Project C: Assessment and Development of Treatment Processes for DBP Precursor and DBP Removal in Small Water Systems

The University of Texas at Austin
Lynn Katz, Desmond Lawler, Frank Seibert, Mitch Bartolo, Frances Sullivan-Gonzales, Nash Mock, Soyoon Kum

March 21, 2016
Introduction

• **Brief Description:** Evaluate Conventional, Emerging and Novel Technologies for Removal of DBP Precursors and DBPs for Small Water Systems
  • Literature Review that re-evaluates technologies specifically for small water systems
  • Laboratory Testing to Assess Potential of Emerging and Novel Applications
  • Comparison of Emerging and Novel Applications to Existing Technologies

• **Anticipated target utility characteristics:**
  - Small water systems using surface waters with elevated DBPs that can benefit from either removal of DBP precursors or DBPs to meet the Stage 2 D/DBR

• **Continuum of technology development:**

![Diagram showing the continuum of technology development: Development, Implementation, Regulation, Outreach](image-url)
Formation of THMs

$\text{Cl}_2 + \text{NOM} \rightarrow \text{THMs and other DBPs}$

NOM: natural organic material
DBP Removal

- Mature Technologies
  - GAC Adsorption
  - Packed Tower Aeration

- Evolving Technologies
  - Nanofiltration
  - Clearwell Stripping
  - Hollow Fiber Membrane Air Stripping
Removing DBP Precursors

• Alternative Disinfectants
  • ClO₂, O₃, NH₂Cl, UV
  • Ferrate

• Mature Technologies
  – Ion Exchange
  – GAC Adsorption

• Evolving Technologies
  – Membrane Filtration
  – Nano, Ultra, RO
  – Enhanced Coagulation

• Novel Technology
  – ED/RO
<table>
<thead>
<tr>
<th>Product</th>
<th>Flow Range (one device)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liqui-Cel® Extra-Flow 2.5 x 8</td>
<td>0.5 - 3 gpm (0.1 - 0.7 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Extra-Flow 4 x 13</td>
<td>2 - 15 gpm (0.5 - 3.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Extra-Flow 4 x 28</td>
<td>4.4 - 30 gpm (1 - 6.8 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Extra-Flow 6 x 28</td>
<td>5 - 50 gpm (1.1 - 11.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Industrial 8 x 20</td>
<td>5 - 50 gpm (1.1 - 11.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® 8 x 20 Stainless Steel</td>
<td>5 - 50 gpm (1.1 - 11.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® High Pressure 8 x 40</td>
<td>30 - 125 gpm (6.8 - 28.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® High Pressure 8 x 80</td>
<td>30 - 125 gpm (6.8 - 28.4 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® 8 x 40/8 x 80 Cartridge</td>
<td>Refer to 8 x 40 and 8 x 80 products for flow rate information</td>
</tr>
<tr>
<td>Liqui-Cel® Extra-Flow 10 x 28</td>
<td>44 - 250 gpm (10 - 57 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Industrial 10 x 28</td>
<td>44 - 210 gpm (10 - 48 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Industrial 14 x 28</td>
<td>70 – 400 gpm (16 – 90.8 m³/hr)</td>
</tr>
<tr>
<td>Liqui-Cel® Industrial 14 x 40</td>
<td>70 – 550 gpm (16 – 125 m³/hr)</td>
</tr>
</tbody>
</table>
Gas Transfer Fundamentals: Absorption/Stripping

• Henry’s Law:
  \[ H_i = \frac{C_{G,i}}{C_{L,i}} \]

• Mass Transfer Coefficients (m/s)
  - \( K_L \): Overall mass transfer coefficient
  - \( k_L \) or \( k_G \): Individual phase mass transfer coefficients

• Diffusivities (m²/s)
  - \( D_L \) or \( D_G \): Diffusion through bulk phases
  - \( D_{Kn} \): Knudsen Diffusion: small pores
  - \( D_c \): Continuum Diffusion: free space

• Stripping Factor:
  - Gas transfer capacity factor
  \[ S = \frac{Q_G H}{Q_L} \]
Hollow Fiber Membrane Air Stripping

• Unbaffled module
Hollow Fiber Membrane Air Stripping

• Unbaffled module
Hollow Fiber Membrane Air Stripping

• Unbaffled module
Hollow Fiber Membrane Air Stripping

- Unbaffled module

<table>
<thead>
<tr>
<th>System Setup</th>
<th>Air-to-Water Ratio</th>
<th>Stripping Factor</th>
<th>Percent Removal</th>
<th>Contaminant(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch</td>
<td>5 - 120</td>
<td>0.85 - 120</td>
<td>~80%</td>
<td>Chloroform</td>
<td>Semmens et al (1989)</td>
</tr>
<tr>
<td>Batch</td>
<td>6 - 16</td>
<td>1.6 - 4.3</td>
<td>80-90%</td>
<td>Toluene</td>
<td>Juang et al (2005)</td>
</tr>
<tr>
<td>Continuous</td>
<td>5 - 46</td>
<td>0.87 - 7.8</td>
<td>~80%</td>
<td>Chloroform, BDCM, Bromoform</td>
<td>Zander et al (1989)</td>
</tr>
<tr>
<td>Continuous</td>
<td>26 - 130</td>
<td>3.2 - 16.2</td>
<td>20-60%</td>
<td>Chloroform</td>
<td>Bhowmick et al (1994)</td>
</tr>
</tbody>
</table>
1. Unbaffled - Batch

- KL (m/s) pred
- KL exp (m/s)

2. Unbaffled - Continuous

- KL pred (m/s)
- KL exp (m/s)
Hollow Fiber Membrane Air Stripping

• Baffled module – Liqui-Cel® Extra-Flow
Hollow Fiber Membrane Air Stripping

- **Baffled module – Liqui-Cel® Extra-Flow**

<table>
<thead>
<tr>
<th>System</th>
<th>Air-to-Water Ratio</th>
<th>Stripping Factor</th>
<th>Percent Removal</th>
<th>Contaminant(s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Continuous (vacuum assisted)</td>
<td>1 - 5</td>
<td>0.43 - 4.9</td>
<td>60-96%</td>
<td>cis-1,2-dichloroethene</td>
<td>Tarafder et al (2007)</td>
</tr>
</tbody>
</table>

Advantages of HFM Air Stripping
- Higher overall mass transfer coefficient (KLa)
- Constant (flow independent) and high mass transfer area
- Reduced dependence of KLa on gas flow rate
- No upper limit on the gas flow rate that can be used
- No need for mist elimination
- No need for tall structures

Disadvantages of HFM Air Stripping
- Large air pressure drops
- Cost?
3. Baffled

![Graph showing KL pred (m/s) vs KL exp (m/s) forTarafder and He](image)
Modeling Liqui-Cel® Extra-Flow

- **Overall** Mass Transfer Coefficient: $K_L$

\[
\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{k_m H} + \frac{1}{k_G H}
\]

- Mass Transfer Coefficient **through the membrane**: $k_m$
- **Shell-side** Mass Transfer Coefficient: $k_L$
- **Tube-side** Mass Transfer Coefficient: $k_G$
Modeling Liqui-Cel® Extra-Flow

- Mass Transfer Coefficient through the membrane: $k_m$

\[
\frac{1}{k_m H} = \frac{\delta \tau}{D_{\text{eff}} \varepsilon H}
\]

\[
D_{\text{eff}} = \left( \frac{1}{D_c} + \frac{1}{D_{Kn}} \right)^{-1}
\]

\[
D_c = 10^{-7} \left( \frac{1}{MW_i} + \frac{1}{MW_G} \right)^{0.5}
\]

\[
D_{Kn} = 4850d_p \sqrt{\frac{T}{MW_i}}
\]
Modeling Liqui-Cel® Extra-Flow

- **Shell-side** Mass Transfer Coefficient: $k_L$

$$k_L = \frac{d_h Sh}{D_L}$$

$$Sh = 0.39 \text{Re}^{0.59} \text{Sc}^{0.33}$$

$$d_h = \frac{d_a^2 - d_d^2 - nd_o^2}{nd_o}$$

$$Sc = \frac{\mu_L}{\rho_L D_L}$$

$$\text{Re} = \frac{u_L d_h \rho_L}{\mu_L}$$
Modeling Liqui-Cel® Extra-Flow

- **Tube-side** Mass Transfer Coefficient: \( k_G \)

\[
\frac{1}{k_G H} = \frac{0.617}{H} \left( \frac{d_i L}{u_G D_c^2} \right)^{0.33}
\]
Stage Efficiency Modeling

• Murphree Efficiency

Mass transfer efficiency at a particular stage:

100% efficiency based on vapor and liquid phases leaving stage in equilibrium (Henry’s Law)

\[ E_m = \frac{\alpha}{1 + \frac{\alpha}{2}} \]

\[ \alpha = \frac{K_L A_i}{Q_G} \]

• Overall Stage Efficiency

\[ E_o = \frac{\ln \left[ 1 + E_m (S-1) \right]}{\ln(S)} \]

\[ S = \frac{Q_G H}{Q_L} \]
Hollow Fibers

Baffle

Effluent

Housing

Radially Forced Liquid Path

Influent

Distribution

Collection

Stage 1

Stage 2

Pore Size – 0.03 to 0.04 microns
Spacing = 40 microns
Stage Efficiency Modeling

![Graph showing predicted versus measured efficiency with data points for Zander, Tarafder, He, (+)20%, and (-)20%.]
## Preliminary Economic Analysis
($/1000$ gal)

<table>
<thead>
<tr>
<th>Treatment Method</th>
<th>Very Small (0.04 mgd)</th>
<th>Small (0.3 mgd)</th>
<th>Medium (1 mgd)</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA 2005 Estimates- adjusted to 2014</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloramine (0.15-mg/L)</td>
<td>1.38</td>
<td>0.26</td>
<td>0.09</td>
</tr>
<tr>
<td>ClO2 (1.25-mg/L)</td>
<td></td>
<td>0.91</td>
<td>0.24</td>
</tr>
<tr>
<td>UV (40-mJ/cm²)</td>
<td>2.01</td>
<td>0.46</td>
<td>0.34</td>
</tr>
<tr>
<td>Ozone (4.5-mg/L with pH adjustment)</td>
<td></td>
<td>4.48</td>
<td>1.52</td>
</tr>
<tr>
<td>GAC (EBCT=20min, 240 day regen. frequency)</td>
<td>8.11</td>
<td>3.09</td>
<td>2.05</td>
</tr>
<tr>
<td>NF</td>
<td>6.18</td>
<td>2.78</td>
<td>1.96</td>
</tr>
<tr>
<td>HF MAS</td>
<td>6.96</td>
<td>2.69</td>
<td>2.17</td>
</tr>
</tbody>
</table>

Objectives

• Quantify THM removal by air stripping in continuous flow baffled membrane systems
• Determine the effect of stripping factor on THM removal
• Determine the effect of THM concentration on THM removal
• Develop a model and estimate the economics of scale for small water systems.
  • This means determining whether these systems should be modeled as stage devices or differential contactors
Liqui-Cel MicroModule

- Liquid Flow Limits = 5-30 mL/min
- Approximate Membrane Surface Area = 100 cm²
- Approximate Priming Volume = 3.5 mL
- Maximum Pressure for 5-25°C Operation = 45.15 psig
Methodology

- Continuous Flow
- THM Dose Varied
  = 50, 100, 150, 200 (μg/L)
- Water Flow Rate Constant
  = 5 mL/min
- Air Flow Rate Varied
  = 195 mL/min to 1640 mL/min
## Trihalomethanes (THMs) Characteristics

<table>
<thead>
<tr>
<th>Compound</th>
<th>Molecular Weight (g/mol)</th>
<th>Henry’s Law Constant (L/L_a)</th>
<th>Henry’s Law Constant (atm/(mol/L))</th>
<th>D_L (x10^-5 cm²/s)</th>
<th>D_c (cm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloroform (TCM)</td>
<td>119.4</td>
<td>0.163</td>
<td>4.00</td>
<td>1.03</td>
<td>0.117</td>
</tr>
<tr>
<td>Bromodichloromethane</td>
<td>163.8</td>
<td>0.091</td>
<td>2.19</td>
<td>0.92</td>
<td>0.110</td>
</tr>
<tr>
<td>Dibromochloromethane</td>
<td>208.3</td>
<td>0.035</td>
<td>0.842</td>
<td>0.96</td>
<td>0.097</td>
</tr>
<tr>
<td>Bromoform</td>
<td>252.8</td>
<td>0.0227</td>
<td>0.556</td>
<td>0.92</td>
<td>0.088</td>
</tr>
</tbody>
</table>
Experiments at 50 μg/L & Stripping Factor 5

Individual THMs

- BDCM
- CDBM
- TBM

THM Mix

- Mix BDCM
- Mix CDBM
- Mix TBM
From Experimental Data:

1. Determine the number of equilibrium stages
2. Determine the overall stage efficiency, $E_0$
3. For 1\textsuperscript{st} pass on data analysis, determine Murphree efficiency from the following equations:
   \[ E_0 = \frac{\ln(1 + E_{mw}(\lambda - 1))}{\ln(\lambda)}, \quad \lambda = \frac{m_tF_s}{F_t} \]
4. Back calculate $\alpha$ from the equation:
   \[ E_{mw} = \frac{\alpha}{1 + \frac{\alpha}{2}} \]
5. Calculate effective $K_{ow}$ from known area and the equation:
   \[ \alpha = \frac{K_{ow}A_i}{Q_t} \]
Summary

• Revised Model for Hollow Fiber Membrane (HFM) Reactor was developed.
• Preliminary economic analysis indicates that the technology is cost competitive for small systems.
• Preliminary evaluation of the technology at bench-scale shows promise.

Future Work

• Continue experiments on THM removal and compare results to modelling predictions.
• Conduct validation experiments at larger scale.
• Refine economic evaluation.
NOM Removal During Alum Coagulation: Insights using infrared spectroscopy

Mitchel J. Bartolo¹, Dr. Lynn Katz¹, Dr. Satish Myneni², Dr. Desmond Lawler¹

¹The University of Texas at Austin, ²Princeton University

March 21, 2016
Hypothesis

• Existing technology: enhanced alum coagulation
• NOM removal can be affected by the presence of anions
• Fluoride results (Project A) emphasized these impacts
Alum Coagulation Process

Jar Testing

Coagulant + Ligand Addition

Rapid Mix

Slow Mix

Settling
Research Goals

• Characterization of Al precipitates
• What are the mechanisms of removal?

Adsorption

Co-Precipitation

Spectroscopy! (FTIR, XPS)

SEM, EDX, XRD, XPS
Impact of F on Particle Size

- Scanning electron microscope (SEM)
  - Imaging of precipitates

- Coulter Counter
  - Particle size distribution

Aluminum precipitates with fluoride
Evidence for Fluoride Co-precipitation

- X-ray photoelectron spectroscopy (XPS)
  - Elemental composition

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Al</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gibbsite</td>
<td>1</td>
<td>1.6</td>
<td>---</td>
</tr>
<tr>
<td>200 mg/L alum</td>
<td>1</td>
<td>2.0</td>
<td>---</td>
</tr>
<tr>
<td>200 mg/L alum (PRE), 5 mg/L F</td>
<td>1</td>
<td>1.8</td>
<td>0.23</td>
</tr>
<tr>
<td>200 mg/L alum (CPT), 5 mg/L F</td>
<td>1</td>
<td>1.7</td>
<td>0.25 (0.43)*</td>
</tr>
<tr>
<td>200 mg/L alum (CPT), 10 mg/L F</td>
<td>1</td>
<td>1.6</td>
<td>0.42</td>
</tr>
</tbody>
</table>

*SEM–EDX (energy dispersive x-ray spectroscopy)
Methods

• 4 weeks of repeated jar tests (0-3 Wks aging)

• Experimental Conditions
  • Fluoride: 5 mg/L
  • NOM surrogate: pyromellitic acid: 5 mg/L as C
  • Sulfate (Alum), Chloride (AlCl₃)
  • Sodium metasilicate: 20 mg/L as SiO₂
  • pH 6.5 and 7.5
  • I = 0.014 M
  • Alk/hardness = 3 meq/L

• Analysis
  • In situ ATR-FTIR
  • Removal data from supernatant
<table>
<thead>
<tr>
<th>Sample #</th>
<th>Coagulant</th>
<th>pH</th>
<th>Organic Acid</th>
<th>Fluoride</th>
<th>SiO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Alum</td>
<td>6.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>2</td>
<td>Alum</td>
<td>6.5</td>
<td>None</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>3</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>4</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Salicylic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>5</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Phthalic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>6</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>7</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Salicylic</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>8</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Phthalic</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>9</td>
<td>Alum</td>
<td>6.5</td>
<td>None</td>
<td>None</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>10</td>
<td>Alum</td>
<td>6.5</td>
<td>None</td>
<td>5 mg/L F</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>11</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>None</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>12</td>
<td>Alum</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>5 mg/L F</td>
<td>20 mg/L</td>
</tr>
<tr>
<td>13</td>
<td>Alum</td>
<td>7.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>14</td>
<td>Alum</td>
<td>7.5</td>
<td>None</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>15</td>
<td>Alum</td>
<td>7.5</td>
<td>5 mg/L Pyromellitic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>16</td>
<td>Alum</td>
<td>7.5</td>
<td>5 mg/L Pyromellitic</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>21</td>
<td>Aluminum Chloride</td>
<td>6.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>22</td>
<td>Aluminum Chloride</td>
<td>6.5</td>
<td>None</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>23</td>
<td>Aluminum Chloride</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>24</td>
<td>Aluminum Chloride</td>
<td>6.5</td>
<td>5 mg/L Pyromellitic</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
<tr>
<td>25</td>
<td>Aluminum Chloride</td>
<td>7.5</td>
<td>None</td>
<td>None</td>
<td>None</td>
</tr>
<tr>
<td>26</td>
<td>Aluminum Chloride</td>
<td>7.5</td>
<td>None</td>
<td>5 mg/L F</td>
<td>None</td>
</tr>
</tbody>
</table>
In Situ ATR-FTIR Insights

- How much
- Mechanism of adsorption
  - Outer or inner sphere
  - Competition between ligands

chemical structures: $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{OH}$, $\text{Al}$, $\text{NOM}$, $\text{Si}$, $\text{F}$
## Colorado Pilot Results

<table>
<thead>
<tr>
<th>Alum Dose (mg/L)</th>
<th>F Removal (%)</th>
<th>Si Removal (%)</th>
<th>Al Residual (mg/L)</th>
<th>UV-254 Removal (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>14.3</td>
<td>4.8</td>
<td>0.475</td>
<td>53</td>
</tr>
<tr>
<td>50</td>
<td>33.9</td>
<td>11.5</td>
<td>0.229</td>
<td>62</td>
</tr>
<tr>
<td>100</td>
<td>52.8</td>
<td>16.7</td>
<td>0.074</td>
<td>65</td>
</tr>
<tr>
<td>150</td>
<td>63.6</td>
<td>21.2</td>
<td>0.056</td>
<td>64</td>
</tr>
<tr>
<td>200</td>
<td>71.2</td>
<td>27.4</td>
<td>0.038</td>
<td>65</td>
</tr>
<tr>
<td>300</td>
<td>79.8</td>
<td>34.0</td>
<td>0.031</td>
<td>66</td>
</tr>
</tbody>
</table>
Pyromellitate as the NOM Surrogate

![Graph showing LMW Organic Removal vs Alum Dose](image)

- **pH**: 6.5 +/- 0.1
- **I**: 0.011 - 0.17 M
- **[F]_i**: 5 mg/L
- **[DOC]**: 5 mg/L

![Graph showing Percent Removed vs Alum Dose](image)

- 5 mg/L DOC
- 5 mg/L DOC, 5 mg/L F

(a) NOM Removal

![Graph with data points and legend](image)
UV-Vis vs DOC

Graphs showing the removal of organic UV-254 nm and organic DOC at different pH levels for Water 1 - TX at different Alum Dose (mg/L) with [F] = 3.04 mg/L and [DOC] = 9.20 mg C/L.
FTIR Results: Pyromellitate Adsorption Mechanism

<table>
<thead>
<tr>
<th>Aqueous Pyromellitate Feature</th>
<th>Wavenumber (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric (v_{C\text{-}O}) Vibration</td>
<td>1562</td>
</tr>
<tr>
<td>Symmetric (v_{C\text{-}O}) Vibration</td>
<td>1412, 1374, 1325</td>
</tr>
<tr>
<td>Aromatic Vibration</td>
<td>1488</td>
</tr>
<tr>
<td>Aromatic C-H Bending</td>
<td>1136</td>
</tr>
</tbody>
</table>

(Adapted from Johnson et al. 2004 and Nordin et al 1998)
Outer-Sphere Complexation of Pyromellitate

Alum, pH 6.5, Pyro 5 mg/L as C (0.042 mM)

<table>
<thead>
<tr>
<th>Aqueous Pyromellitate Feature</th>
<th>Wavenumber (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymmetric $\nu_{C=O}$ Vibration</td>
<td>1562</td>
</tr>
<tr>
<td>Symmetric $\nu_{C=O}$ Vibration</td>
<td>1412, 1374, 1325</td>
</tr>
<tr>
<td>Aromatic Vibration</td>
<td>1488</td>
</tr>
<tr>
<td>Aromatic C-H Bending</td>
<td>1136</td>
</tr>
</tbody>
</table>
Carbonate Adsorption Mechanism

- Carbonate coordination determined by the degree of splitting at the $v_3$ C-O vibration

<table>
<thead>
<tr>
<th>Anion</th>
<th>$v_3$ Frequency (cm$^{-1}$)</th>
<th>$\Delta v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Carbonate</td>
<td>1383</td>
<td>-</td>
</tr>
<tr>
<td>Monodentate Carbonate</td>
<td>1448 1575 1580</td>
<td>1354 1455 1420</td>
</tr>
<tr>
<td>Bidentate Carbonate</td>
<td>1590 1710</td>
<td>1282 1315</td>
</tr>
<tr>
<td>0.01M carbonate + am-Al(OH)$_3$ (Su et al.)</td>
<td>1490</td>
<td>1420</td>
</tr>
</tbody>
</table>

Adapted from Su et al. 1997 and Wijnja et al. 1998
Inner-Sphere Complexation of Carbonate

Δν₃ ~ 65 cm⁻¹

Alum, pH 6.5, no additional ligands
## Effect of Al Salt on Carbonate

<table>
<thead>
<tr>
<th>Age</th>
<th>$v_3$</th>
<th>$\Delta v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Wk</td>
<td>1501.3</td>
<td>1437.6</td>
</tr>
<tr>
<td>1Wk</td>
<td>1501.3</td>
<td>1443.4</td>
</tr>
<tr>
<td>2Wk</td>
<td>1501.3</td>
<td>1434.7</td>
</tr>
<tr>
<td>3Wk</td>
<td>1502.2</td>
<td>1438.6</td>
</tr>
</tbody>
</table>

### Sulfate, pH 6.5

<table>
<thead>
<tr>
<th>Age</th>
<th>$v_3$</th>
<th>$\Delta v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Wk</td>
<td>1497.4</td>
<td>1427</td>
</tr>
<tr>
<td>1Wk</td>
<td>1506.1</td>
<td>1400</td>
</tr>
<tr>
<td>2Wk</td>
<td>1501.3</td>
<td>1406.8</td>
</tr>
<tr>
<td>3Wk</td>
<td>1498.4</td>
<td>1407.7</td>
</tr>
</tbody>
</table>

### Chloride, pH 6.5

<table>
<thead>
<tr>
<th>Age</th>
<th>$v_3$</th>
<th>$\Delta v_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0Wk</td>
<td>1498.4</td>
<td>1423.2</td>
</tr>
<tr>
<td>1Wk</td>
<td>1504.2</td>
<td>1399.1</td>
</tr>
<tr>
<td>2Wk</td>
<td>1505.1</td>
<td>1400</td>
</tr>
<tr>
<td>3Wk</td>
<td>1505.1</td>
<td>1400</td>
</tr>
</tbody>
</table>

### Chloride, pH 7.5
Sulfate Adsorption Mechanism

Sulfate Species and Their Infrared Active Bands

- **Species**
  - Aqueous sulfate
  - Outer-Sphere sulfate
  - Monodentate (M = Metal or Proton)
  - Bidentate Binuclear (Me = Metal)
  - Bidentate Mononuclear

- **Symmetry**
  - $T_d$
  - $T_d$ (distorted)
  - $C_{3v}$
  - $C_{2v}$

- **Infrared Active Bands**

  - $v_1$
  - $v_3$

- **Peak at** ~1100 cm$^{-1}$
Outer-Sphere Complexation of Sulfate

[Graph showing absorbance vs. wavenumber cm\(^{-1}\) with peaks around 1099 cm\(^{-1}\).]

Alum, pH 6.5, varied Pyro and F
## Silicate Adsorption Mechanism

Adapted from Gaggiano et al. 2013

<table>
<thead>
<tr>
<th>Silicate Feature</th>
<th>Wavenumber cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O bending</td>
<td>800</td>
</tr>
<tr>
<td>Si-O (4NBO) stretching</td>
<td>850-855</td>
</tr>
<tr>
<td>Si-O (3NBO) stretching</td>
<td>898-920</td>
</tr>
<tr>
<td>Si-O (2NBO) stretching</td>
<td>938-953</td>
</tr>
<tr>
<td>Si-O (1NBO) stretching</td>
<td>1040-1050</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>985-1003</td>
</tr>
<tr>
<td>Si-OH</td>
<td>1093-1120</td>
</tr>
</tbody>
</table>

Swedlund et al. 2009

![Silicate Adsorption Mechanism Graph](image-url)
Inner Sphere Complexation of Si w/ Polymerization

<table>
<thead>
<tr>
<th>Silicate Feature</th>
<th>Wavenumber cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si-O bending</td>
<td>800</td>
</tr>
<tr>
<td>Si-O (4NBO)</td>
<td>850-855</td>
</tr>
<tr>
<td>Si-O (3NBO)</td>
<td>898-920</td>
</tr>
<tr>
<td>Si-O (2NBO)</td>
<td>938-953</td>
</tr>
<tr>
<td>Si-O (1NBO)</td>
<td>1040-1050</td>
</tr>
<tr>
<td>Si-O-Si</td>
<td>985-1003</td>
</tr>
<tr>
<td>Si-OH</td>
<td>1093-1120</td>
</tr>
</tbody>
</table>

Alum, pH 6.5, 20 mg/L as SiO\(_2\) (0.3 mM Si)

~990 cm\(^{-1}\)
Graphs showing the changes in Sulfate : Silica Intensity for different conditions:

1. Si: No change observed in intensity across weeks.
2. Si+F: A decrease in intensity from Week 0 to Week 3.
3. Si+Pyro: A decrease in intensity from Week 0 to Week 3.
4. Si+Pyro+F: A decrease in intensity from Week 0 to Week 3.
# Summary of Mechanism Findings

<table>
<thead>
<tr>
<th>Mechanism</th>
<th>Mechanism Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyromellitate</td>
<td>Outer-Sphere</td>
</tr>
<tr>
<td>Sulfate</td>
<td>Outer-Sphere</td>
</tr>
<tr>
<td>Carbonate</td>
<td>Inner-Sphere Monodentate</td>
</tr>
<tr>
<td>Silicate</td>
<td>Inner-Sphere with Silicate Polymerization</td>
</tr>
<tr>
<td>Fluoride</td>
<td>Co-precipitation and Inner-Sphere (prior findings in this study)</td>
</tr>
</tbody>
</table>
Inner Sphere Competition

F% Removal vs Silica % Removal for different aging periods with and without fluoride and silicate treatments.
Conclusions

• ATR-FTIR allows us to determine both magnitude and mechanism of adsorption
  • Sulfate and Pyro: Outer-sphere
  • Carbonate, Silicate, and F: Inner-sphere

• Mechanism-based competition between ligands provides an understanding of the impacts that background water chemistry will have on NOM precursor removal
C: Coupled ED and RO/NF Treatment

Soyoon Kum
University of Texas at Austin
ED and RO/NF

- A coupled ED and RO/NF system that utilizes
  - Electrodialysis to isolate salts that increase fouling in RO or NF
  - Reverse Osmosis or Nanofiltration to remove NOM

- Hypothesis: The treatment efficiency and number of treatment cycles of RO or NF can be improved by isolating salts temporarily prior to either RO or NF.
Coupled ED/RO or NF system

- Schematic diagram of ED/RO NOM removal system

Feed → Electrodialysis (ED) → ED dilute with low salt conc. and high conc. NOM → Reverse Osmosis (RO) → RO concentrate with low salt conc. and high conc. NOM → Mixing → RO permeate with low salt conc. and low conc. NOM → Treated water with normal salt conc. and low conc. NOM.
Introduction to Electrodialysis

![Diagram of electrodialysis process]

- **Cathode**
  - **H₂**
  - **OH⁻**
- **Anode**
  - **O₂**
  - **H⁺**
- **Electrolytes**
  - **AEM** (Anion Exchange Membrane)
  - **CEM** (Cation Exchange Membrane)

The process involves the separation of ions across the membranes, leading to the concentration of substances on one side and dilution on the other. The diagram illustrates the movement of ions and gases, highlighting the fundamental principles of electrodialysis.
Experimental Setup: batch-recycle

Walker, et al., 2014
Whole system of lab-scale ED experiment

Photo by Soyoon Kum
Current Status and Future Work

Current Status:
• Verifying treatment of salt water w/ NOM and w/o NOM by ED

Future Work:
• Changing the conditions of electrodialysis system, such as voltage, superficial velocity, and pH, find the optimum condition of electrodialysis operation to achieve high water recovery of NOM contained water in RO membrane process
• Conducting experiments using different ion exchange membranes to verify salt ion removal characteristics in different ion exchange membranes
• Conducting NOM removal experiment of ED/RO combined system by applying selected optimum ED experiment condition using different water resources.
Treatment of Salt Water w/ NOM and w/o NOM by ED

- Compare salt and NOM removal performance with electrodialysis by comparing both salt only solution and salt with NOM solution

250 mg/L NaCl + 0.01 M Na₂SO₄ solution w/o NOM

250 mg/L NaCl + Concentrated Lake Austin water w/ NOM (DOC 5 mg/L)

Conductivity ≅ 0.82 mS/cm and pH 7.4
## Composition of concentrated Lake Austin water (NOM source)

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration (mg/L)</th>
<th>Component</th>
<th>Concentration (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl⁻</td>
<td>136.5</td>
<td>Ca²⁺</td>
<td>35</td>
</tr>
<tr>
<td>NO₂⁻</td>
<td>0.0</td>
<td>Mg²⁺</td>
<td>1.7</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.5</td>
<td>K⁺</td>
<td>1.5</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>8.4</td>
<td>Na⁺</td>
<td>8.0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>-</td>
<td>DOC</td>
<td>269.9</td>
</tr>
</tbody>
</table>

1:20 dilution of Concentrated Lake Austin water
### Experiment Operation Condition

<table>
<thead>
<tr>
<th>Variable</th>
<th>Standard value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane type</td>
<td>CMV/AMV</td>
<td>4 cell pairs</td>
</tr>
<tr>
<td>Stack voltage</td>
<td>1 V/CP</td>
<td>4.0 V/Stack</td>
</tr>
<tr>
<td>Flow rate</td>
<td>0.4 L/min</td>
<td>Superficial velocity $\approx 2.12$ cm/s</td>
</tr>
<tr>
<td>Feed water</td>
<td>Synthetic water</td>
<td>250 mg/L NaCl+ 0.01 M Na$_2$SO$_4$ solution w/ and w/o NOM</td>
</tr>
<tr>
<td>Removal ratio</td>
<td>80 %</td>
<td></td>
</tr>
</tbody>
</table>
Treatment of Salt Water w/o NOM
Treatment of Salt Water w/ NOM
Comparison of Salt Removal w/ and w/o NOM
NOM Concentration Change with Time

<table>
<thead>
<tr>
<th></th>
<th>Final Conc. in Diluate</th>
<th>Final Conc. in Concentrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>DOC (mg/L)</td>
<td>4.72 mg/L</td>
<td>4.68 mg/L</td>
</tr>
</tbody>
</table>
Conclusions

• Effective Removal of salt was achieved
• TOC removal was minimal
• RO has been demonstrated to remove NOM
• These very preliminary results are promising!
Outputs and Outreach

Completed:

Scheduled:
None

Anticipated:
Manuscript for submission to a technical Journal on FTIR results, late spring 2016
Manuscript for submission to a technical Journal on HFM modeling and cost analysis, summer 2016

WINSSS or US EPA Small Systems Webinar – late 2016 or 2017
Questions?
Inner versus outer-sphere

Figure 5-1: Common aqueous complexes between aluminum and organic acids (adapted from Vance et al. 1996)
Aqueous pyromellitate as a function of protonation state (Johnson et al. 2004)
LMW Organic UV Removal (%)

pH

Salicylic Acid (296 nm)
Phthalic Acid (240 nm)
Pyromellitic Acid (296 nm)

Alum Dose = 200 mg/L
I = 0.011-0.017 M
[DOC] = 5 mg/L
Phthalic Acid

Pyromellitic acid

Salicylic acid
# XPS Bond Strength

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Binding Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O 1s</td>
</tr>
<tr>
<td>200 mg/L alum</td>
<td>529.81</td>
</tr>
<tr>
<td>200 mg/L alum (PRE), 5 mg/L F</td>
<td>529.41</td>
</tr>
<tr>
<td>200 mg/L alum (CPT), 5 mg/L F</td>
<td>529.51</td>
</tr>
<tr>
<td>200 mg/L alum (CPT), 10 mg/L F</td>
<td>529.51</td>
</tr>
</tbody>
</table>
Exciting the molecule

\[ \nu_1 \quad \text{symmetric stretch} \]
\[ \nu_2 \quad \text{asymmetric stretch} \]
\[ \nu_3 \quad \text{bend} \]
\[ x \quad \text{librations} \]

http://www1.lsbu.ac.uk
Fluoride Removal

Jar Number

Non-Aged
1 Wk-Aged
2 Wk-Aged
3 Wk-Aged
Organics Removal

UV-Vis % Removal

Jar Number

Non-Aged

1 Wk-Aged

2 Wk-Aged

3 Wk-Aged
Silica Removal

0.0% 10.0% 20.0% 30.0% 40.0% 50.0% 60.0% 70.0%

Jar Number

Non-Aged 1 Wk-Aged 2 Wk-Aged 3 Wk-Aged
Aluminum Residuals

Al Residual (log M)

Jar Number

3 Wk-Aged

2 Wk-Aged

1 Wk-Aged

Non-Aged
Experimental Setup (contd.)

1. Conduct jar tests, quiescent aging (1-3 wks)
2. Centrifuge solids in Princeton
   • Filter and save supernatant
3. Dry portion of bulk water, run on FTIR
4. Test for residual concentrations in supernatant at UT
What is ATR?
ATR-FTIR: How it works

1. Source
2. Interferometer
3. Sample
4. Detector

Interferogram → FFT → Spectrum

Polystyrene run as film

Wavenumbers (cm⁻¹)

% T

4000 3000 2000 1000 900
Sample absorbs 5 units of e
ATR-FTIR: How it works contd.