
Arsenic Removal by Coagulation & Precipitation Processes

Presentation Prepared by:

Joe Chwirka - Camp Dresser & McKee
(chwirkajd@cdm.com)

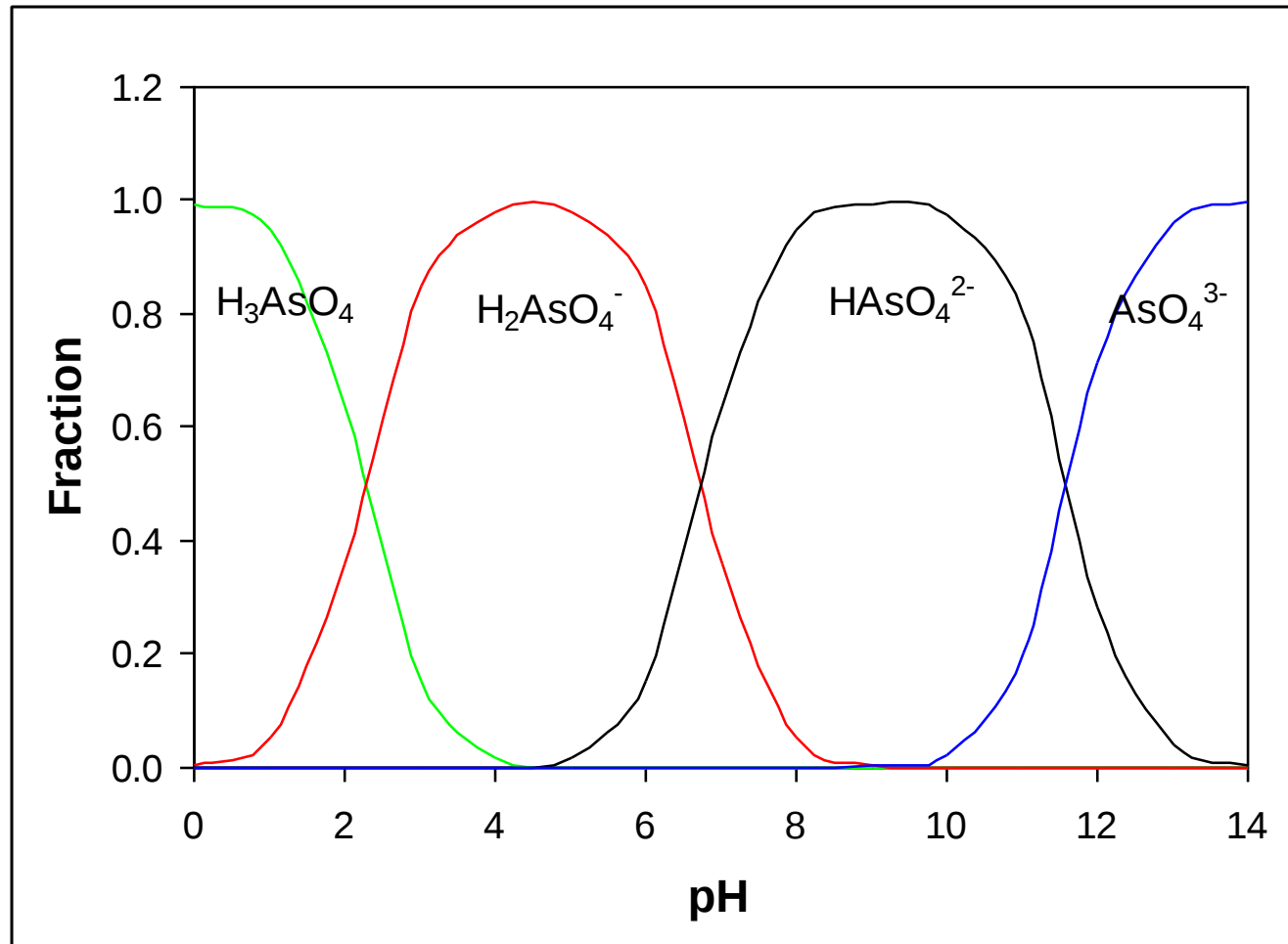
Bruce Thomson - University of New Mexico
(bthomson@unm.edu)

Presented by: YuJung Chang – HDR Engineering, Inc.

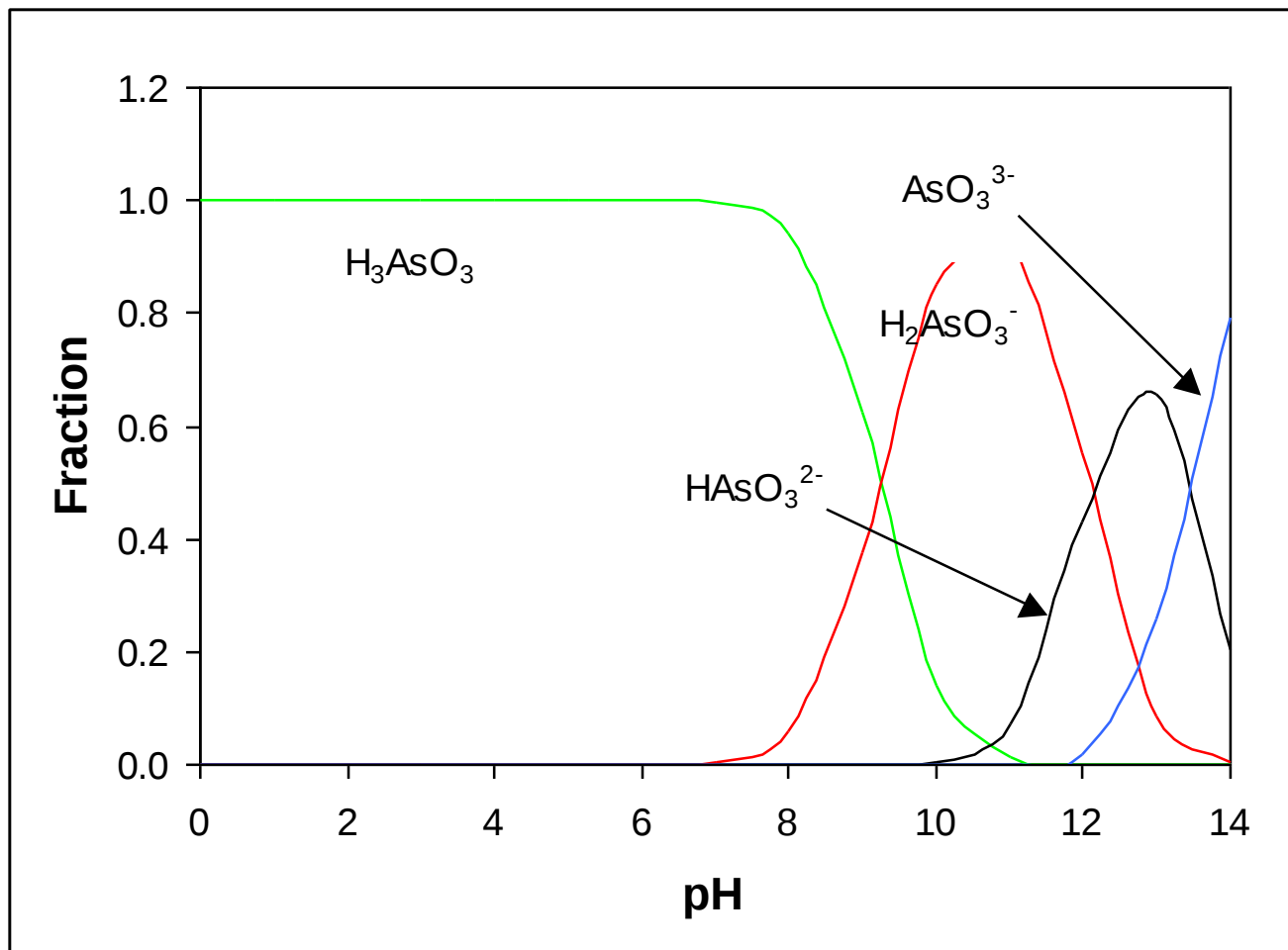
Introduction

- Arsenic removal by coagulation & filtration is effective for many applications
- Presentation will discuss:
 - Chemistry of the process
 - Variables affecting process performance (especially pH & coagulant dose)
 - Process variations
 - Coagulation & granular media filtration
 - Coagulation & membrane filtration
 - Design considerations

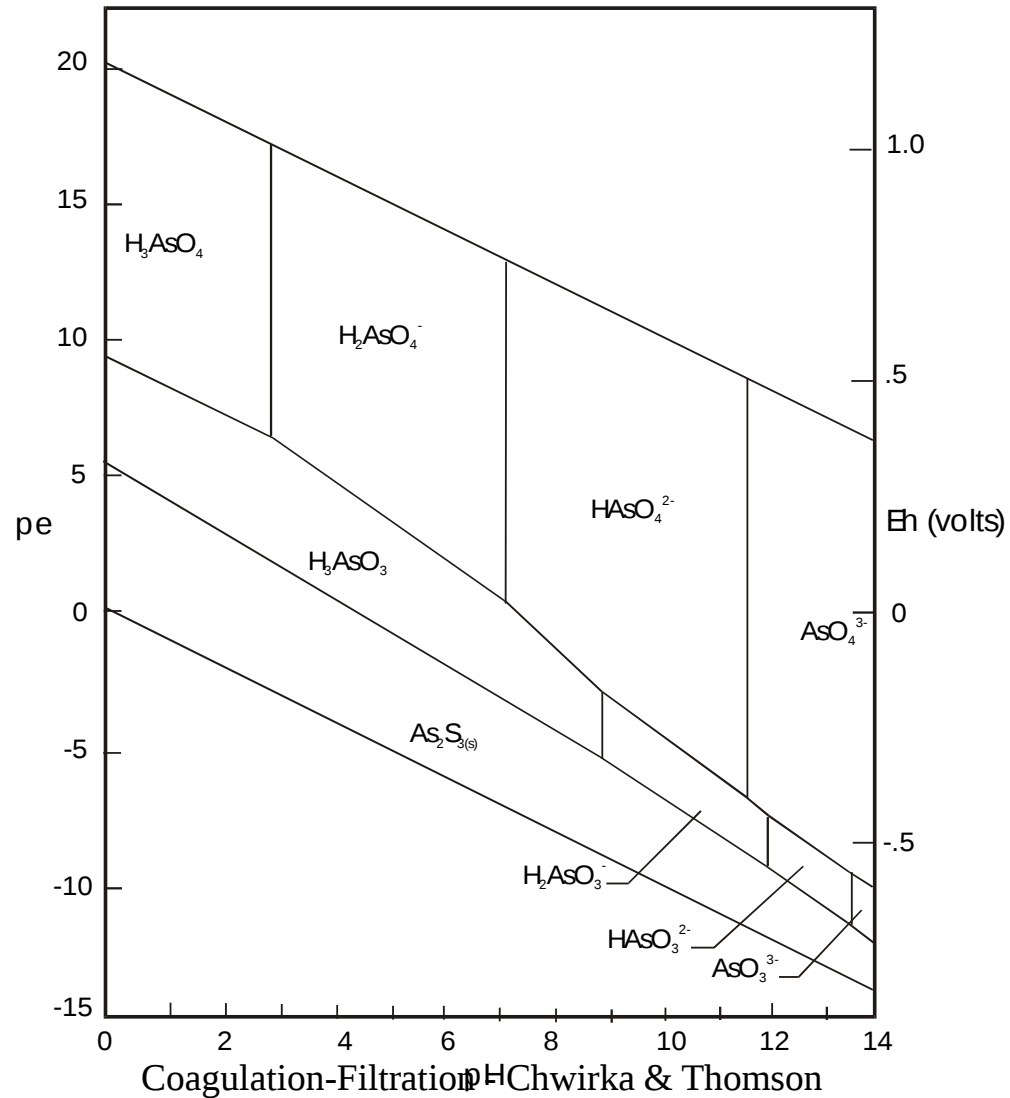
Acid-Base Chemistry of As(V)



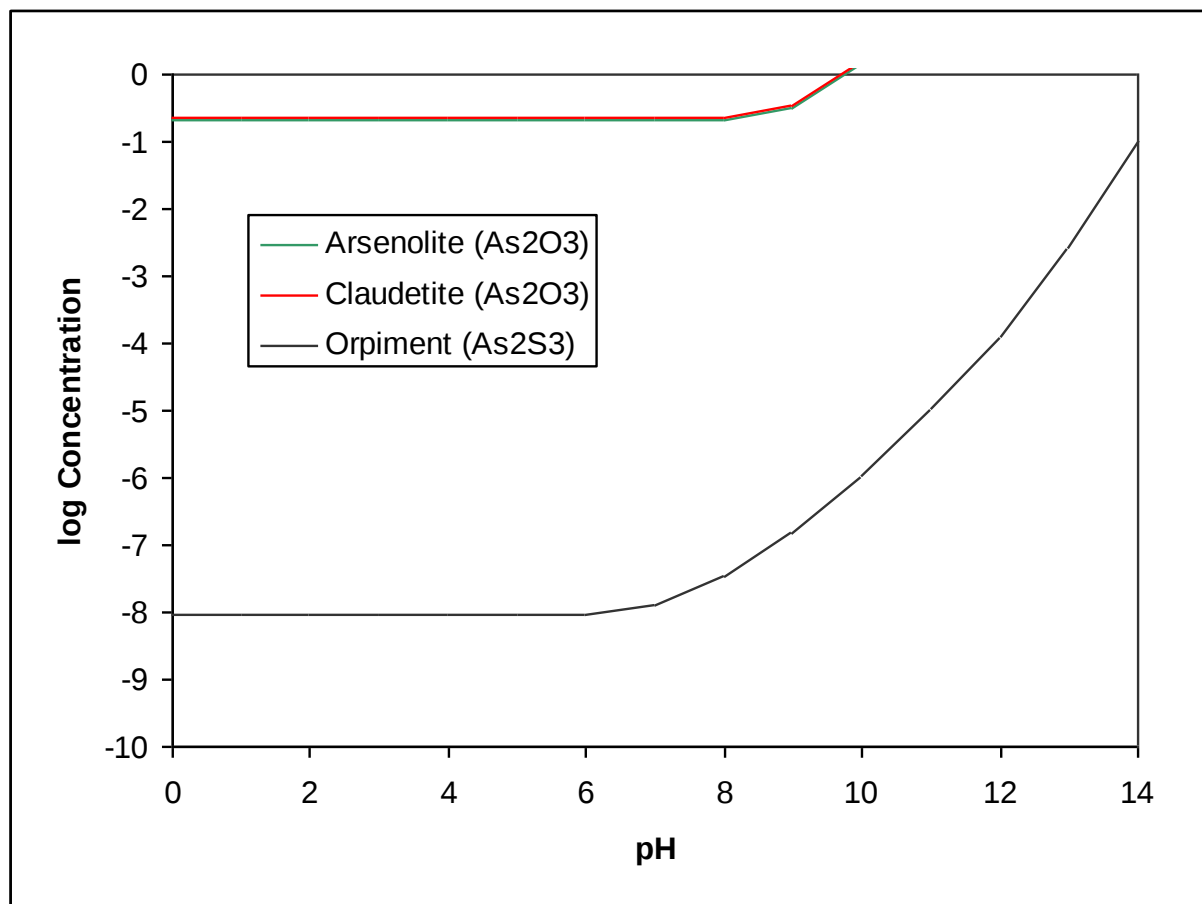
Acid-Base Chemistry of As(III)



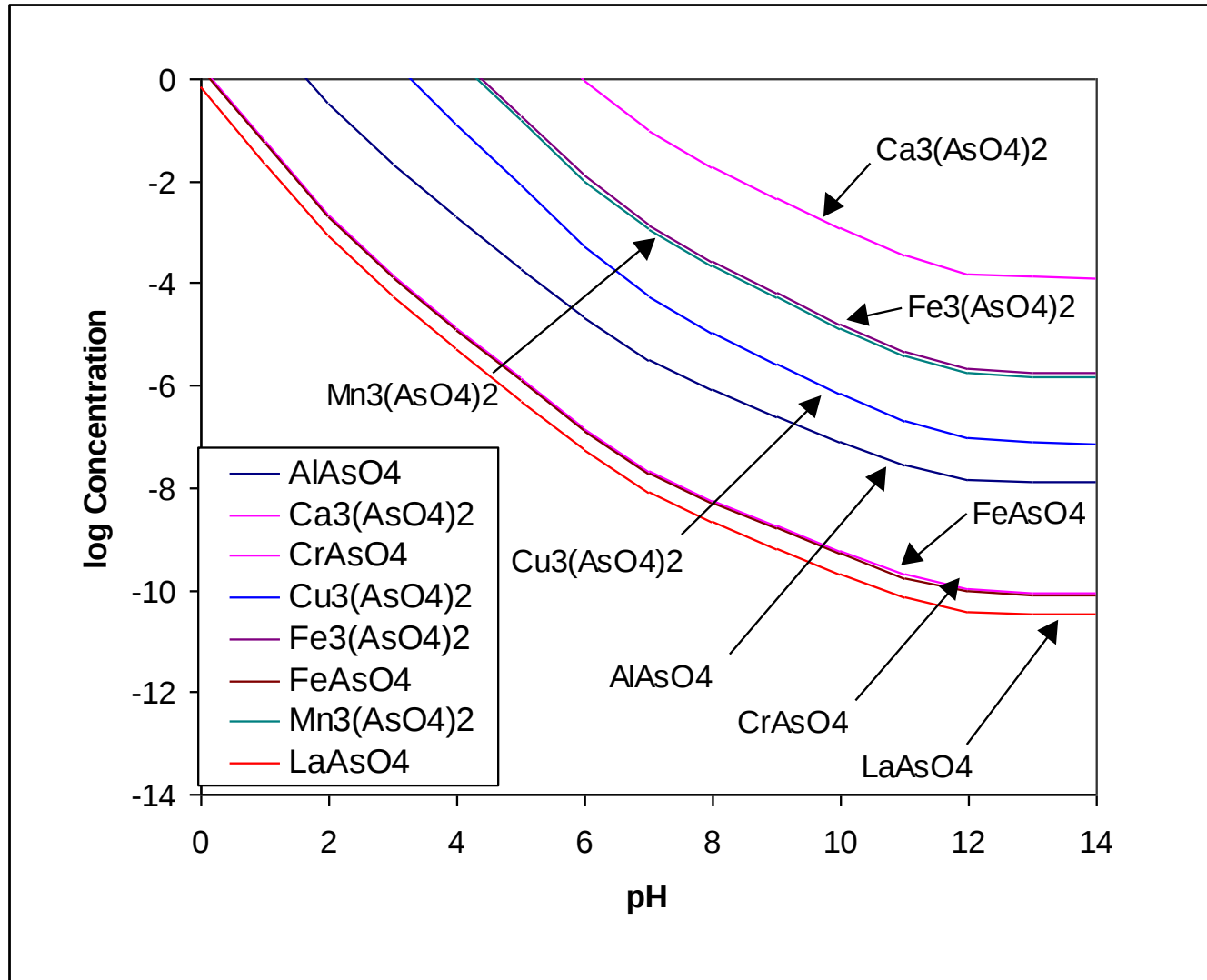
Redox Chemistry of As



Solubility of As(III) Compounds



Solubility of As(V) Species

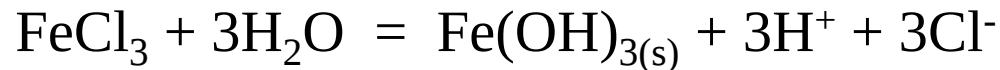


Important Points

- As has two oxidation states - As(III) & As(V)
- As(III)
 - Non-ionic (H_3AsO_3) at neutral pH
 - High solubility
 - More toxic to many organisms
- As(V)
 - Ionic ($\text{H}_2\text{AsO}_4^-/\text{HAsO}_4^{2-}$) at neutral pH
 - Some phases are less soluble
 - More reactive in solution:
 - Membranes
 - IX
 - Adsorption

Coprecipitation

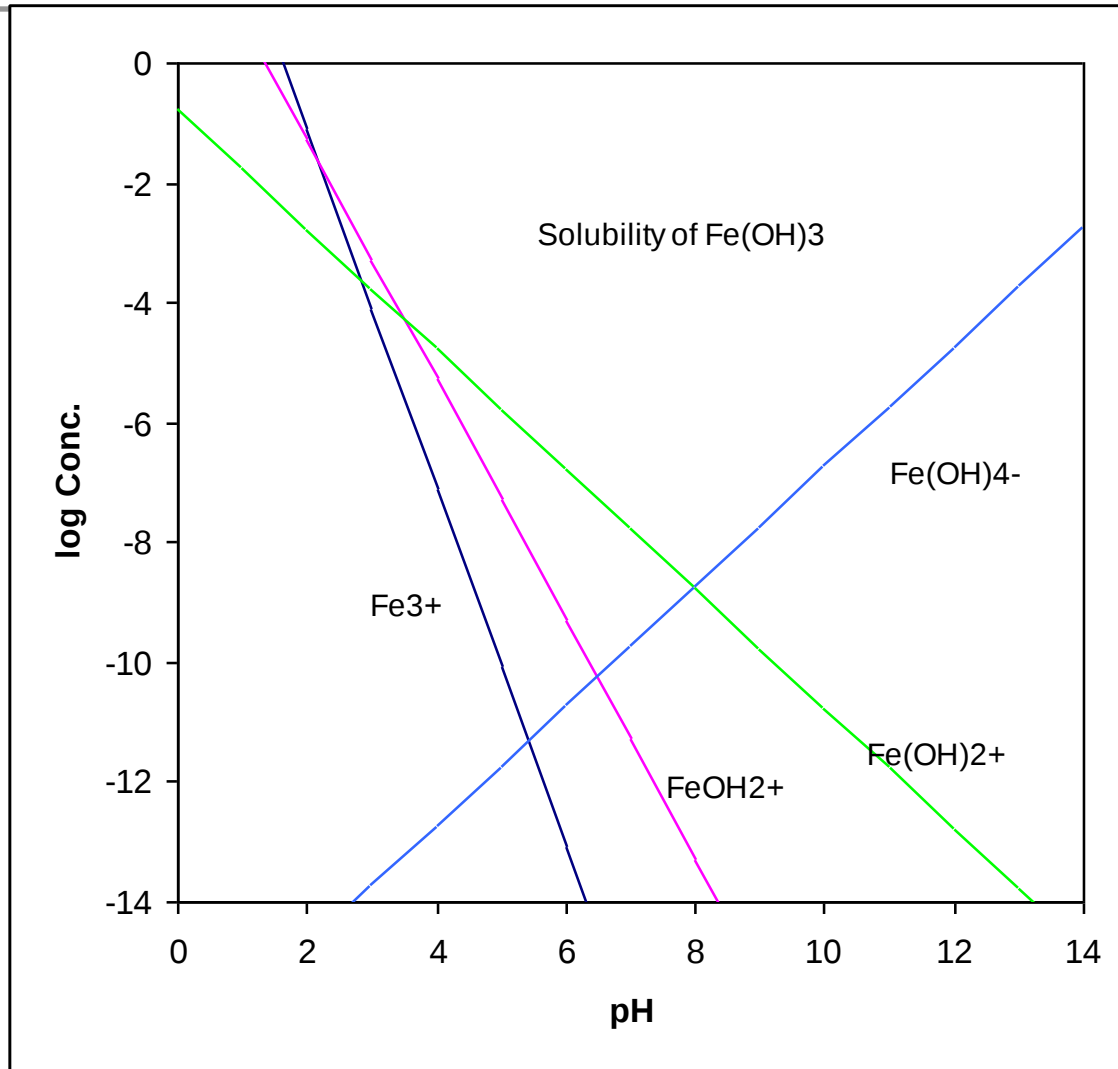
- Coprecipitation involves removal of two or more constituents by a precipitation reaction. Coprecipitation of As with $\text{Fe}(\text{OH})_3$ is an effective treatment process:



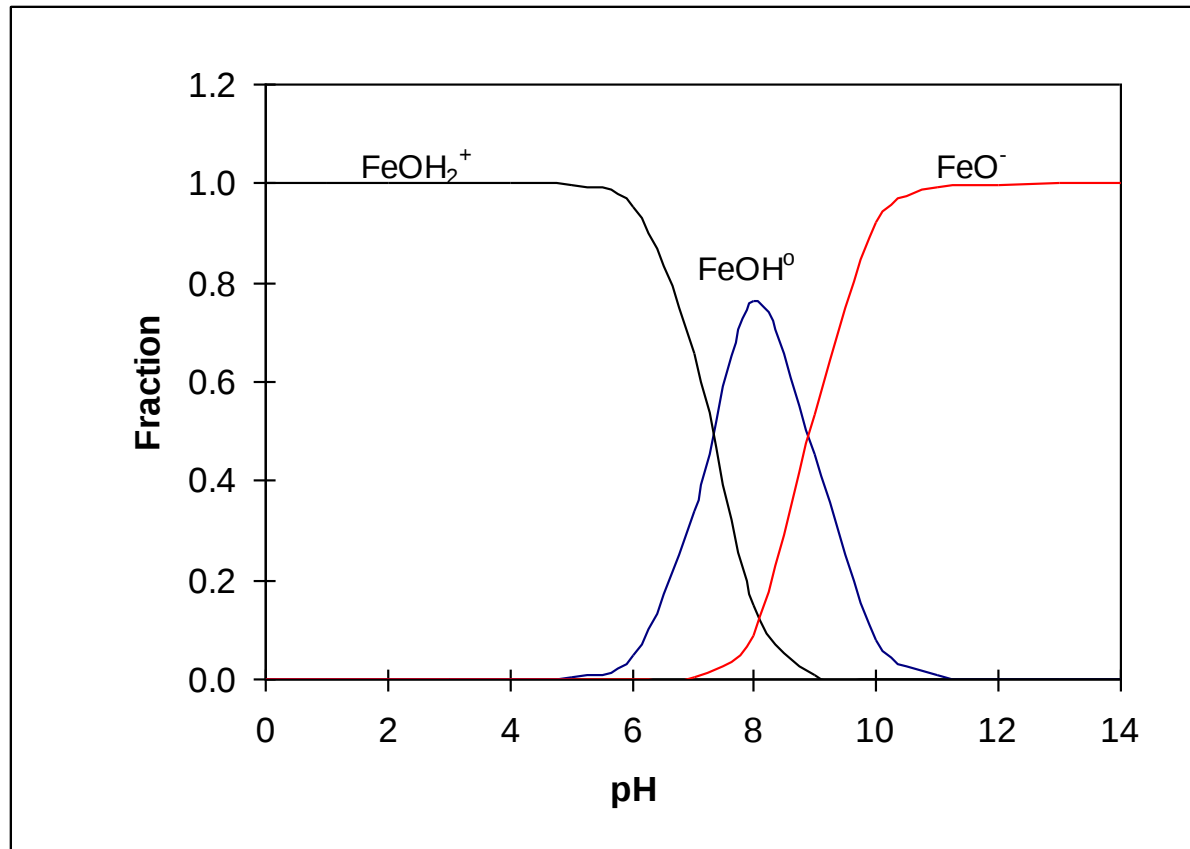
Points:

- Produces HCl which will lower pH
- Typical Fe dose $\sim 10^{-4}$ M, whereas As conc. $\sim 10^{-7}$ M, hence As is minor component within precipitate
- As likely removed by adsorption onto $\text{Fe}(\text{OH})_3$ surface with subsequent enmeshment as floc particle grows
- $\text{Al}(\text{OH})_3$ also effective

Solubility of $\text{Fe}(\text{OH})_3$

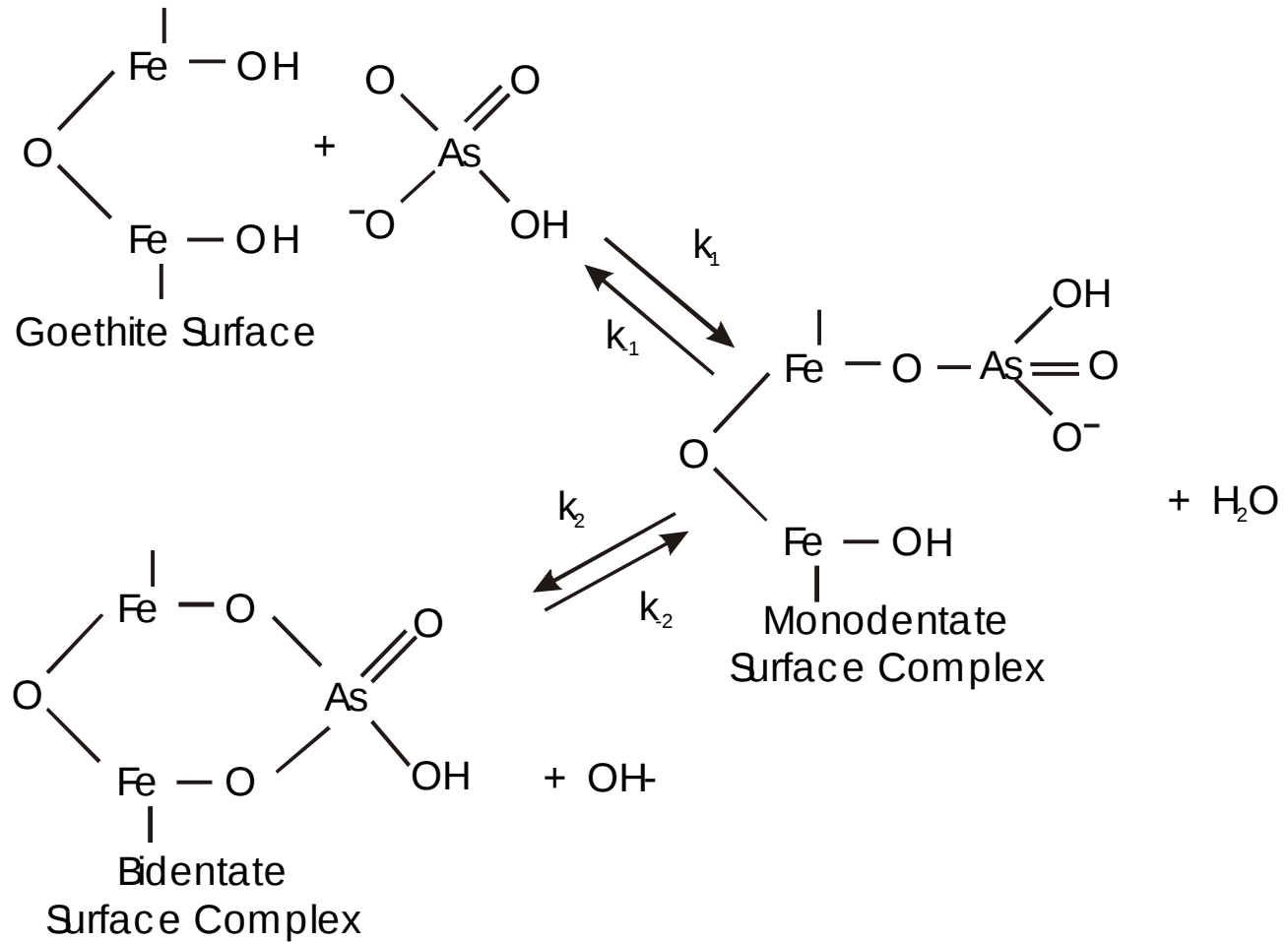


Effect of pH on Surface Charge of $\text{Fe}(\text{OH})_3$



Covalent Bond Formation

(Grossl et al., 1997)



pH of Zero Point of Charge

- Electrostatic attraction is important first step in adsorption
- $\text{pH}_{\text{zpc}} = \text{pH}$ at which net surface charge = 0
 - Surface is positive at $\text{pH} < \text{pH}_{\text{zpc}}$
- Most clay minerals have $\text{pH}_{\text{zpc}} < 6$
 - Hence poor adsorption
 - Clays dominate surface chemistry of soils
- $\text{Fe}(\text{OH})_3$ and Al_2O_3 have relatively high pH_{zpc}
 - Good adsorbents of $\text{As}(\text{V})$

As Removal by Conventional Treatment

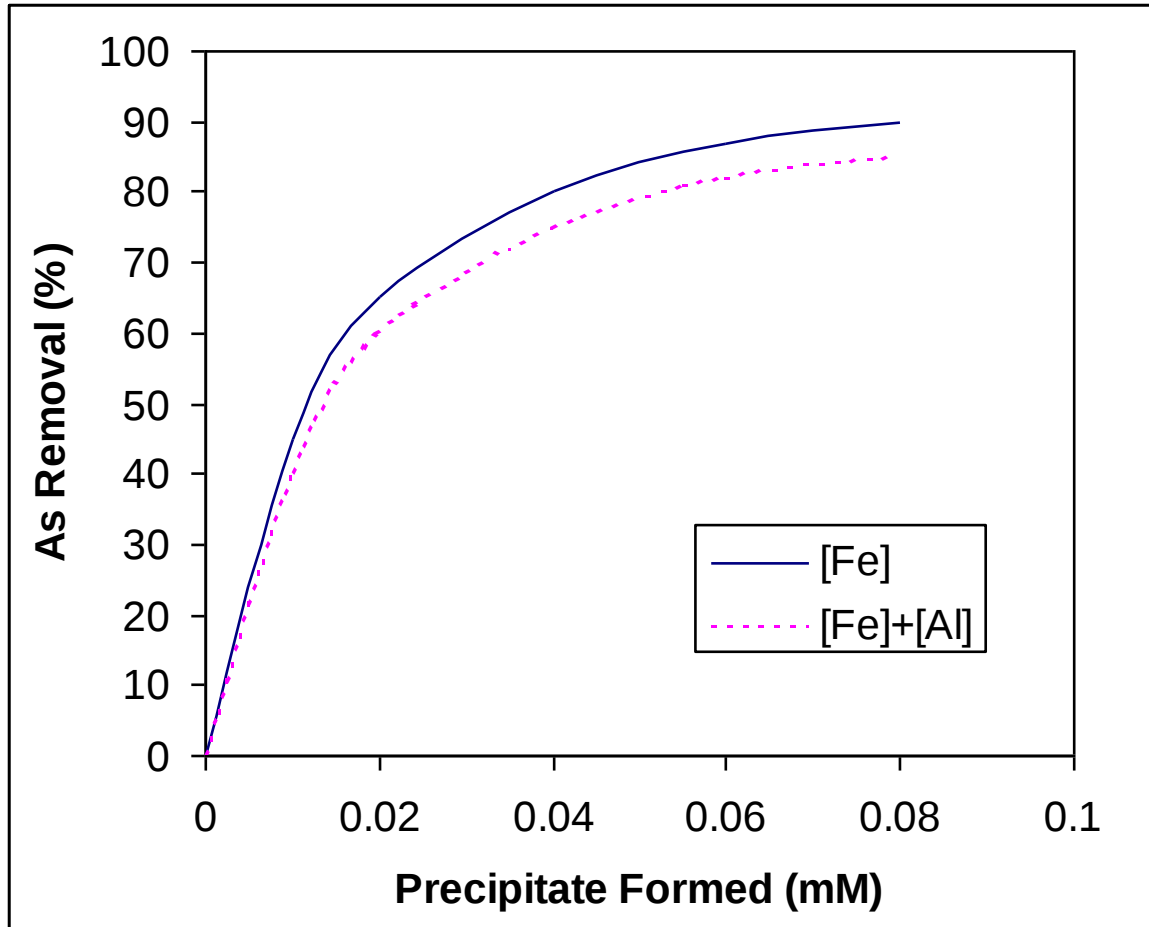
(McNeill & Edwards 1997)

- Survey of conventional coagulation-flocculation water treatment plants
- Correlate As removal to removal of Fe, Mn, & Al

$$\text{As Fraction Removed} = \frac{K[\text{Fe}]}{1 + K[\text{Fe}]}$$

- $[\text{Fe}]$ = Iron Precip. Formed (mM)

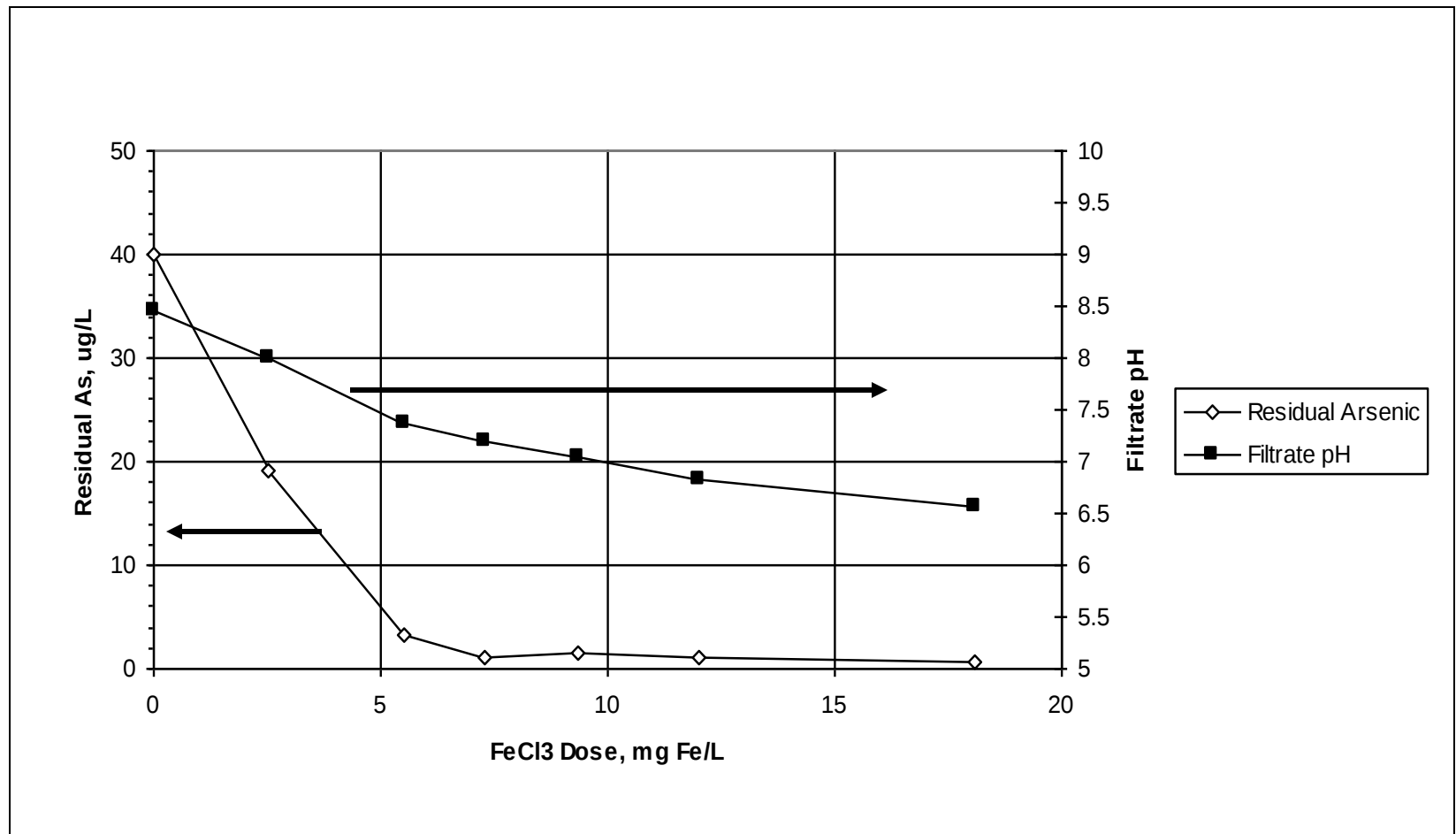
As Removal by Conventional Trt. - 2



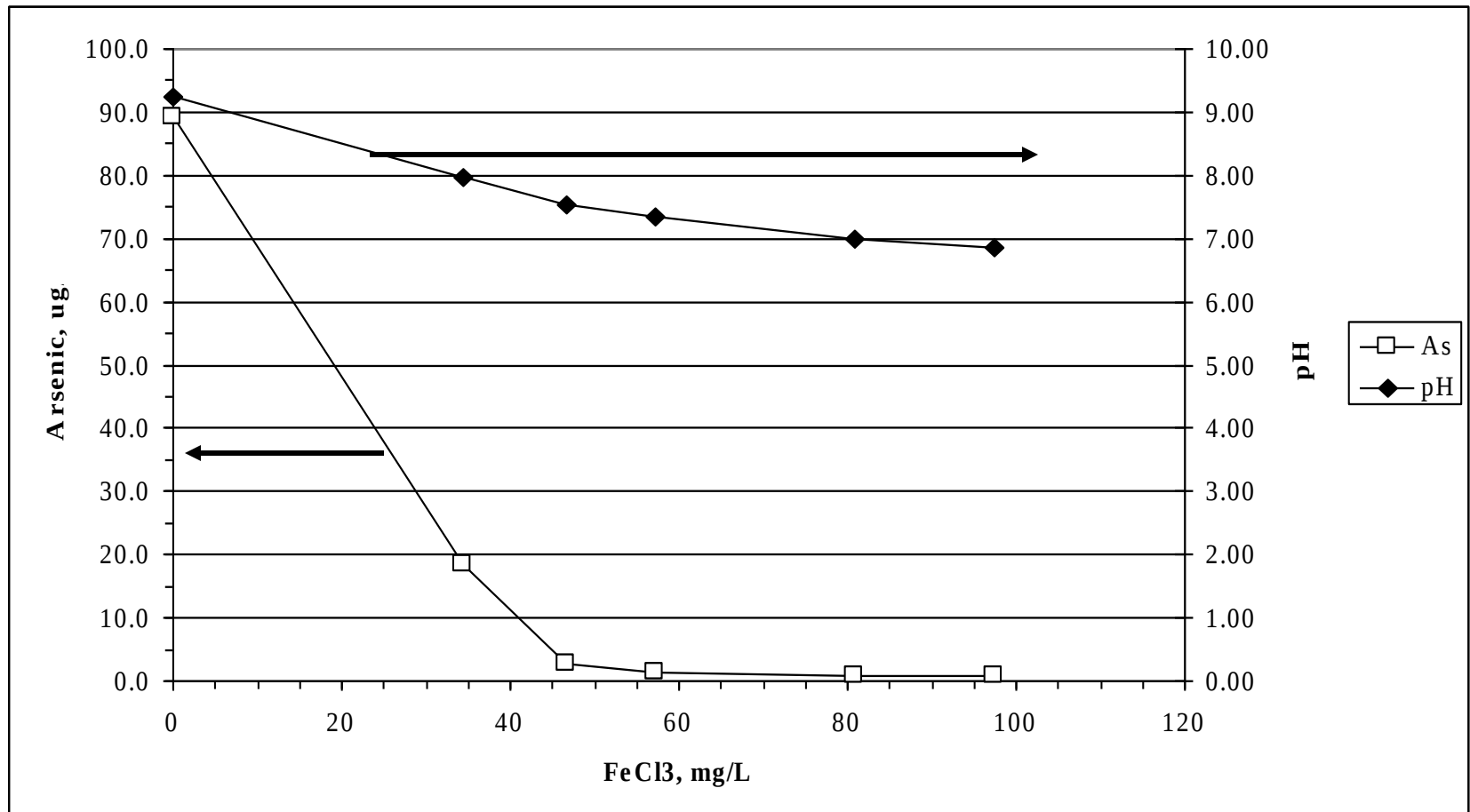
As Removal by Conventional Trt. - 3

- Strong correlation to removal of Fe & use of FeCl_3 as coagulant
- Weaker correlation to removal of Al & use of Alum
 - Possible sorption onto colloidal $\text{Al}(\text{OH})_3$ which passes through granular media filters
 - Improved As removal achieved by minimizing effluent total Al concentration
- Note the importance of particulate As

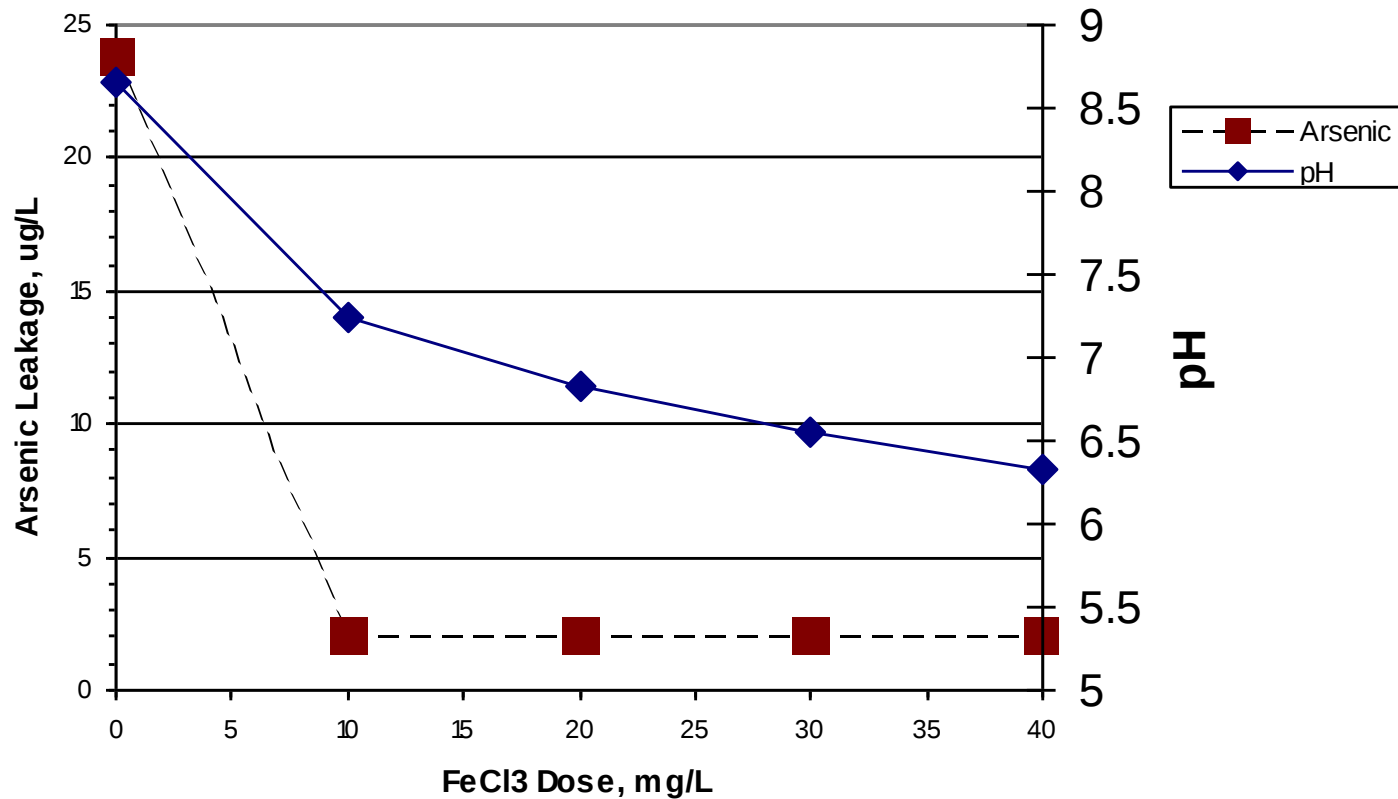
Arsenic Removal vs FeCl_3 Dose, Albuquerque NM



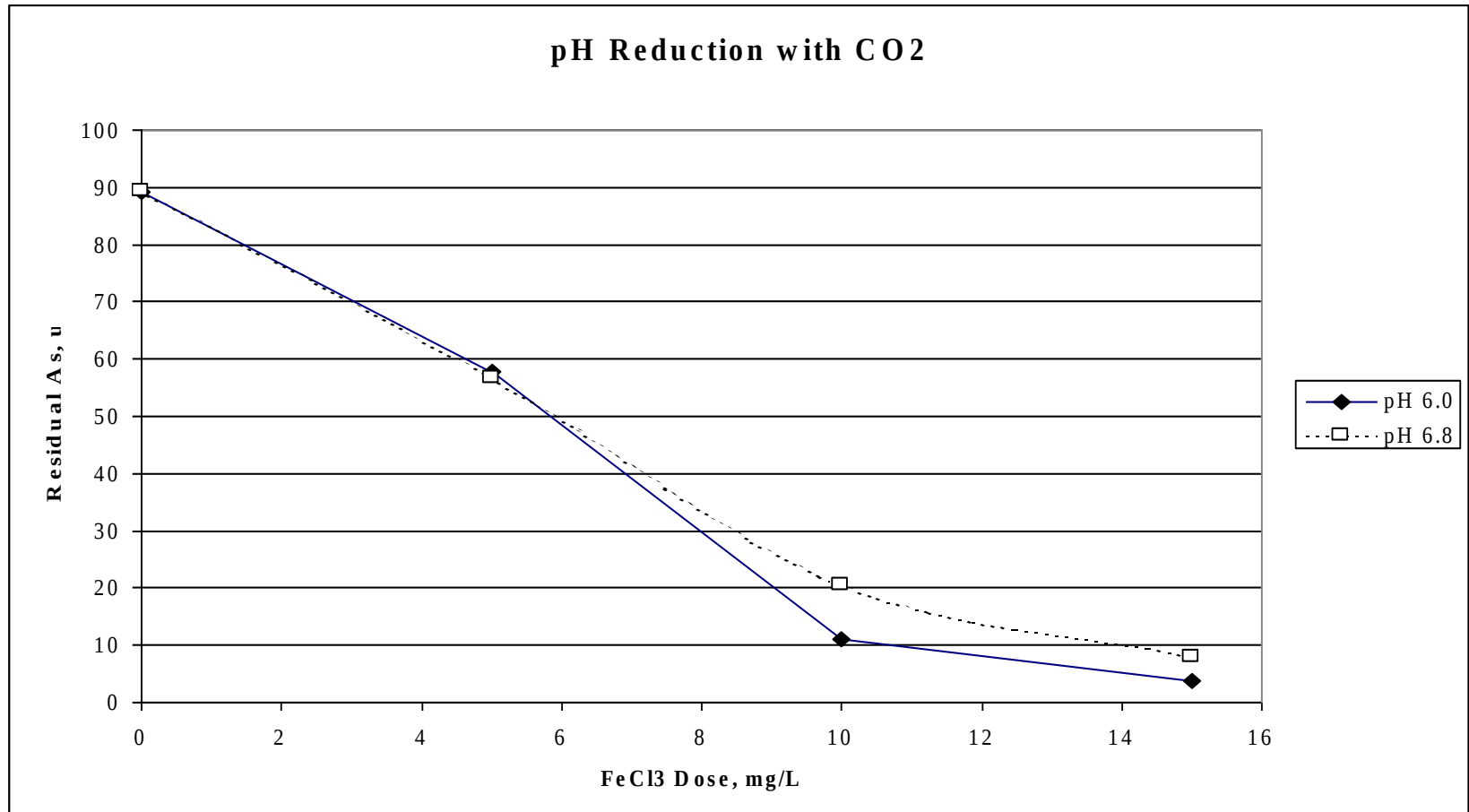
Ambient pH: FeCl₃ vs As Leakage, NAS Fallon



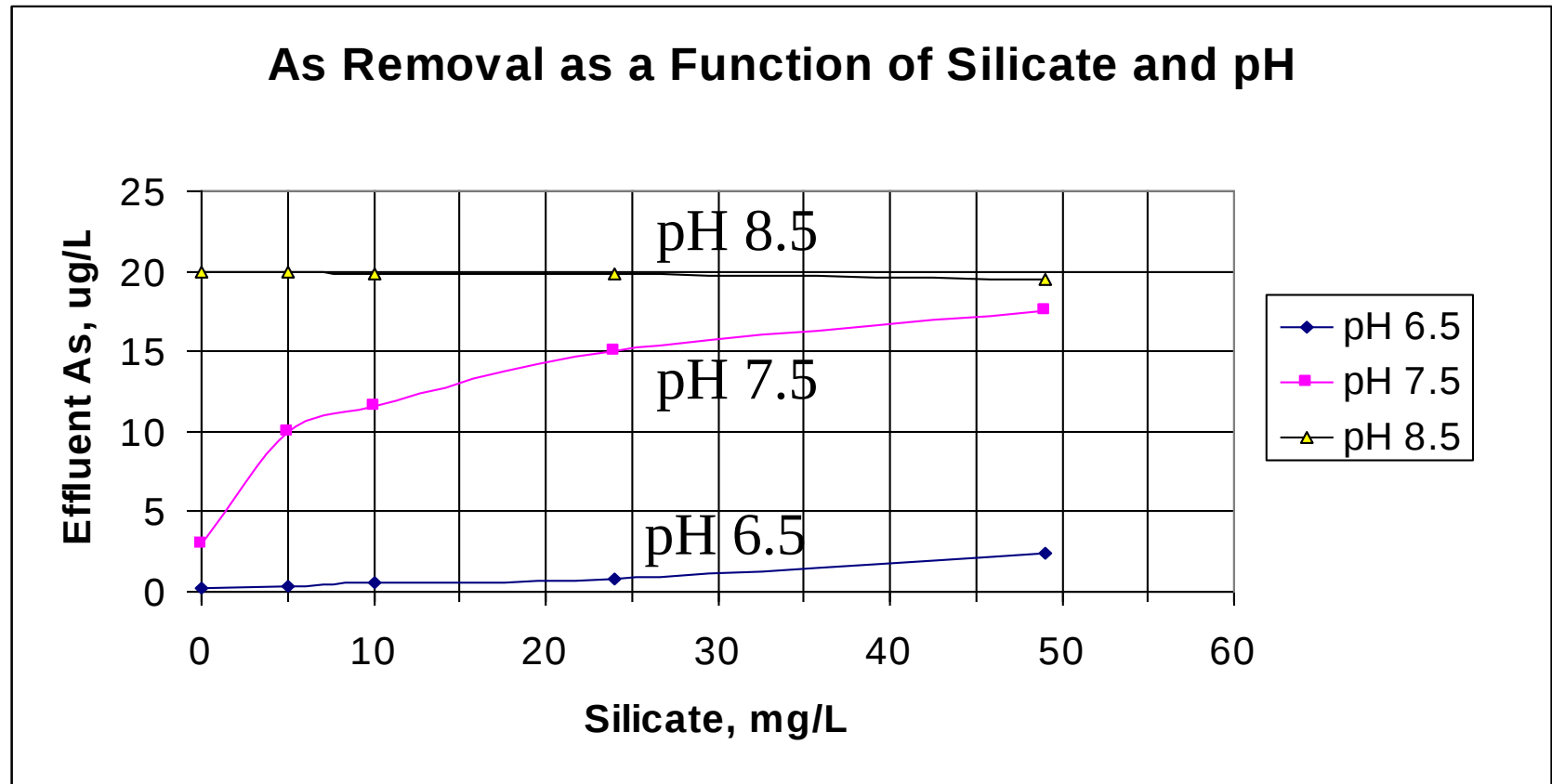
El Paso Jar Testing



pH Adjustment with CO₂, NAS Fallon, NV

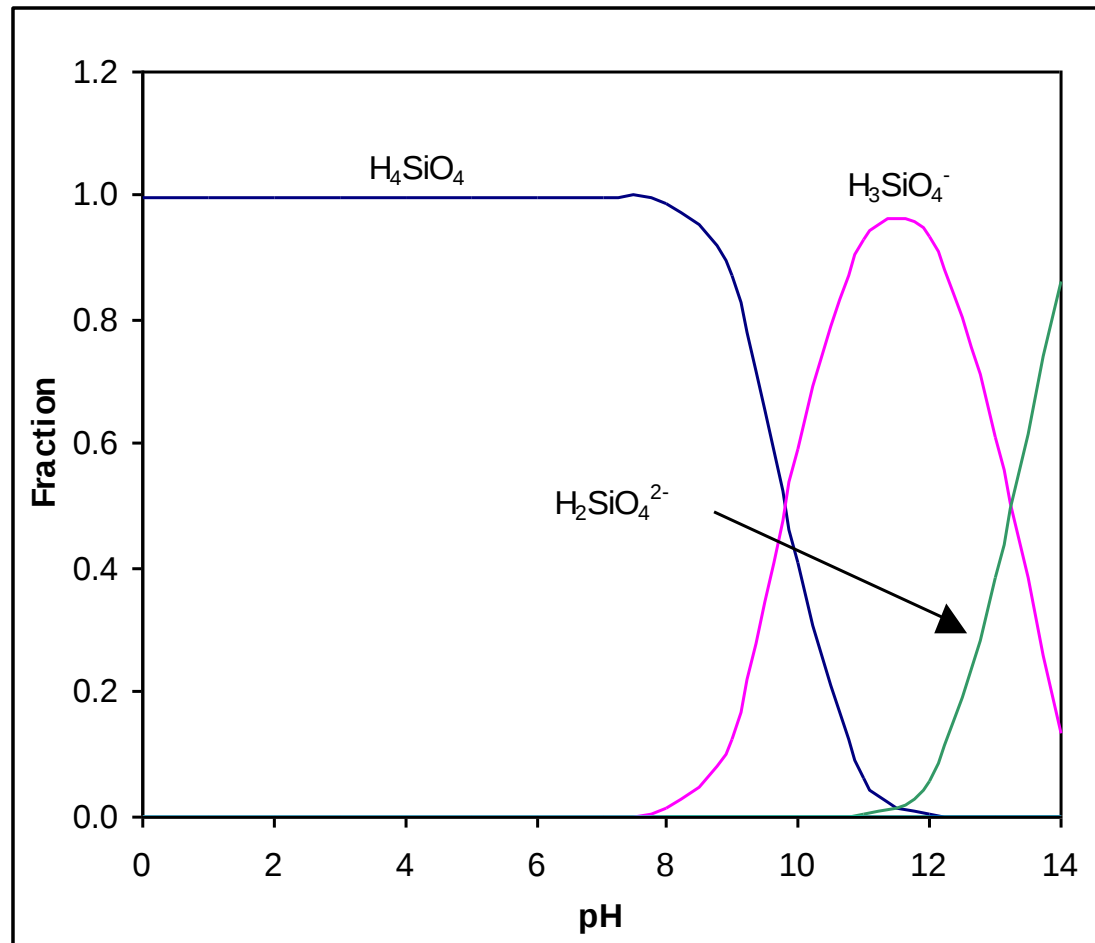


Silica Impacts Arsenic Removal at pH 7.0 and Above

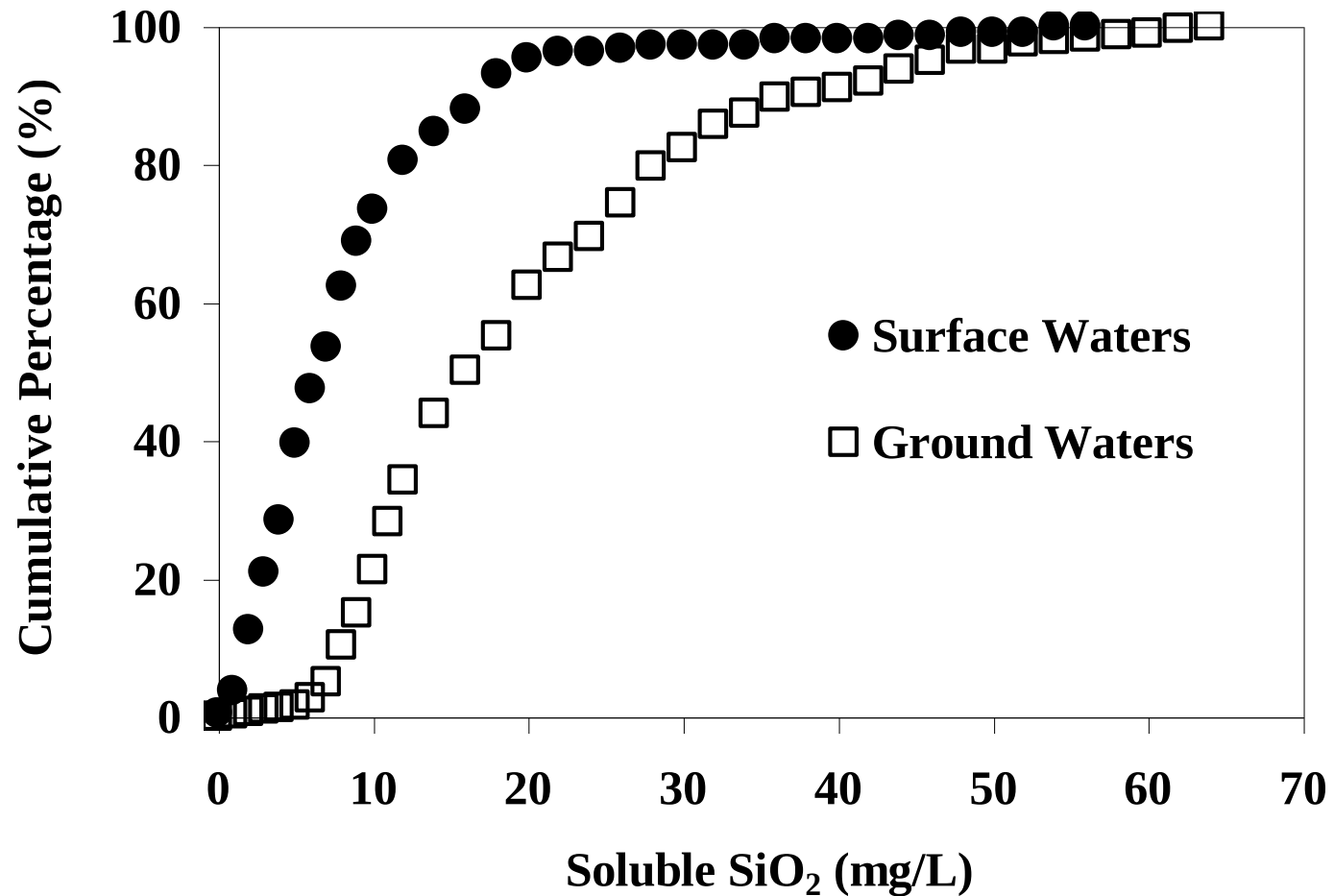


FeCl₃ Dose: 4 mg/L

Silica Speciation with pH

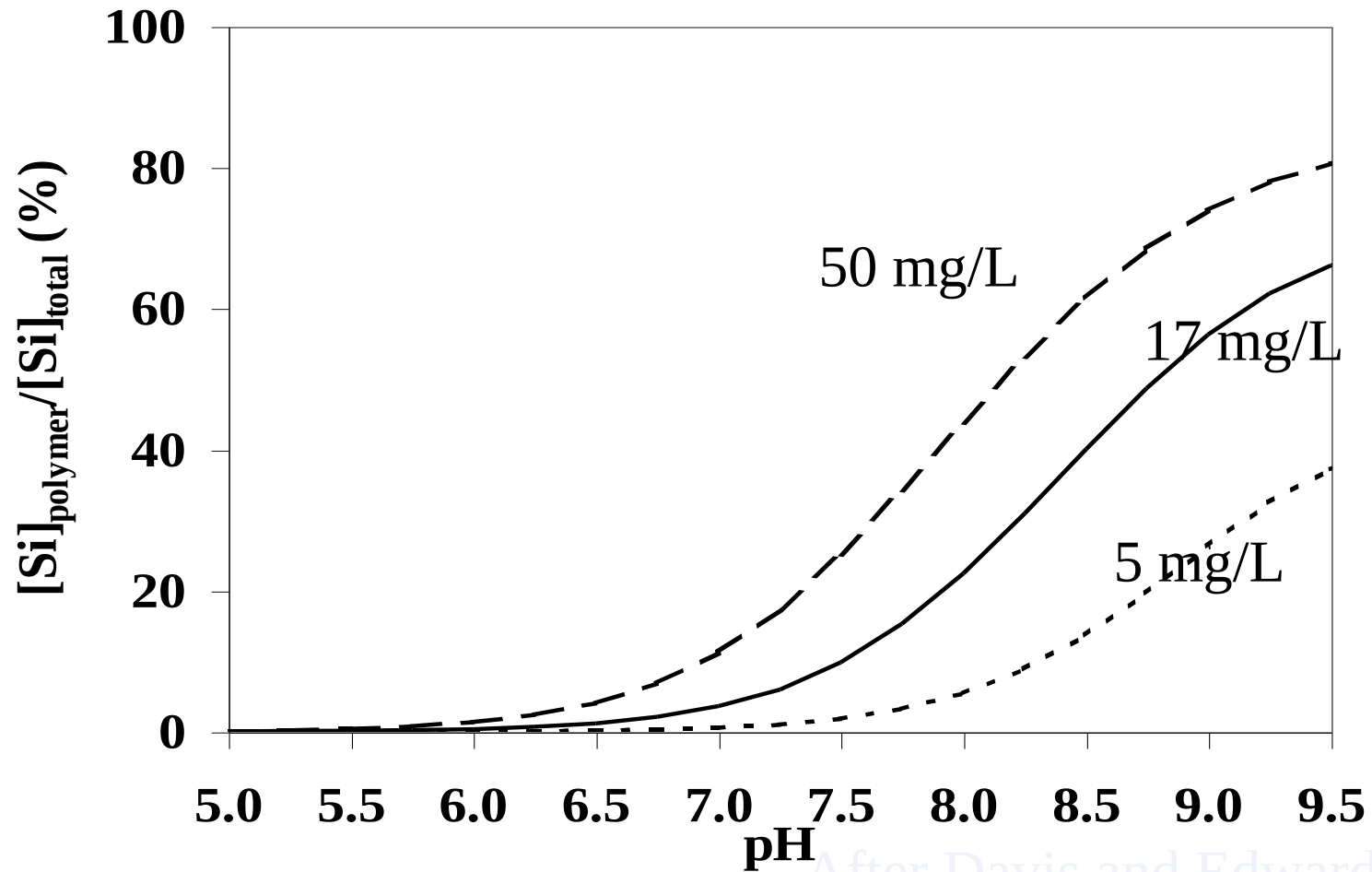


Silica in US Water Supplies (NAOS)



After Davis and Edwards

Polymeric Silica

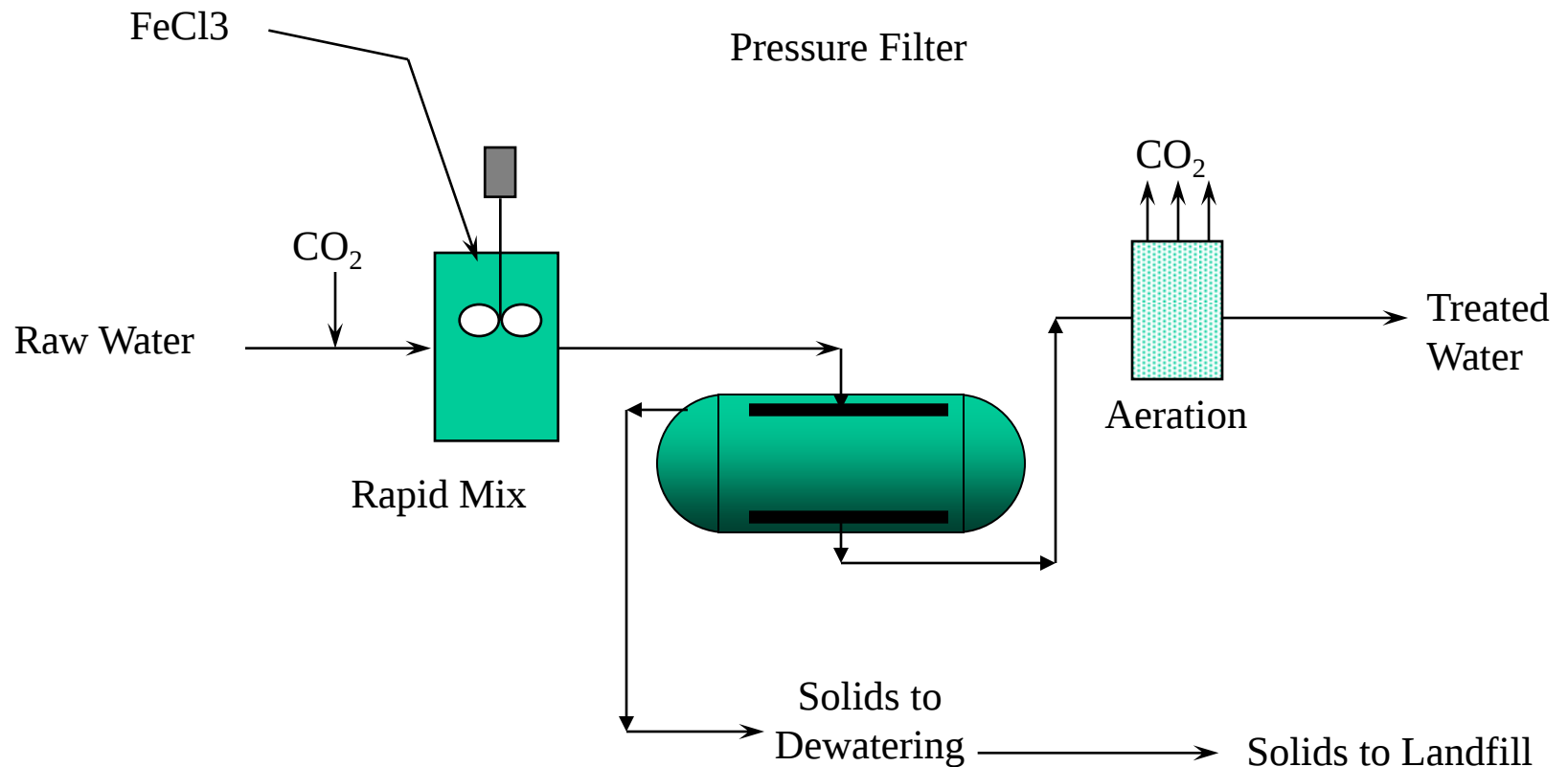


After Davis and Edwards

Coagulation/ Filtration

- Use pressure filters
- Direct Filtration frequently used for iron and manganese removal.
- Limited to low ferric dose applications.
- High coagulant dose will result in frequent backwash requirements
 - Increased residuals production & handling costs
 - Increased production of wastewater

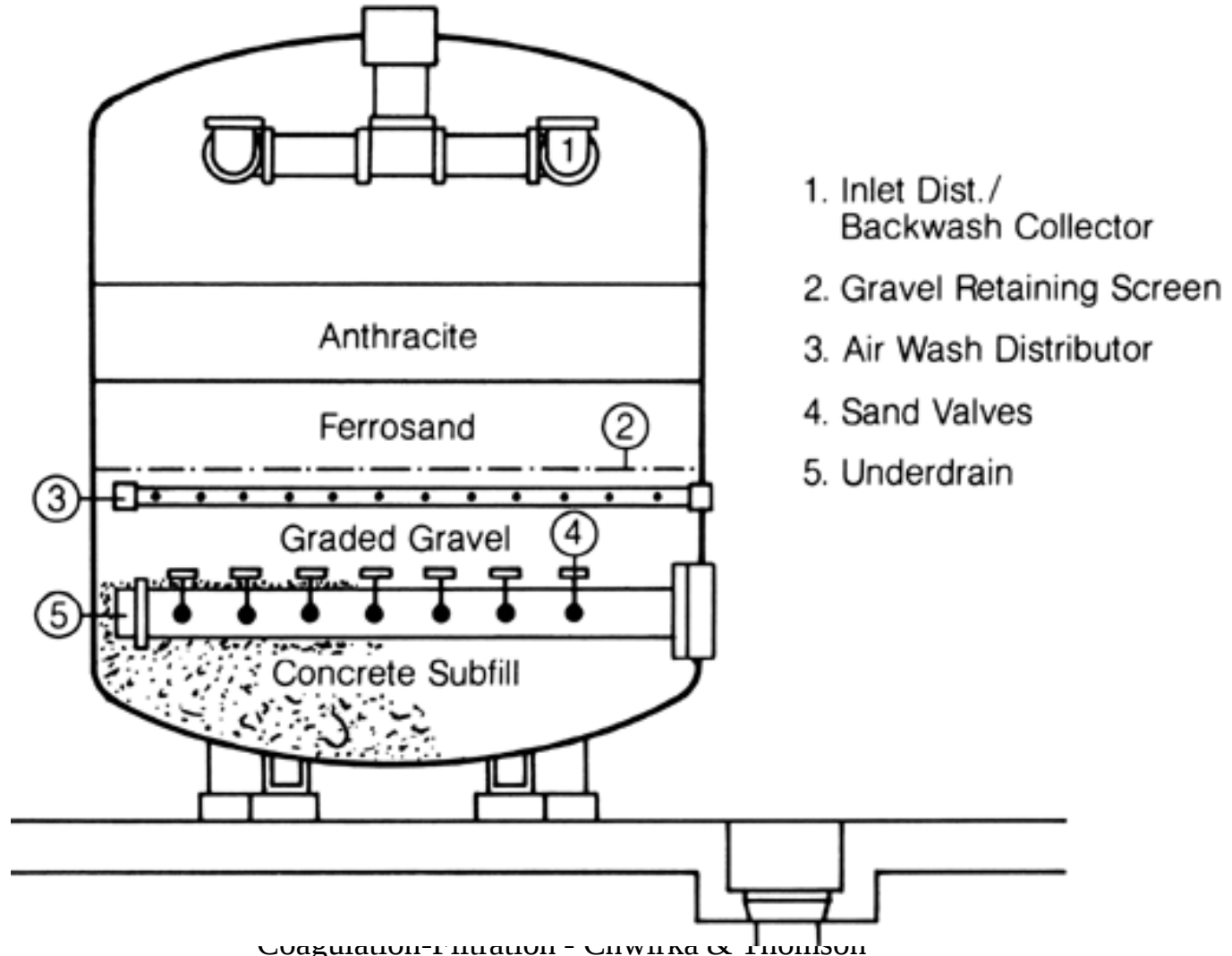
Schematic of Coagulation/ Filtration



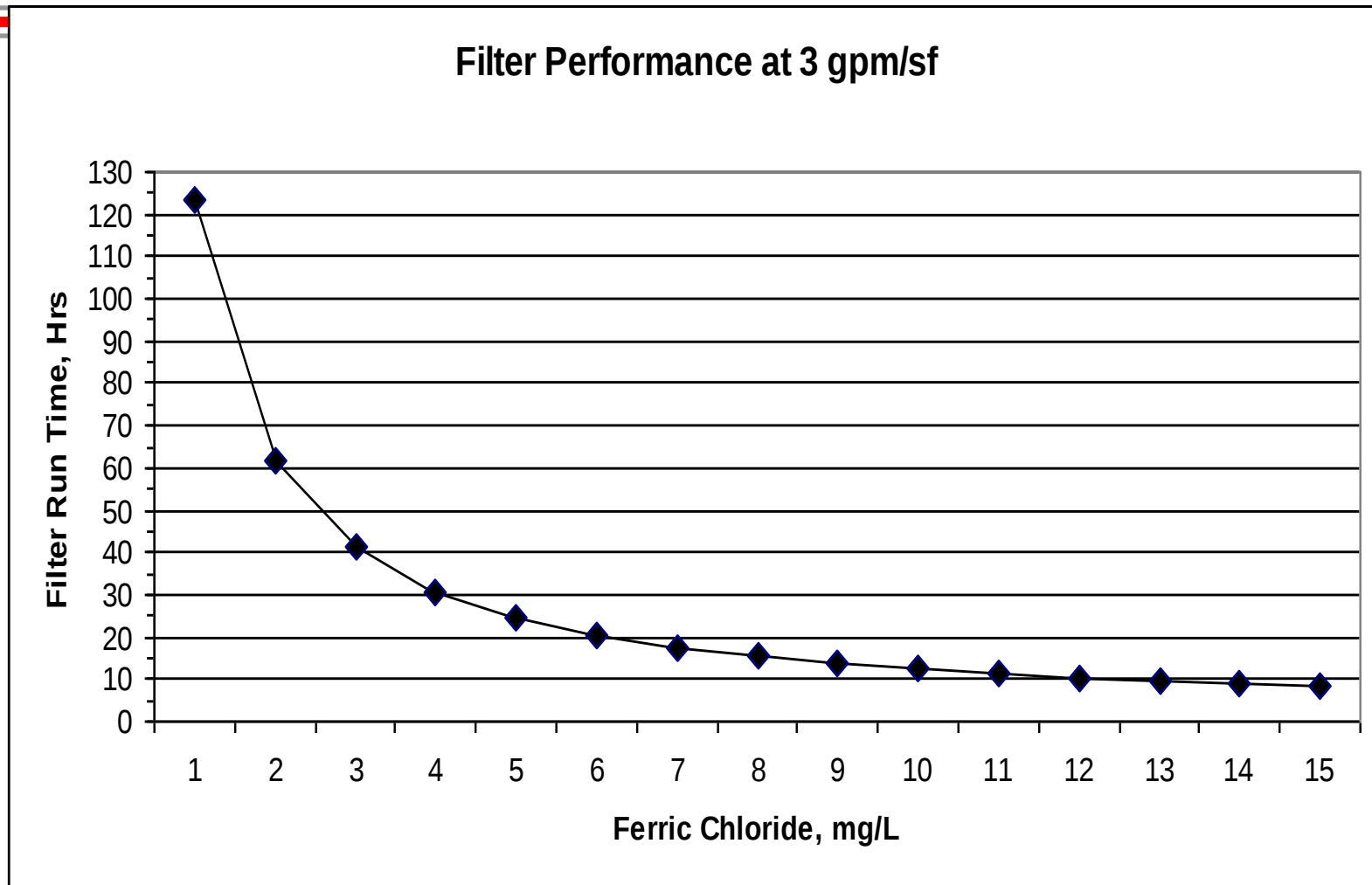
Calculation of Filter Loading Limitation

- Rule of Thumb, no more than 10 mg/L of FeCl_3
- Limit Solids Loading to 0.1 lbs/SF
- May need to add sedimentation

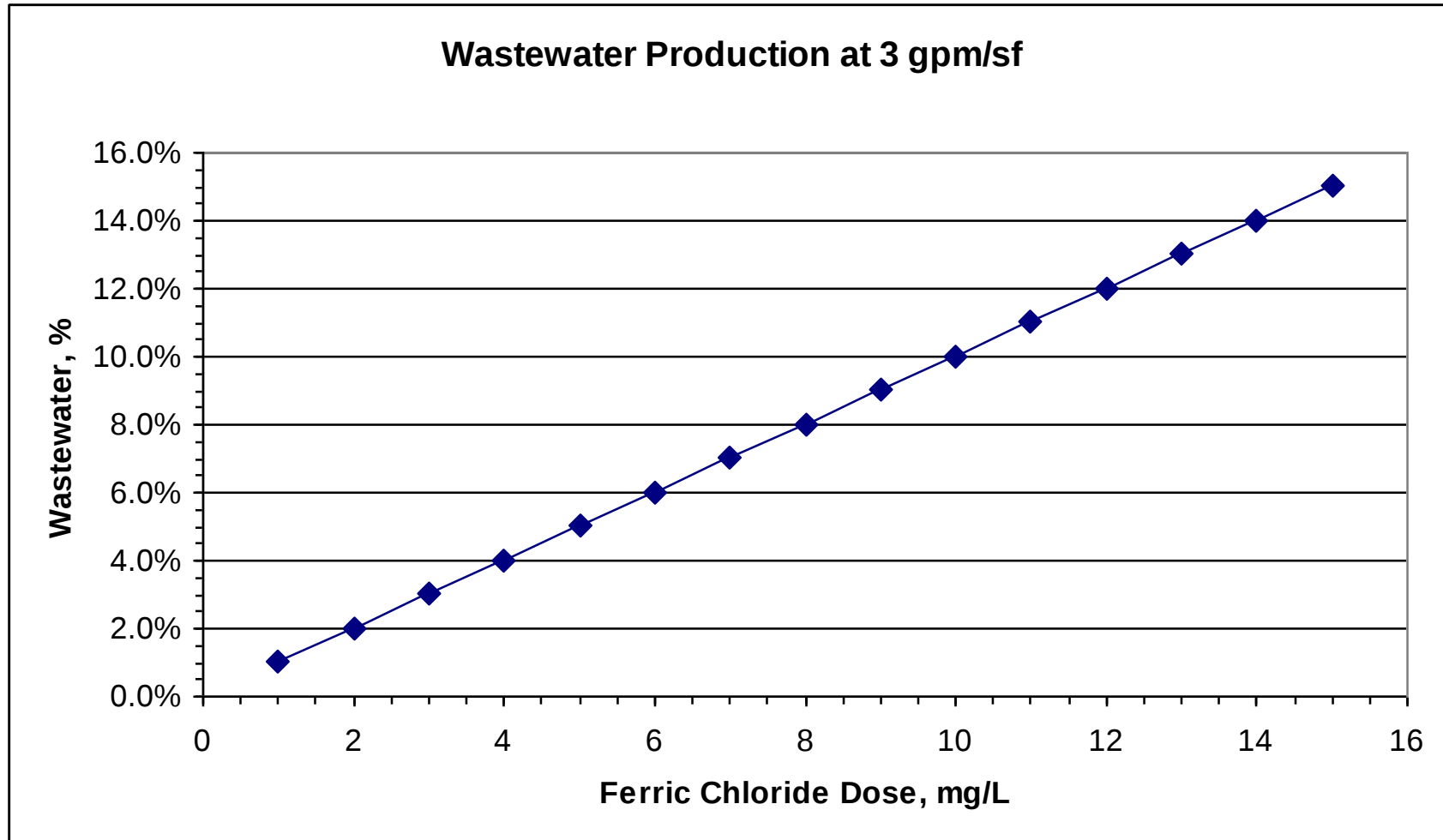
Vertical Pressure Filter



Direct Filtration Performance (Based on 0.1 lbs Solids/sf)



Backwash Water as Percent of Production (Based on 250 gal/sf)



C/F O&M Issues

- Large backwash volume (20 gpm/sf for 10 minutes)
- Tanks may need internal painting, 10 yr intervals. Use 316 SST.
- Standby filters, typically provided, but need to evaluate.
- Pneumatic or electric valve operators.

Coagulation/ Pressure Filtration

- Particle size
- Particle breakthrough
- backwash requirements
- filter ripening
- Backup Filters

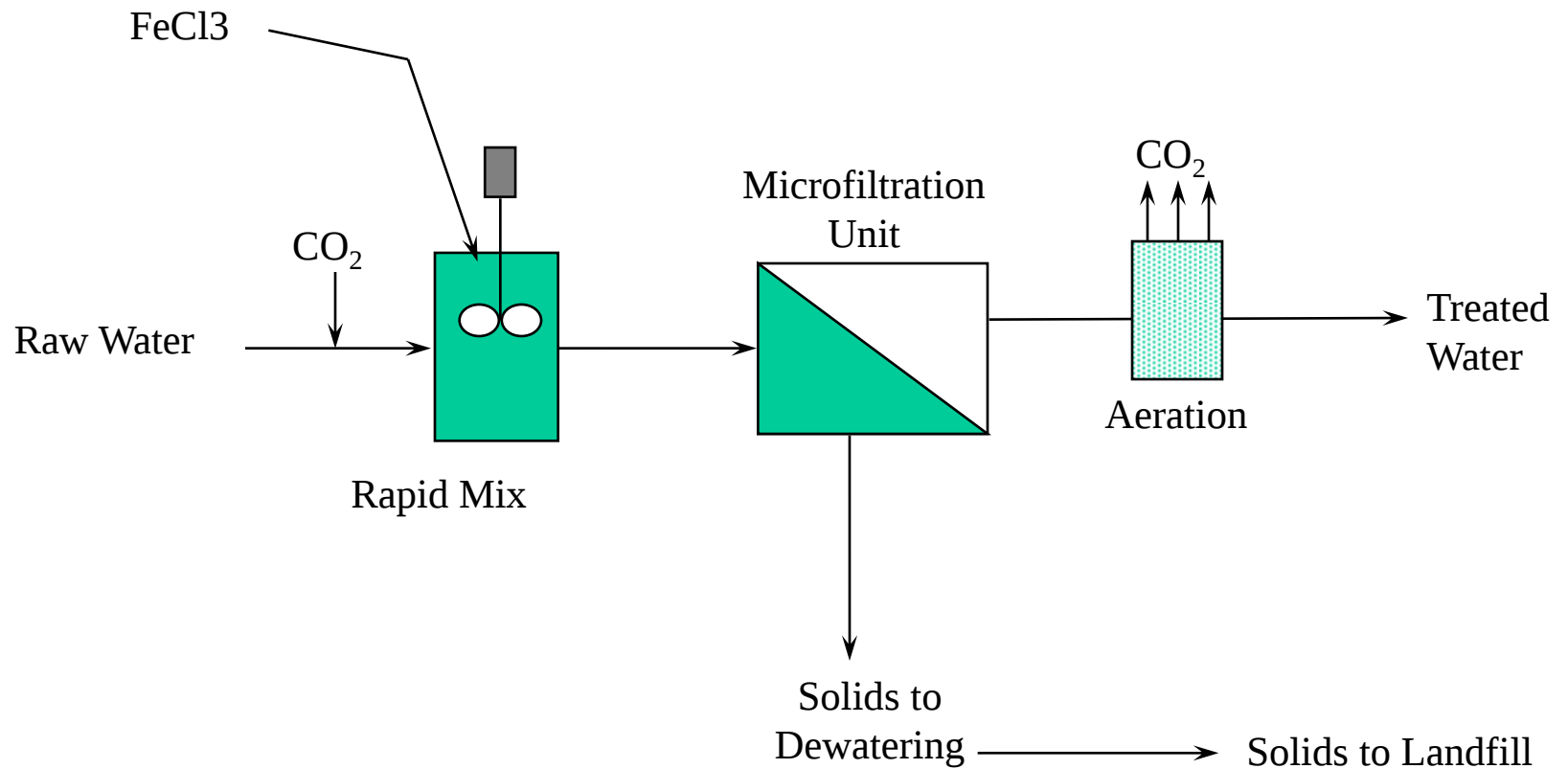
Coagulation/ Microfiltration

- Pilot tested in Albuquerque, 1998
- Pilot tested in NAS Fallon, NV, 2001
- Pilot tested in El Paso, TX, 2001/2002
- Fallon Paiute Shoshone Tribe: 0.5 mgd
- City of Albuquerque: 2.3 mgd

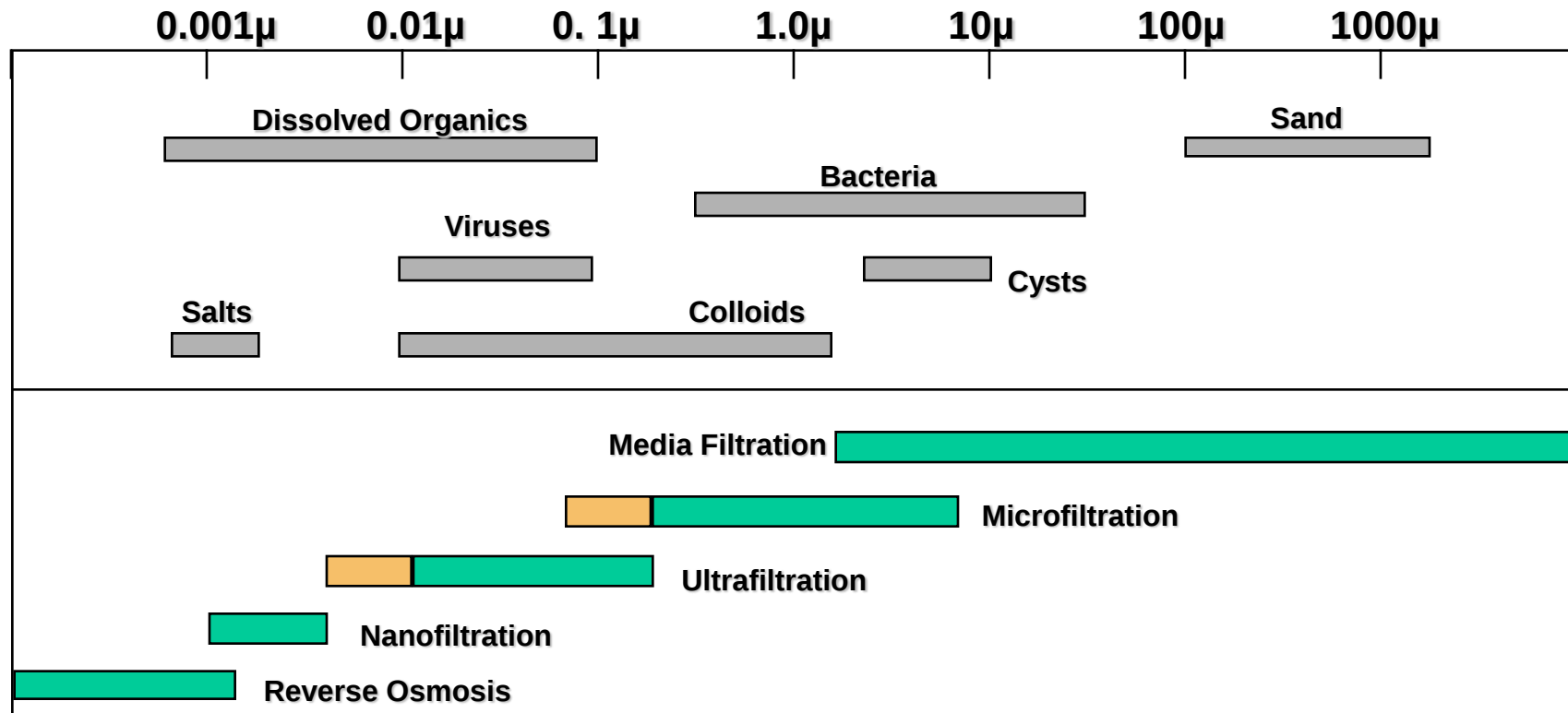
Microfiltration General Concepts

- Low Operating Pressure, 5 - 30 psi
- 0.1 to 0.2 micron pore size
- Water flow from Outside to the Inside
- Air-Water Backwash
- Backwash Every 25 to 30 minutes (95% recovery)
- Flux rate defined as Gallons/SF/Day (GFD)
- Chemical Cleaning Frequency > 30 days

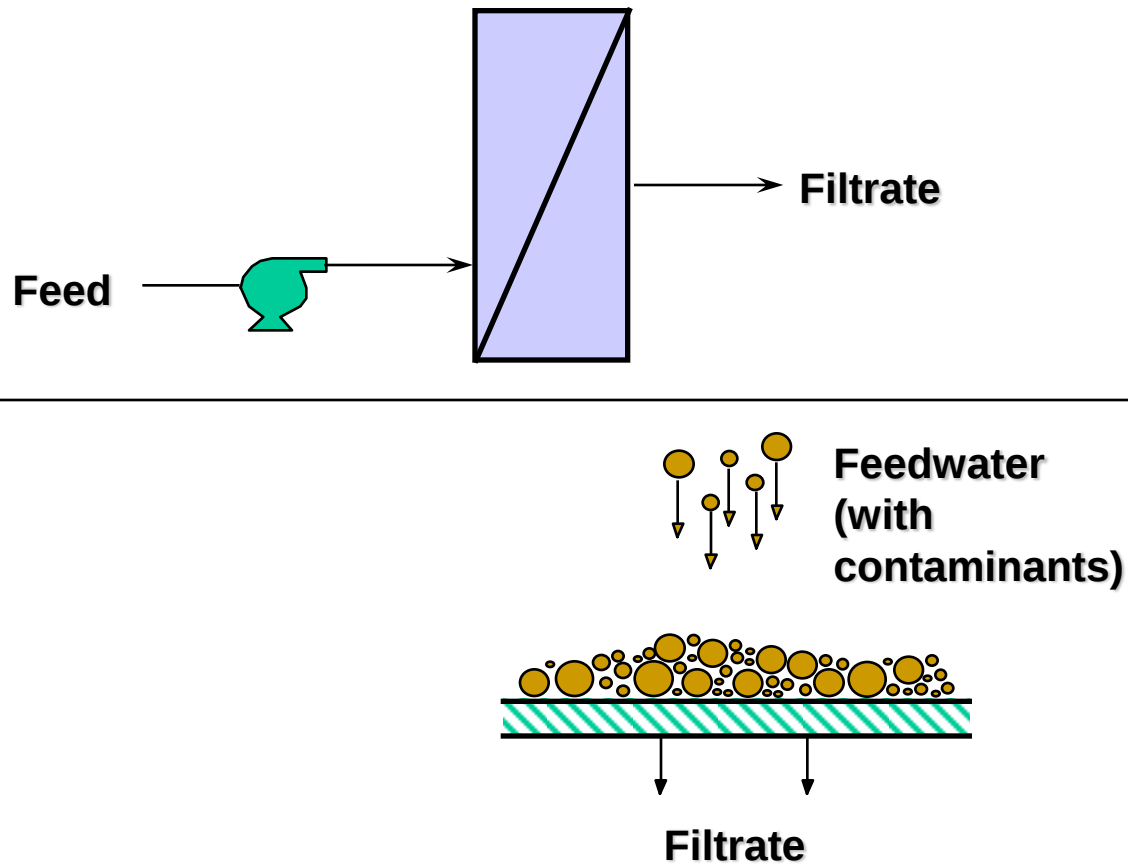
What is C/MF?



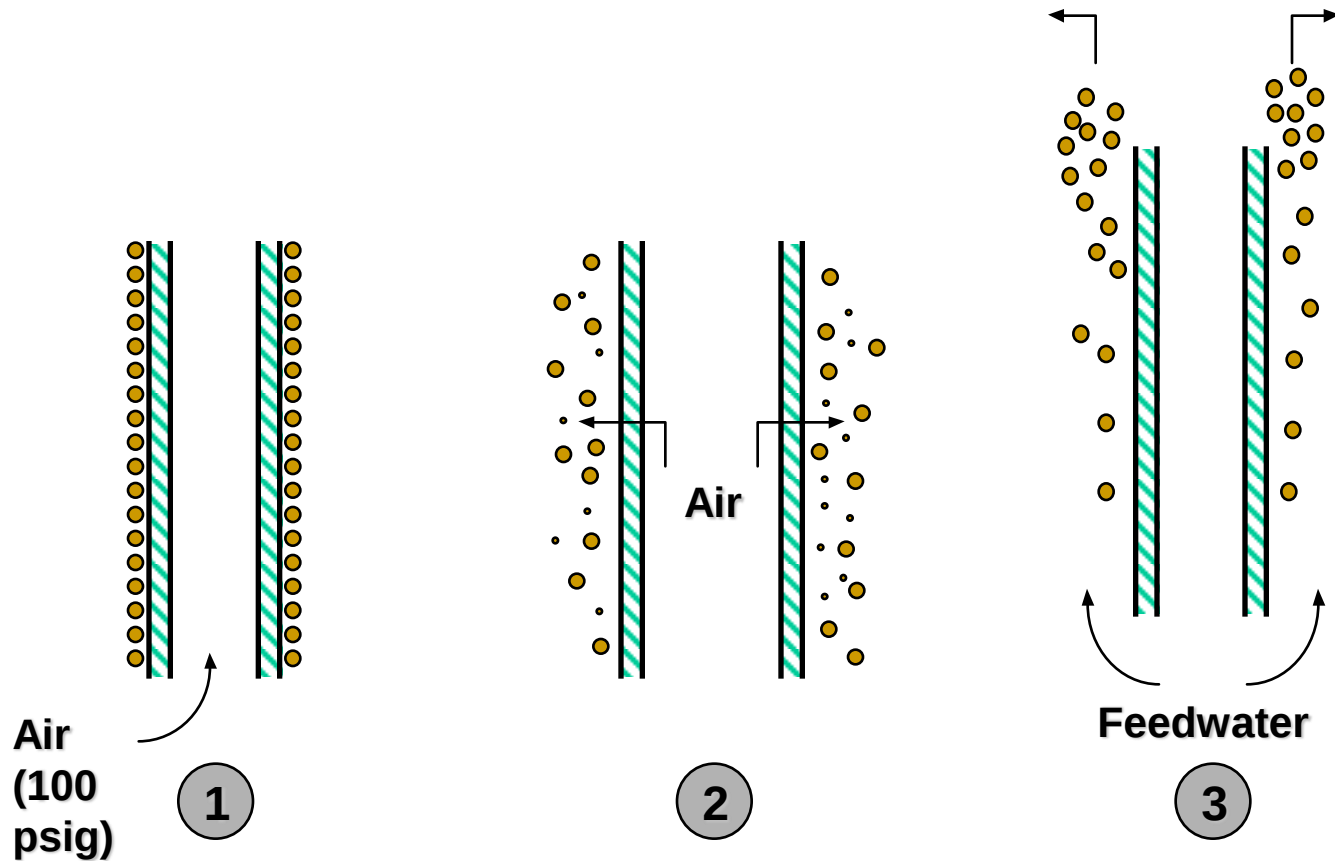
Pressure Driven Membranes



MF Process Operates in Direct Filtration Mode



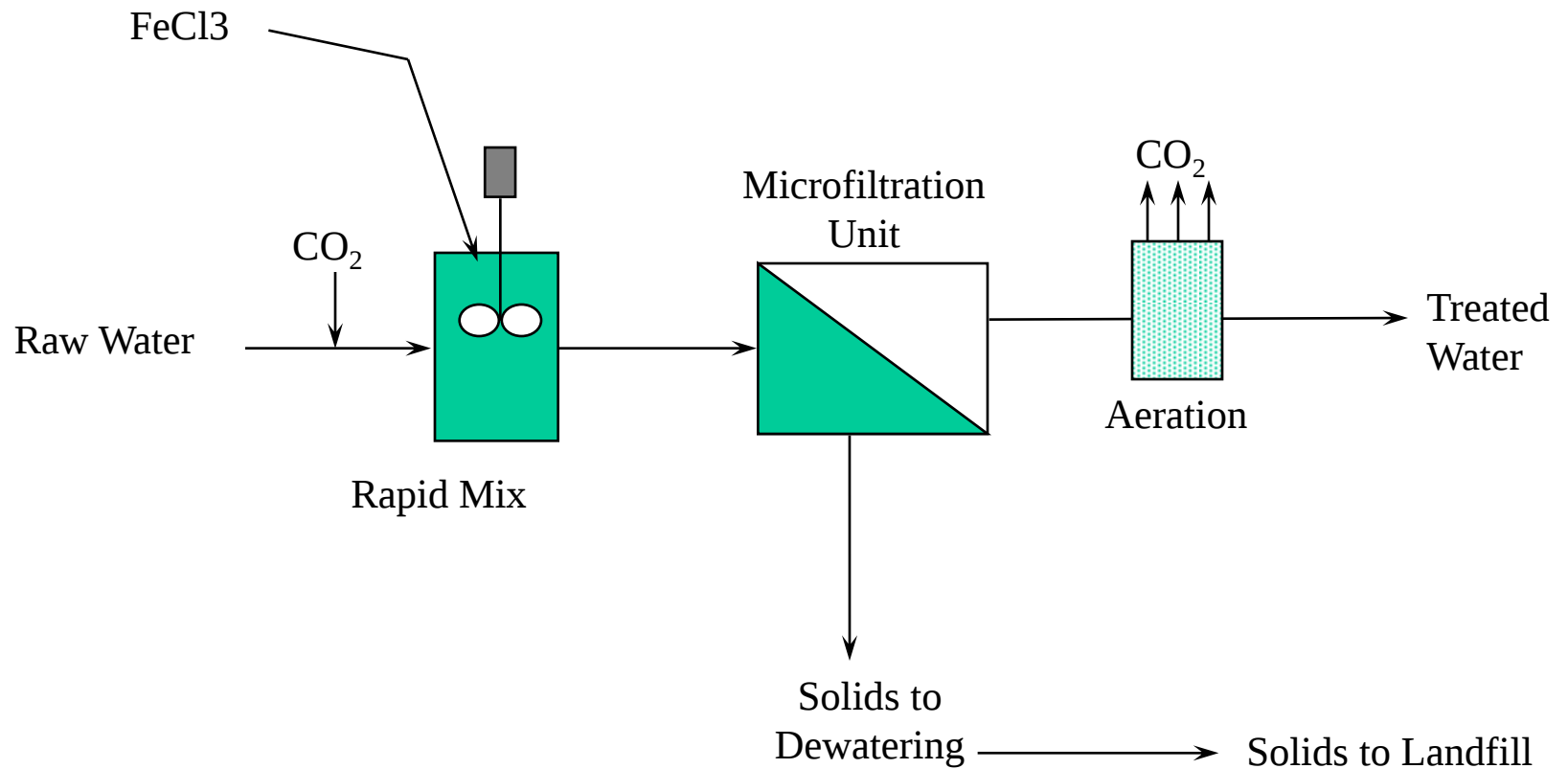
Solids are Removed from Module by an Air-Water Backwash



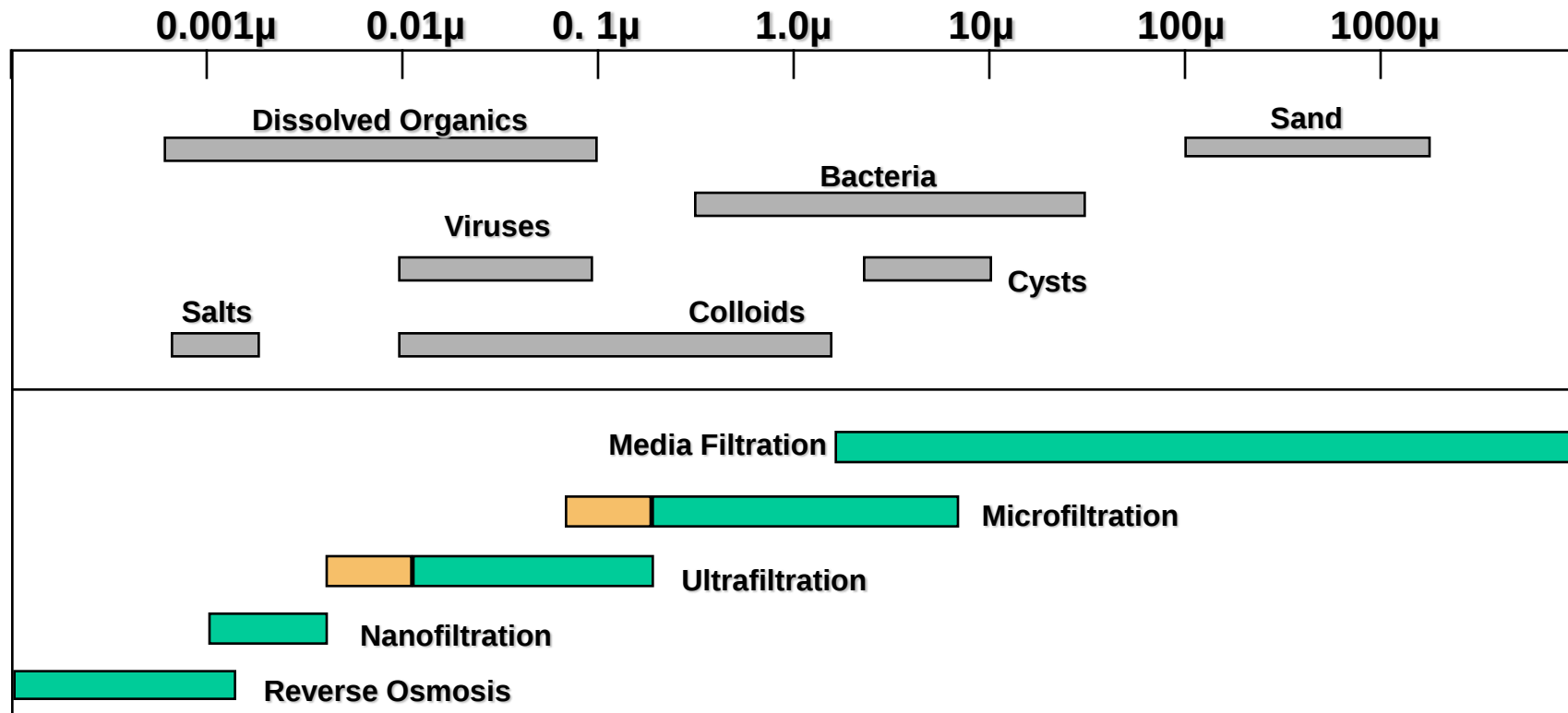
Coagulation/ Microfiltration

- Pilot tested in Albuquerque, 1998
- Pilot tested in NAS Fallon, NV, 2001
- Pilot tested in El Paso, TX, 2001/2002
- Fallon Paiute Shoshone Tribe: 0.5 mgd
- City of Albuquerque: 2.3 mgd

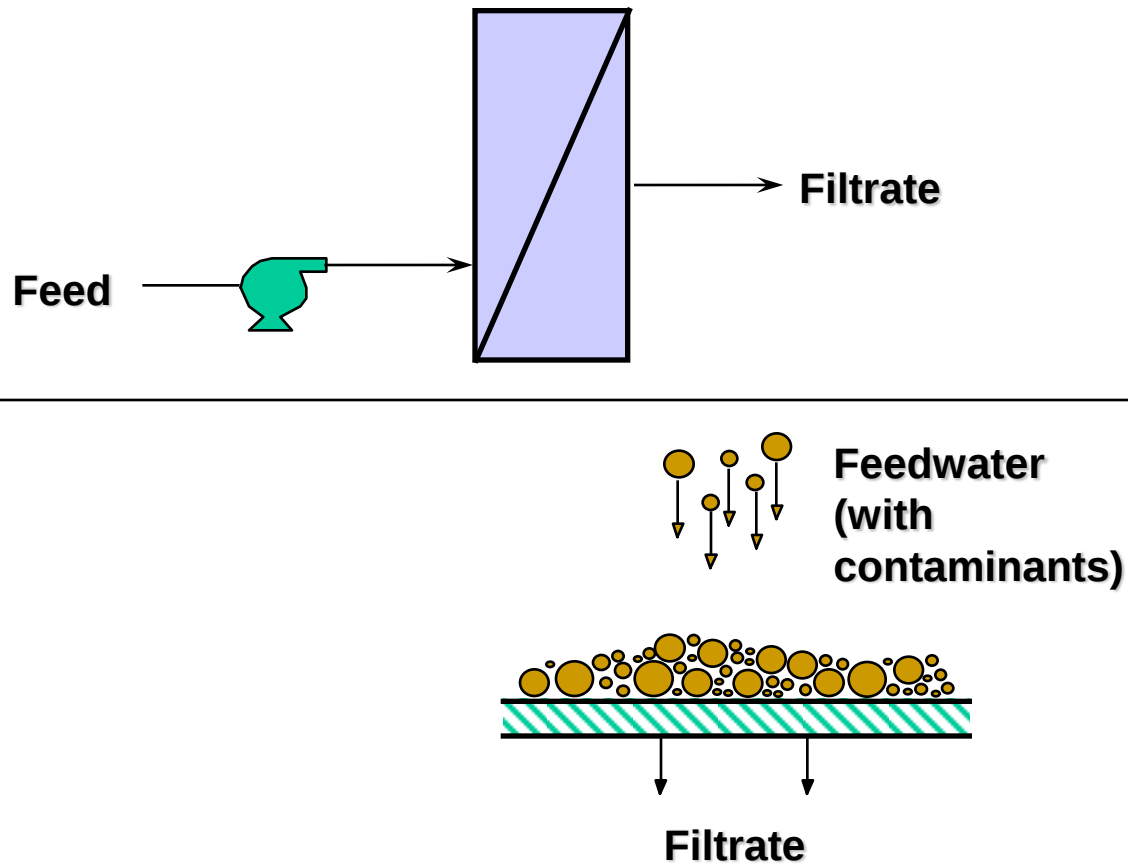
What is C/MF?



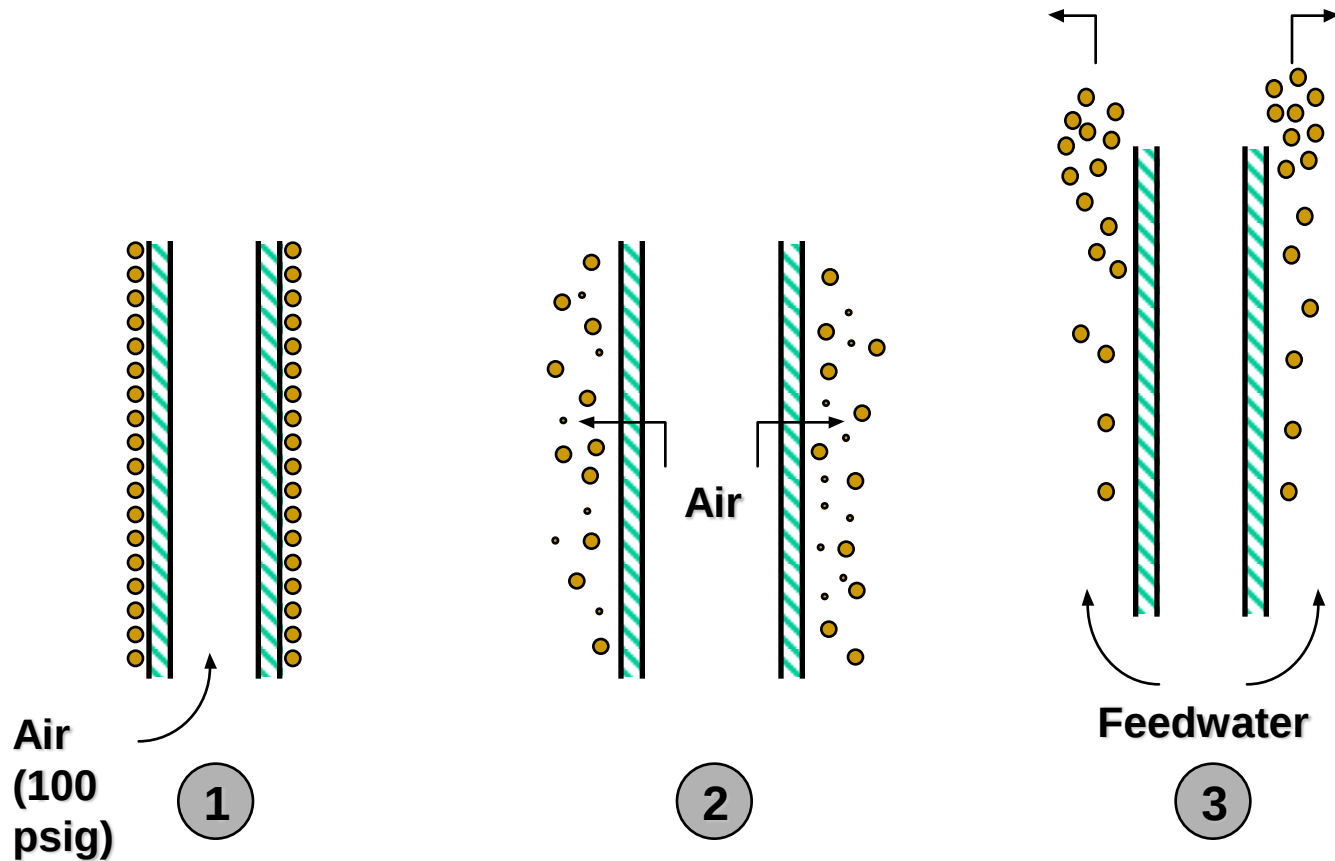
Pressure Driven Membranes



MF Process Operates in Direct Filtration Mode



Solids are Removed from Module by an Air-Water Backwash

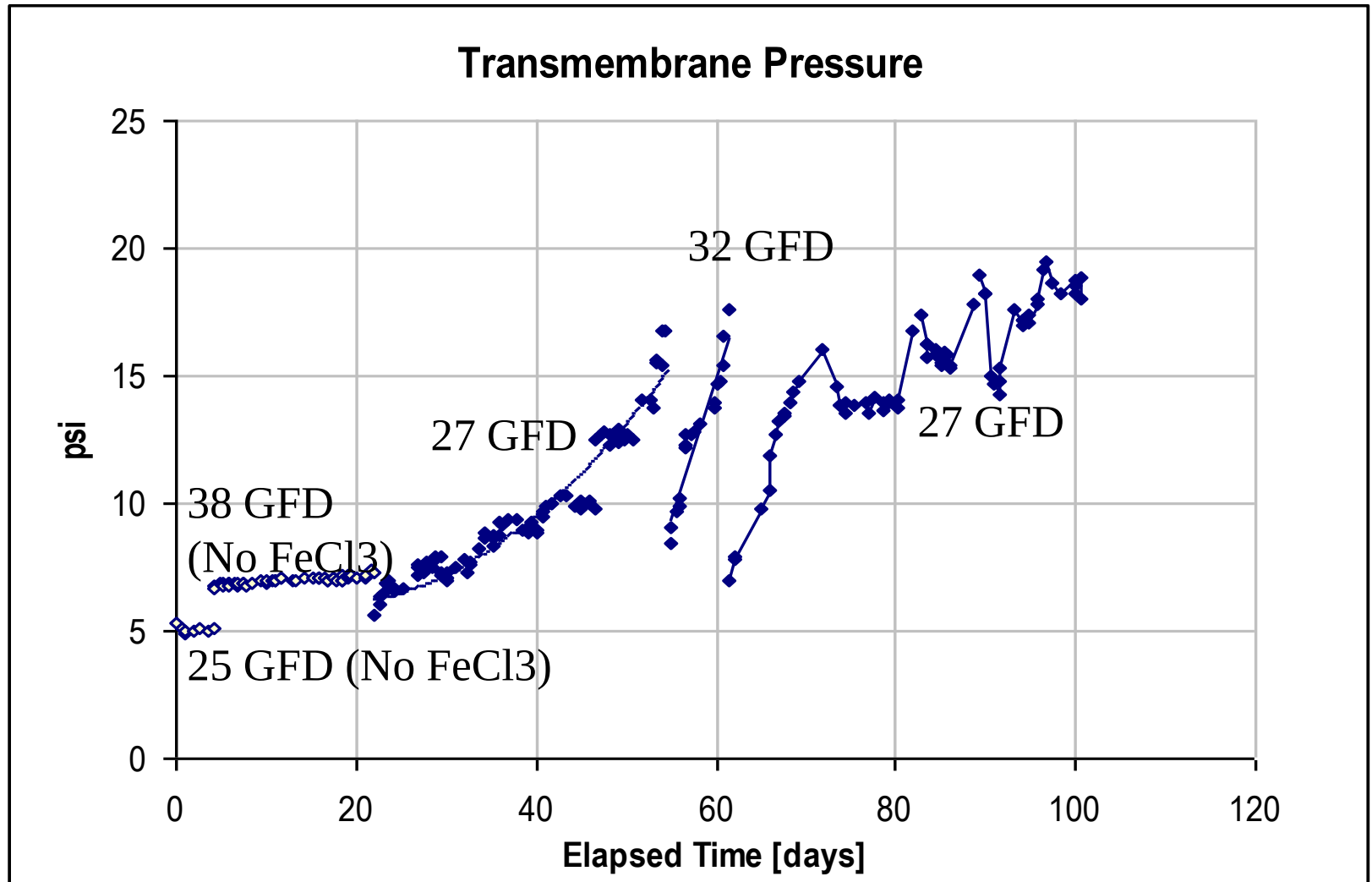


Pall Microfilter



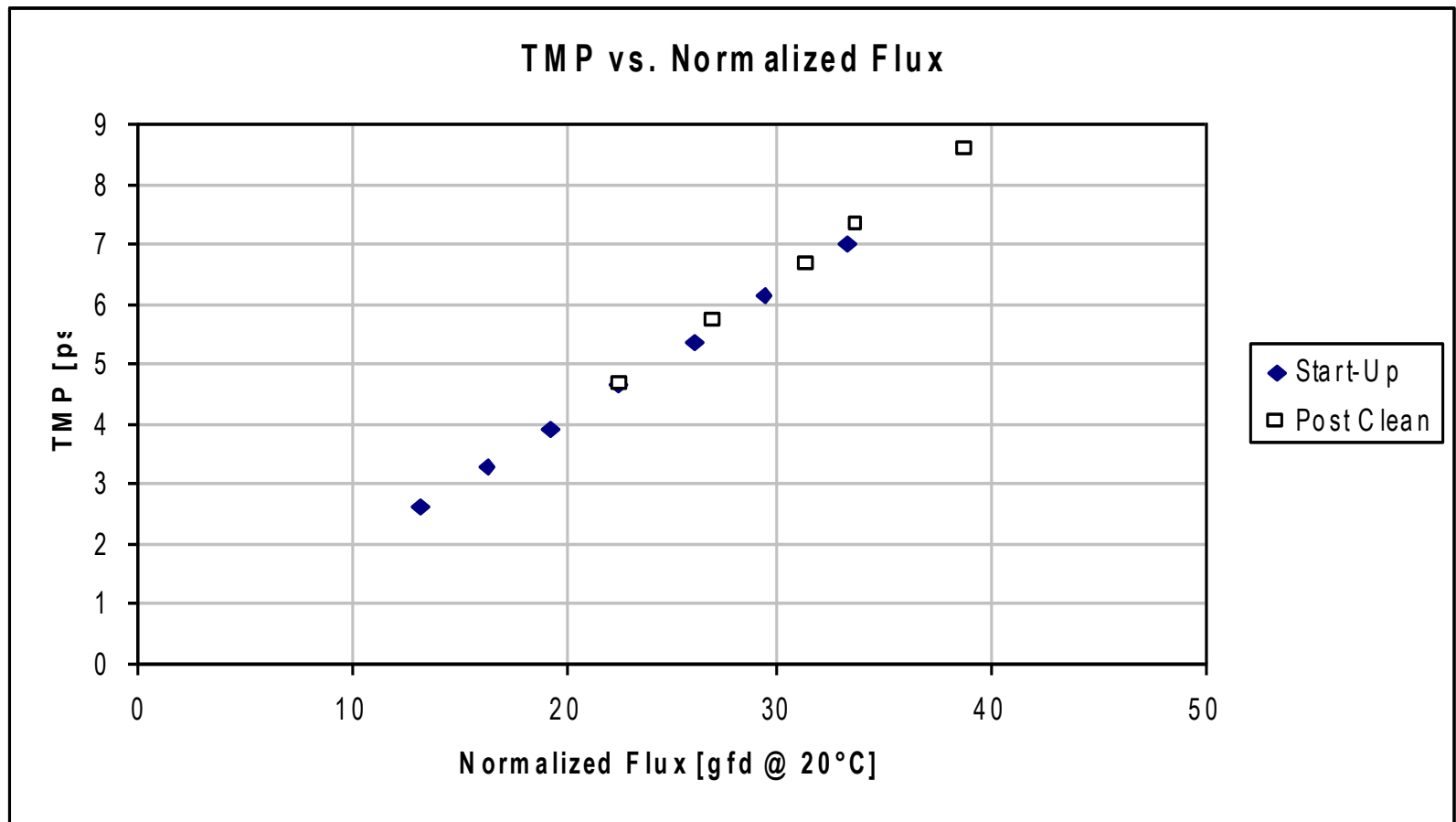
Memcor Performance

NAS Fallon, 15 mg/L FeCl₃



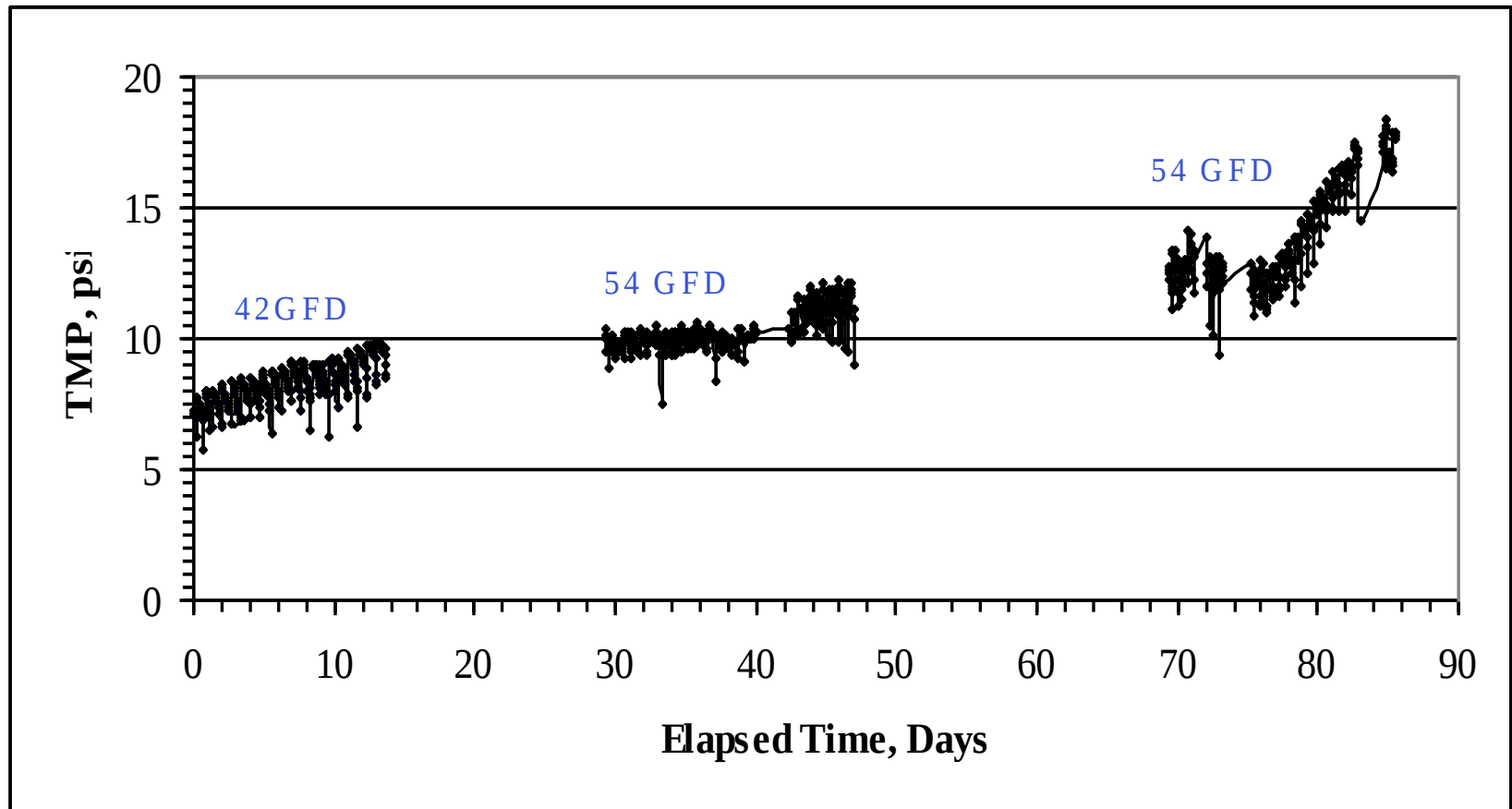
Memcor Cleaning Efficiency

NAS Fallon, Citric Acid



Pall Performance

NAS Fallon, FeCl₃ 45 mg/L



El Paso C/MF Pilot Studies

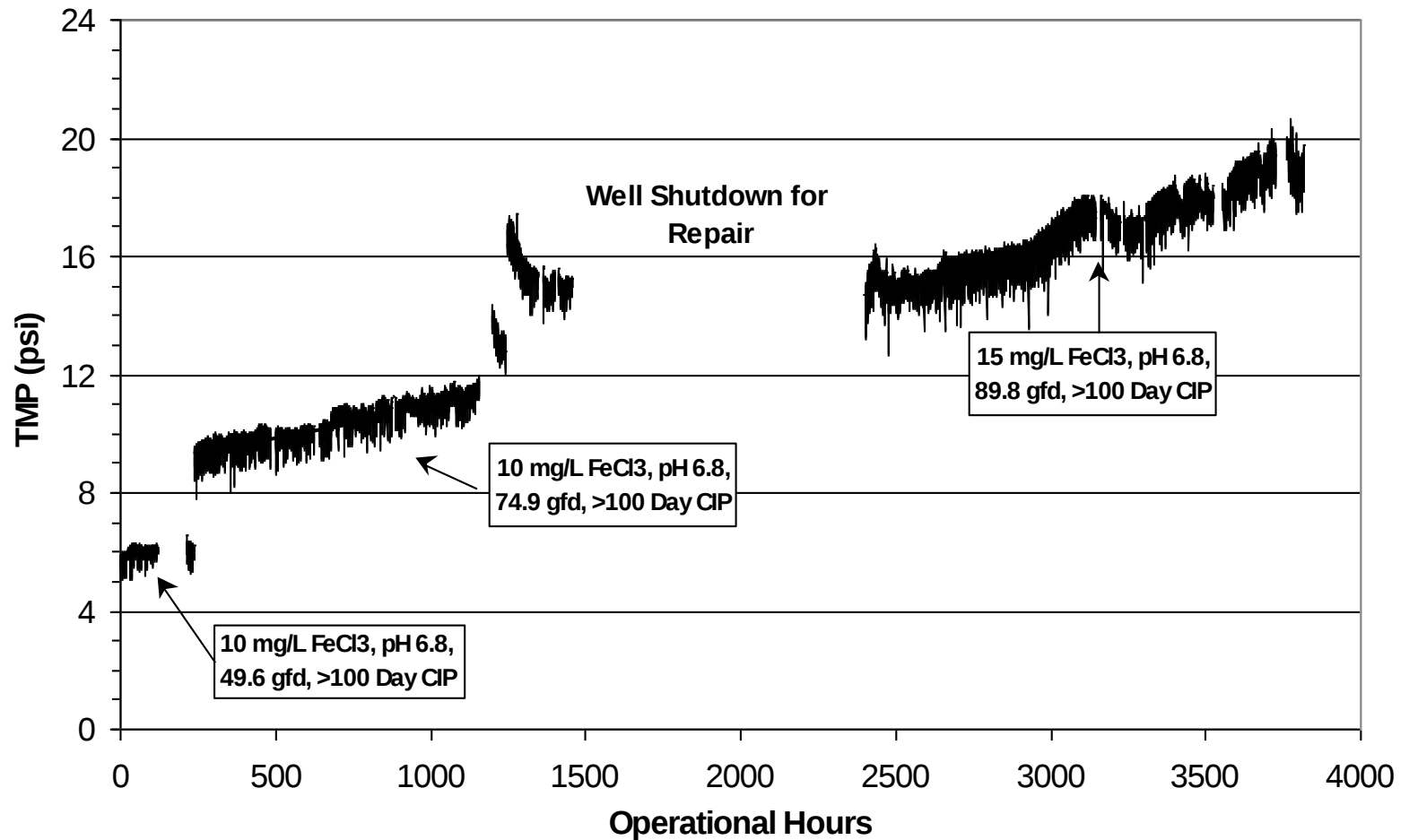


El Paso Pilot Studies

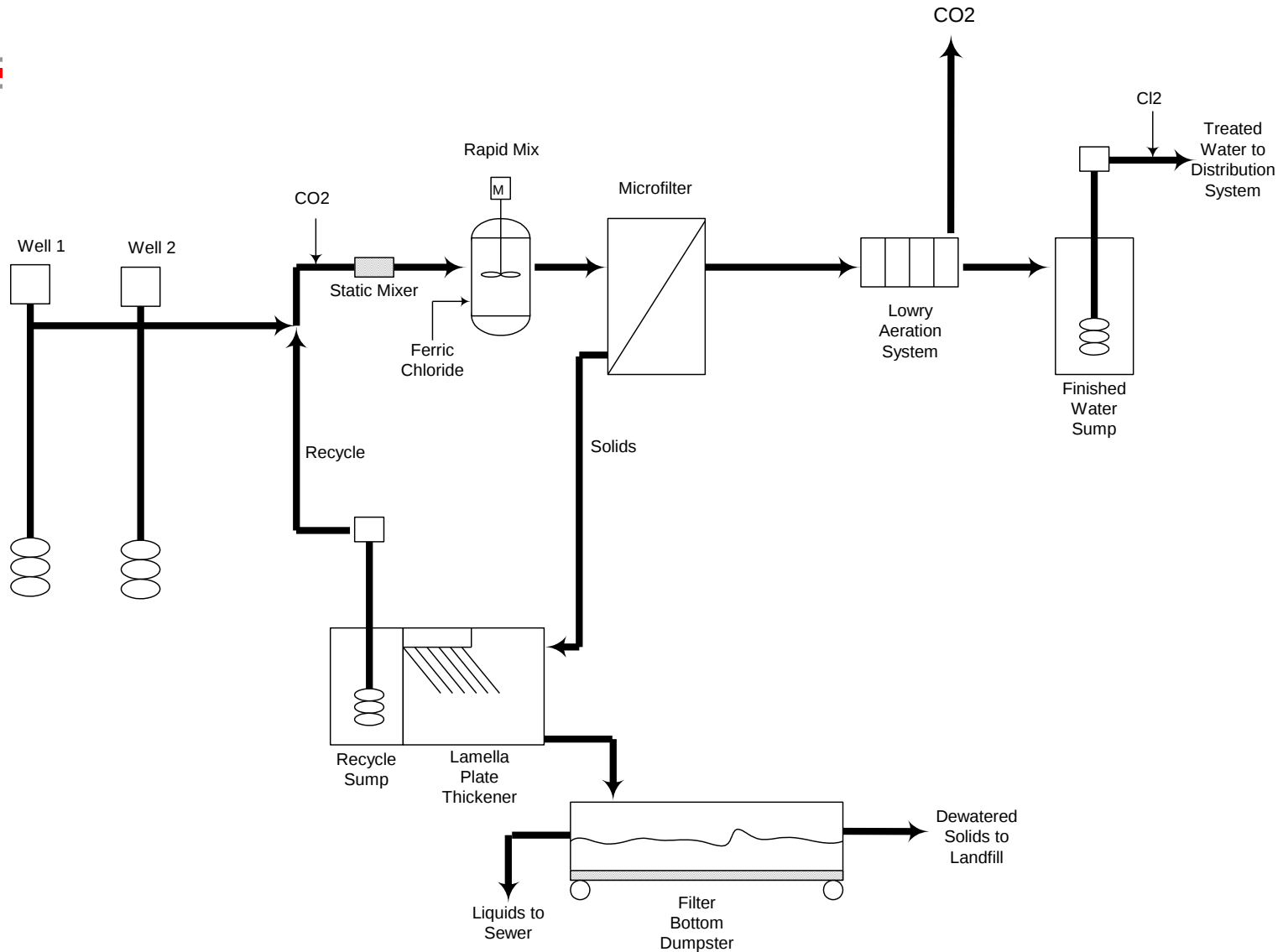
- Only Pall MF tested
- Ferric dose 10 mg/L
- pH lowered to 6.8 with CO₂

El Paso

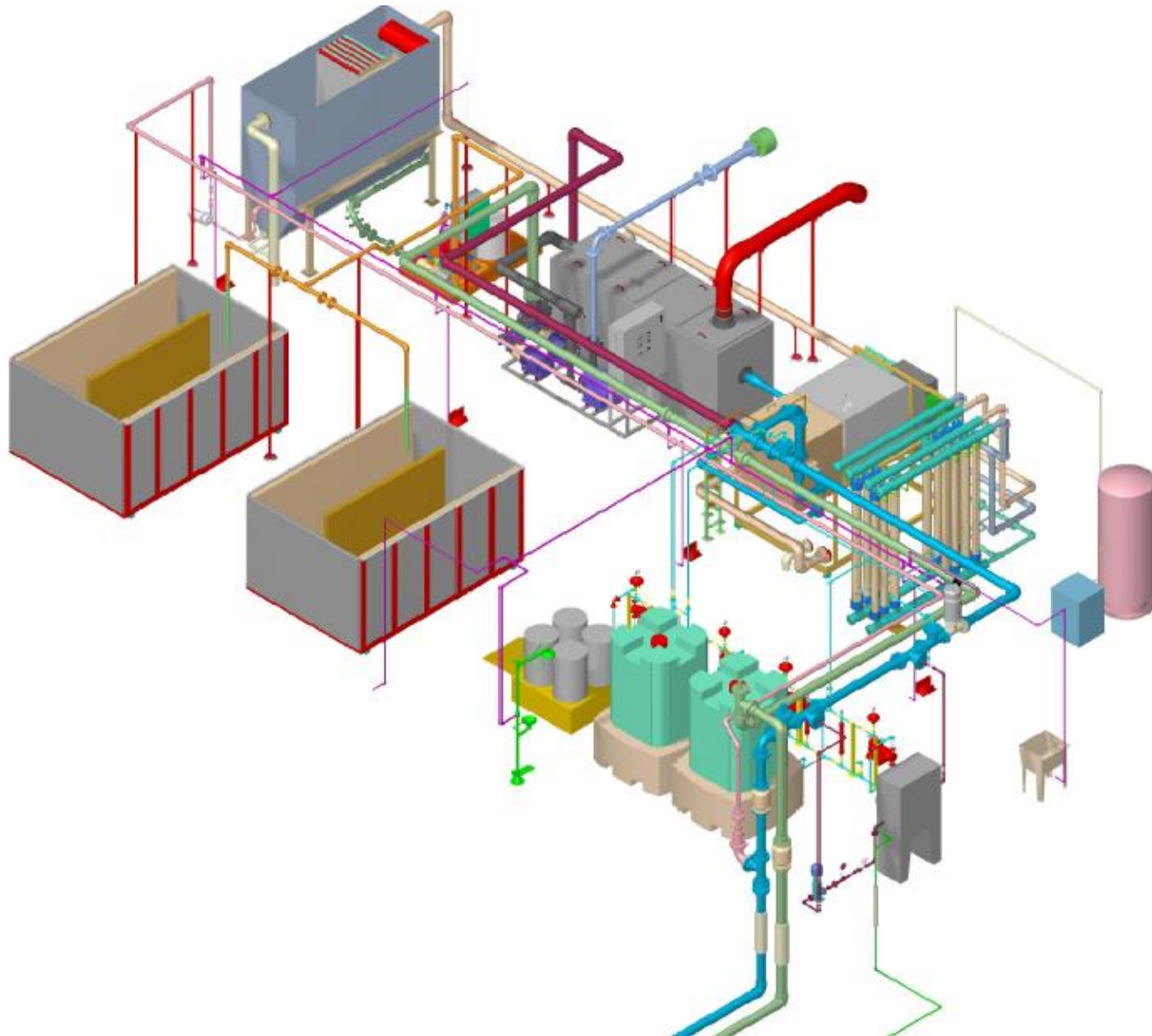
Pall Performance



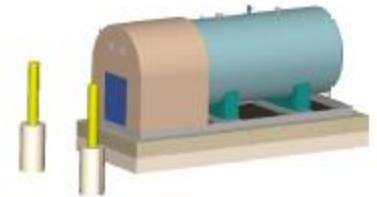
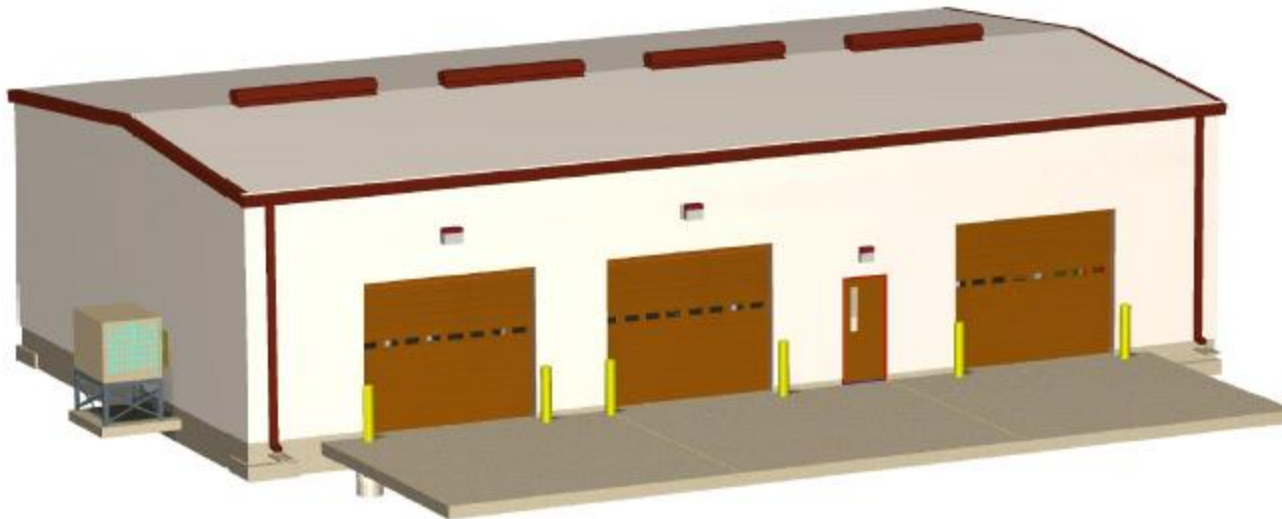
Fallon Paiute Shoshone Tribe C/MF PFD



Fallon Paiute Shoshone Tribe C/MF

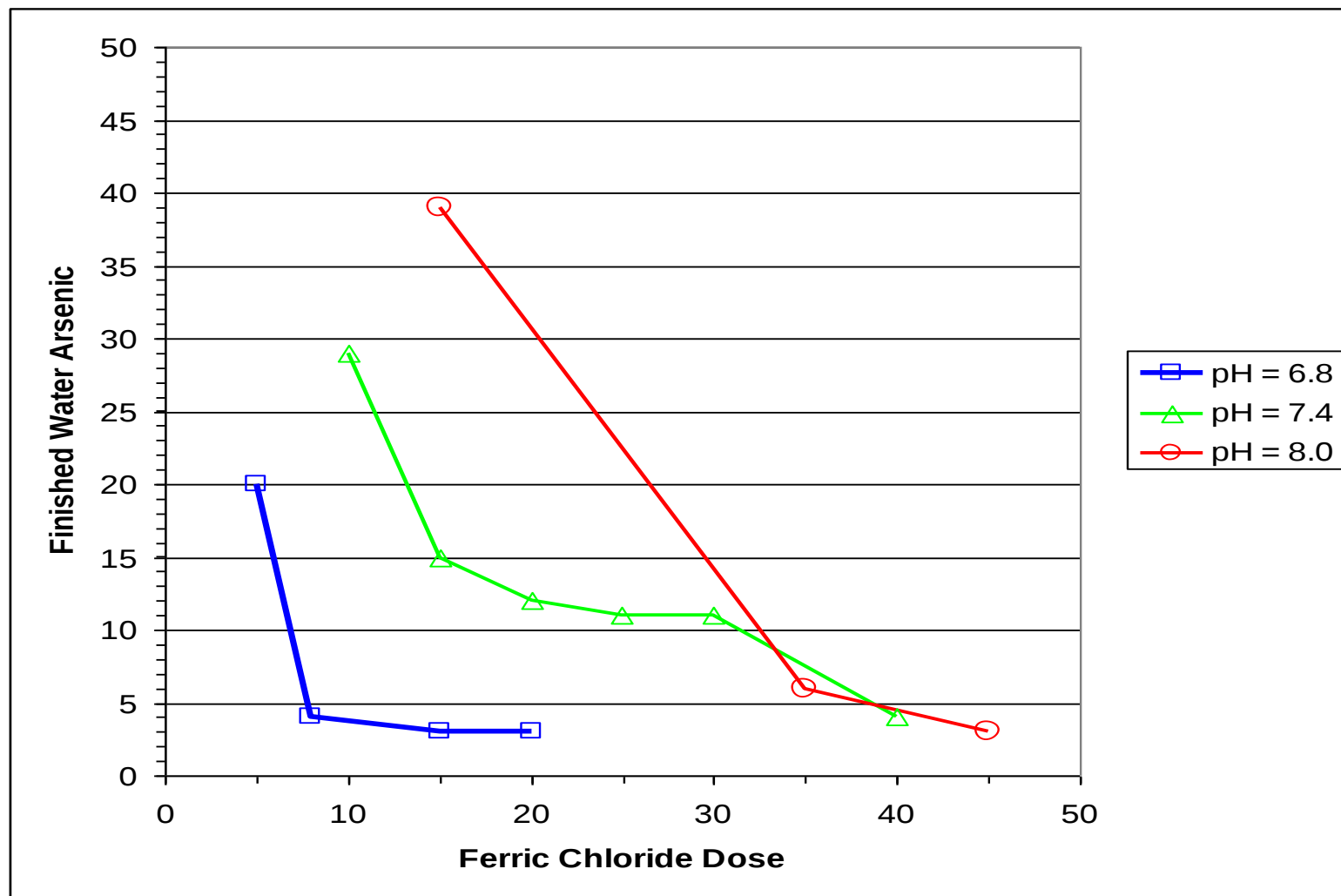


Fallon Paiute Shoshone Tribe As Treatment Facility



Fallon Paiute Shoshone Tribe Start-up

December 2004

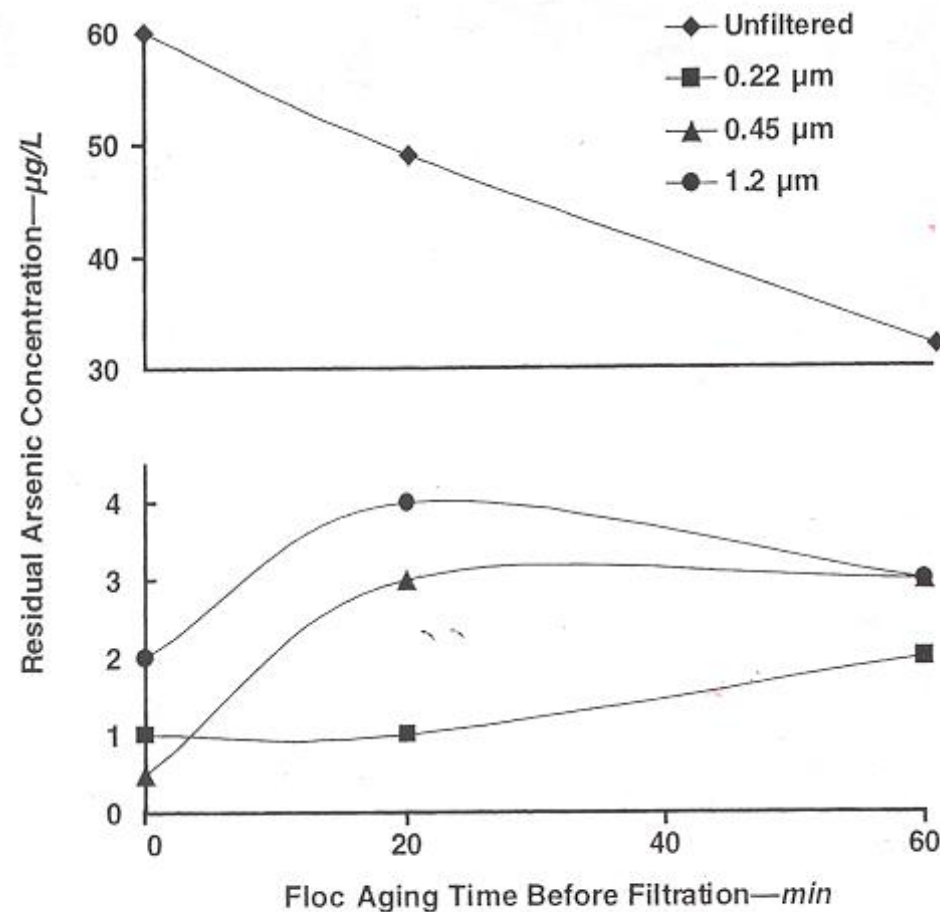


C/MF Summary

- Emerging Technology for Arsenic Treatment
- Can be designed for high flux rates with Low TOC groundwater
- Optimize solids loading by pH pre-treatment
- Cost competitive with other technologies

Recent Studies on Particle Size Filtration and Arsenic Removal

FIGURE 7 Variation of residual arsenic concentration as a function of floc aging and membrane pore size



C/MF O&M Issues

- Membrane Replacement: Pall warrants membranes for 10 years, prorated.
- Chemical cleaning with citric acid, can not be recycled, must be disposed of.
- Provide sufficient replacement parts, not system redundancy.

Comparison of C/MF to Pressure Filters at the Fallon Paiute Shoshone Tribe

Capital Cost Summary	Pressure Filters	C/MF
Total Estimated C/MF Facility Cost	\$1,252,998	\$987,898
Summary of Annual O&M Costs		
Total Estimated O&M for Treatment, \$/yr	\$71,436	\$82,392
Unit O&M Costs for C/MF	\$0.77	\$0.89
Present Worth Analysis		
Total Present Value of Facilities	\$2,087,000	\$1,948,000
Annual Amortized Cost of Capital & O&M	\$125,220	\$116,880
Total Unit Cost of Water Produced, \$/1,000 gals	1.38	1.29

Residuals Characteristics for C/MF and C/F

- C/MF around 4% to 5 % Backwash.
- C/F around 5% to 10% Backwash.
- Recycle the backwash water to minimize wastewater.
- Ferric residuals will pass TCLP, however, may not pass the Cal WET.

Residuals Handling

- Mechanical dewatering will be complicated: Ferric sludge is difficult to dewater
- Need body additives, Diatomaceous Earth
- Filter Bottom Dumpsters and polymer for small applications.
- Solids drying ponds:
 - Ponds need to be lined.
 - Anaerobic conditions may release the As.
 - Provide access for sludge removal equipment.

Concurrent Iron, Manganese, and Arsenic Drinking Water Standards

- Fe: Secondary Standard of 0.30 mg/L
- Mn: Secondary Standard of 0.05 mg/L

Iron and Arsenic Removal

- Oxidize Fe with Cl_2 or O_3
- Adsorb As onto $\text{Fe}(\text{OH})_3$ precipitate
- pH needs to be around 7.3

Manganese and Arsenic Removal

- As requires low pH for adsorption
- Mn requires high pH (>10) for oxidation with Cl_2
- Mn oxidation by ClO_2 is rapid & appears to be independent of pH
 - ClO_2 reported to be ineffective for As(III) oxidation.
 - May need to add Cl_2 in addition