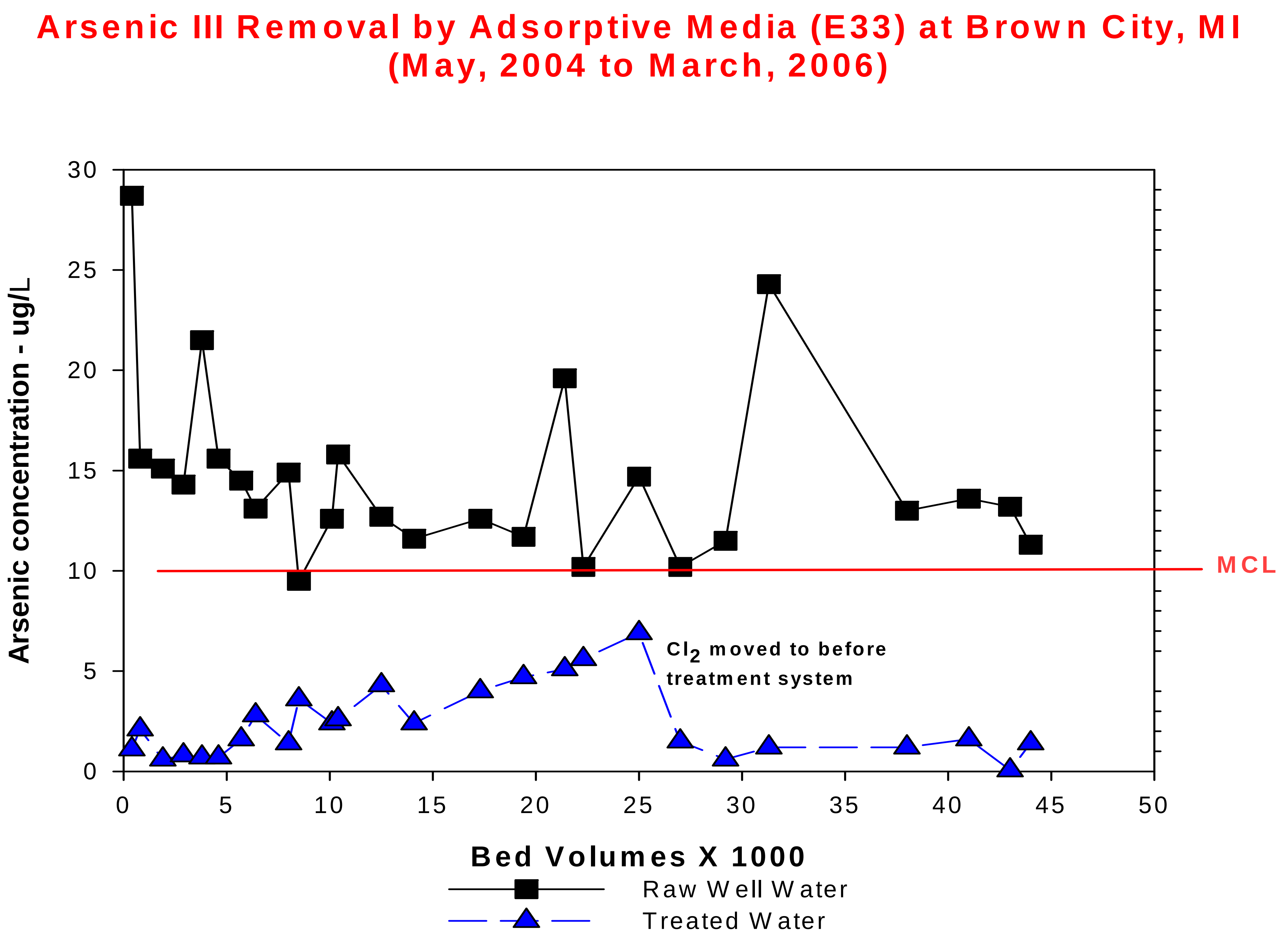


Freeboard

Bed expansion
15 - 50 %

Bed depth
3-6 ft

Brown City, MI Adsorptive Media System


Arsenic III Removal by Adsorptive Media (E33) at Brown City, MI
(May, 2004 to March, 2006)
Arsenic concentration - ug/L
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
40
45
50
Bed Volumes X 1000
MCL
Cl2 moved to before
treatment system
Raw Well Water
Treated Water

Alumina Based Media

- Act similar to iron based medias by removing As by adsorption
- Usually do not remove As as efficient as Fe based medias (media needs replacement quicker)
- Media cost is usually lower then Fe media

Titanium Based Media

- Act similar to iron based medias by removing As by adsorption
- Can remove As more efficiently than Fe based medias (media last longer)
- Media cost is usually higher then Fe media

Adsorption medias Evaluation Criteria

- Cost
- As(III) vs. As(V) in raw water
- Bed Volumes before disposal/regeneration
- Iron concentrations
- Competitive adsorption (competing ions)
- Other chemicals (CL2, KMn04) needed
- Backwash disposal options

Adsorptive Media

Some medias can also remove……..

<u>Co-contaminants</u>

Uranium, Antimony, and Radium

<u>Competing anions</u>

Silicon, Vanadium, Phosphorus, Fluoride

Can decrease media efficiency and useful life!

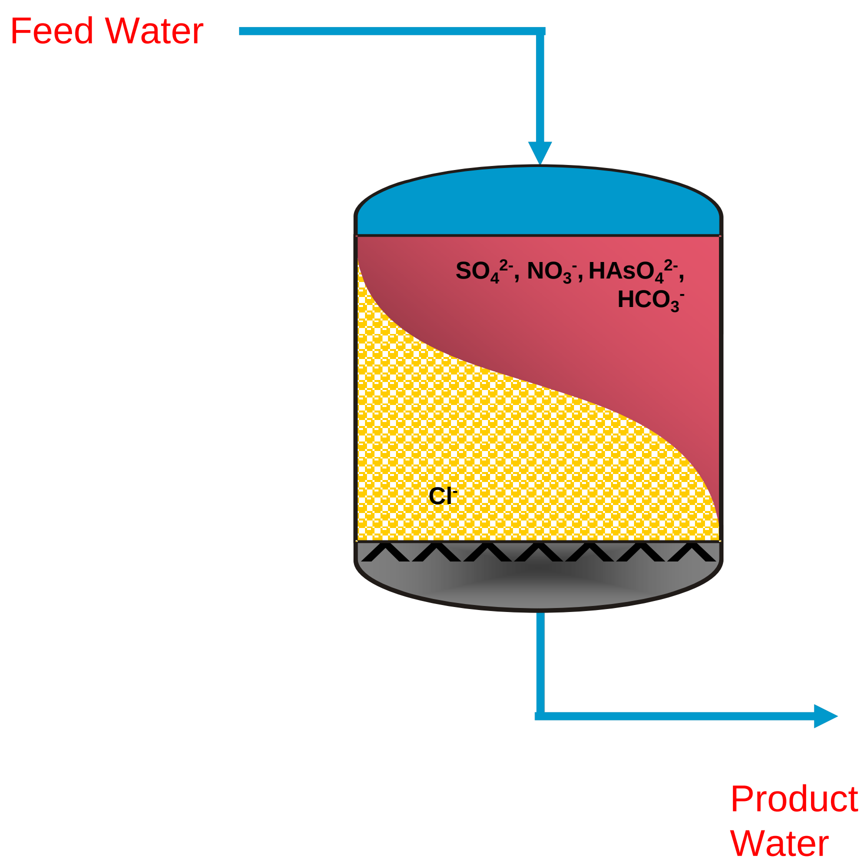
Ion (Anion) Exchange

- Similar to water softeners, but uses a negatively (anion) charged resin
- Arsenic must be in As (V) state
- pH must be in 6.5 – 9.0 range
- Sulfate should be < 50 mg/l
- “Dumping” is a concern (As released from resin by competing ions)
- Chloride exchanged 2:1 for each sulfate and arsenic ion removed

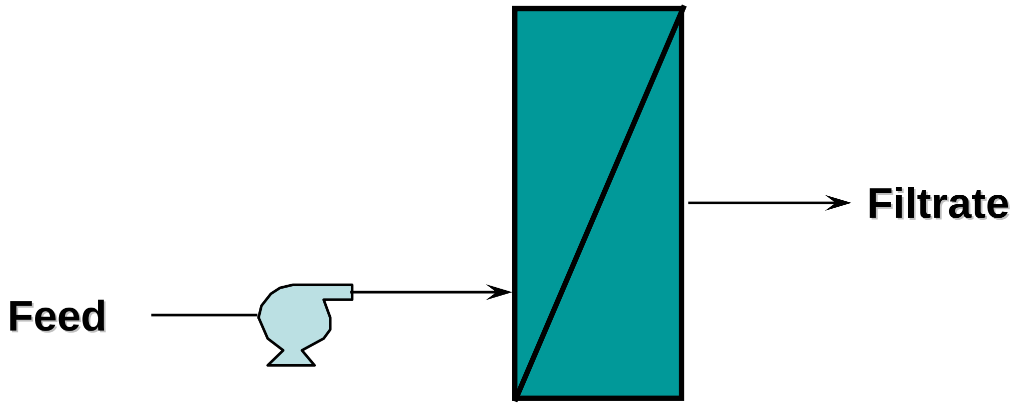
Anion Exchange Process

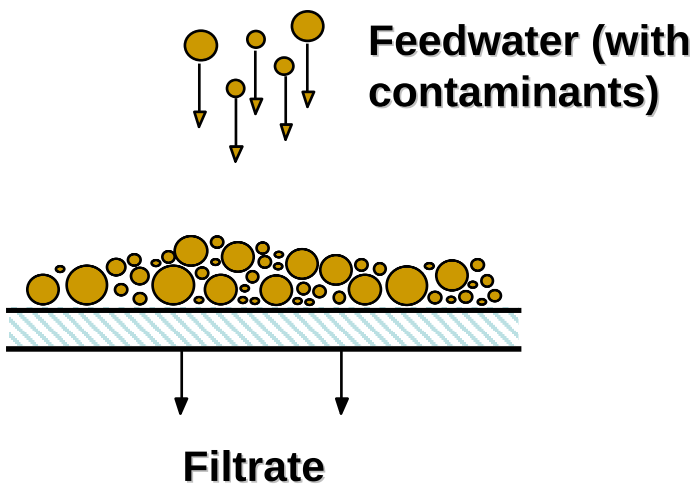
- Exchange chlorides on strong base anion exchange resin with arsenic in raw water
- Ion selectivity:

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



Reverse Osmosis Process

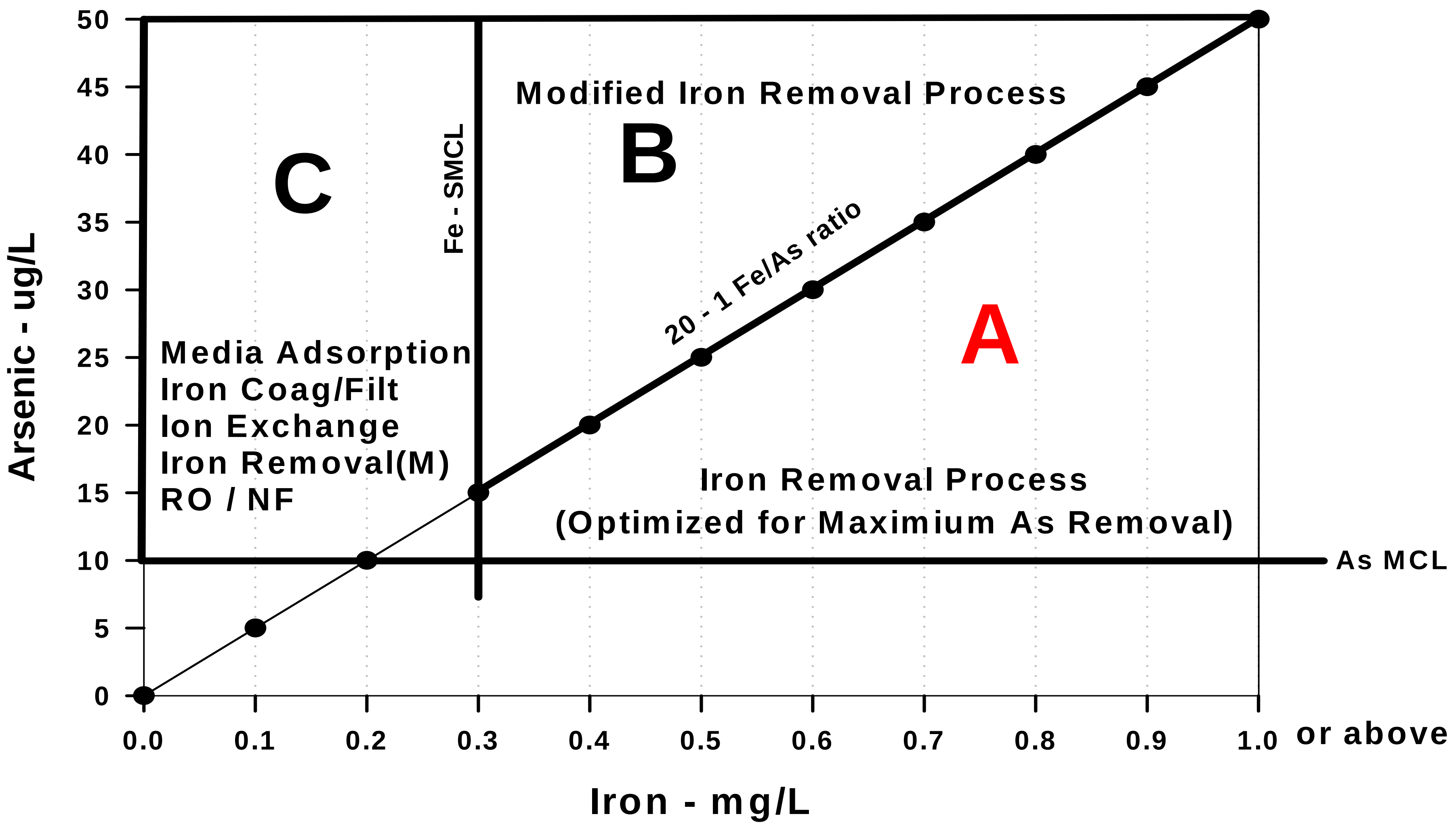




pH adjustment

- Reducing influent pH can increase arsenic removal capacity
- Adds O&M complexity
- Loss of pH adjustment can cause an arsenic spike in the treated water

Arsenic Treatment Process Selection



Backwash Water Considerations

<u>Conventional iron, modified iron and IX</u>

1-7 days and will contain arsenic in the backwash water

<u>Adsorption based medias</u>

every 7-30 days depending a raw water quality

Usually contains elevated levels of As

As bound to the naturally occurring iron in the raw water is not adsorbed onto the media

MI Preliminary Numbers (2003)

- Based on historical sample results it was expected that as many as 160 Community Water Systems (CWS) and 330 Nontransient Noncommunity water systems (NTNCWS) would exceed the 10 ppb standard.

- Inventory of MI Public Water Supplies
  - ~1,400 CWS
  - ~1,530 NTNCWS
  - ~8,750 TNCWS

MI Numbers (cont)

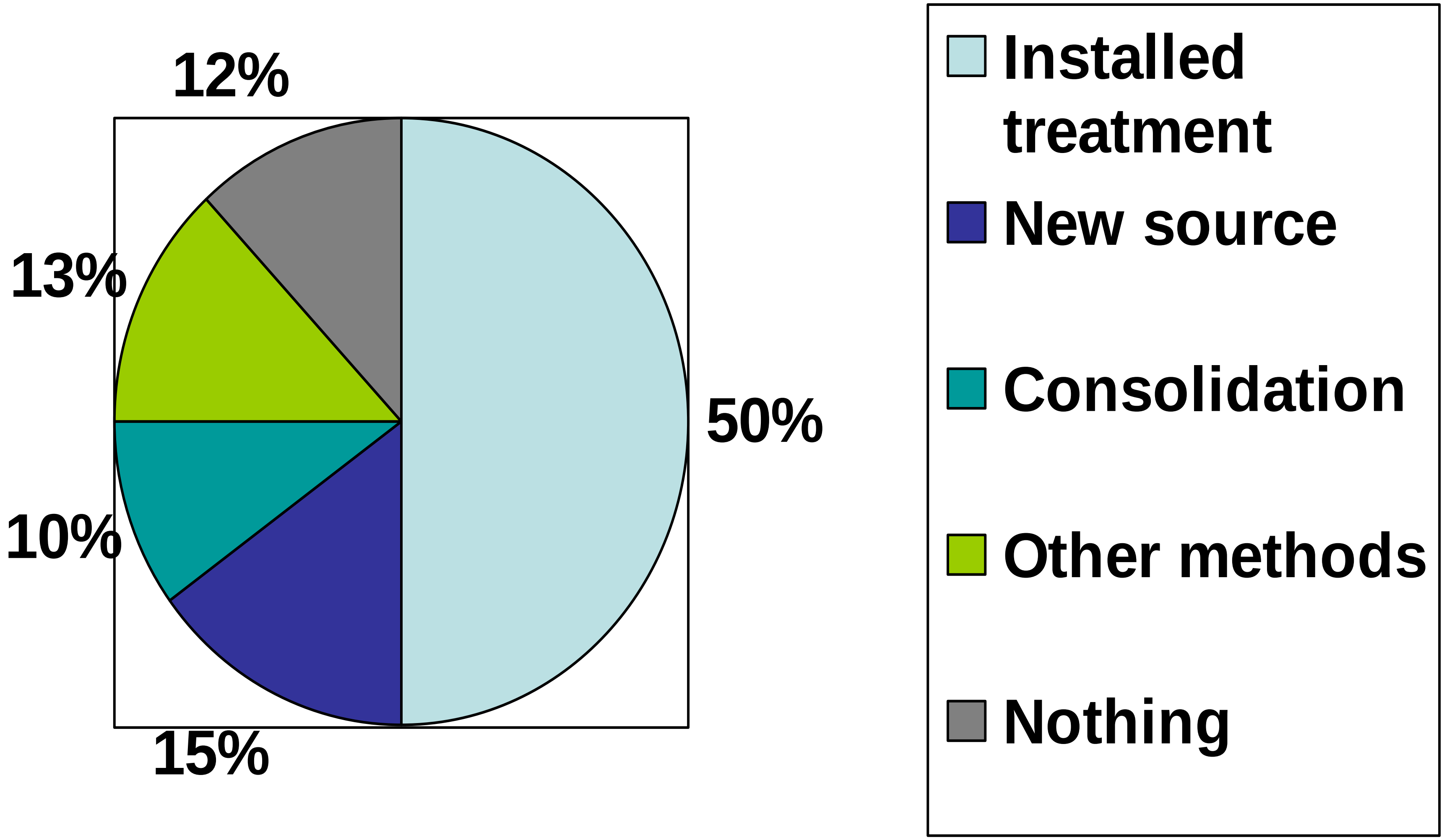
Since Jan 2006

- 111 CWS violated the 10 ppb MCL
- 164 NTNCWS violated the MCL

As of Jan 2009

- 24 CWS still exceed the standard
- 12 NTNCWS still exceed the standard

Compliance Methods



Questions