Use of Biotechnology for Air Pollution Control at Produced Water Evaporation Facilities

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Use of Biotechnology Colorado

- July 2014 Permit - 1\textsuperscript{st} time biotechnology has been proposed as an air pollution control technology in Colorado.

- Previously had to assume that 100\% of VOCs dissolved in the evaporation pond water ends up in the atmosphere.

- Our permit quantified mass of VOCs removed by metabolism at the facility.
Developed Predictive Model

- For each month it calculates:
  - mass removal by metabolism.
  - mass emitted to the atmosphere.

- For the covered bioreactor and uncovered evaporation ponds.

### Overall Mass Balance Summary

<table>
<thead>
<tr>
<th>Percentage</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.3%</td>
<td>of Methanol gets biodegraded in Primary Bioreactor.</td>
</tr>
<tr>
<td>59.6%</td>
<td>of Methanol gets biodegraded in Secondary Bioreactors (Evaporation Ponds).</td>
</tr>
<tr>
<td>14.1%</td>
<td>of Methanol gets discharged to the atmosphere.</td>
</tr>
<tr>
<td>100.0%</td>
<td><strong>Mass Balance</strong></td>
</tr>
<tr>
<td>86%</td>
<td>of Methanol will be biologically metabolized..</td>
</tr>
</tbody>
</table>
Successful Anaerobic Treatment Requires 10 Things

1. Right Microorganisms
2. Substrate (Food)
3. Water
4. Proper Temperature
5. Proper pH / Alkalinity
6. Macronutrients
7. Micronutrients
8. Control of Toxicity
9. Contact between Microbe and Substrate
10. Reaction Time
RNI Bacteria Populations

Total Eubacteria (EBAC)

Microbial Insights - CENSUS Method  DNA/RNA Extraction - ID gene sequences
Anaerobic Digestion

\[
\text{CH}_3\text{CO OH} = \text{Acetic Acid}
\]

Acidogens metabolize hydrocarbons faster than methanogens.
Sampling of Produced Water

- Sampled three evaporation facilities each quarter for one year.
- Elevated Methanol – Freeze protection
- BTEXH, methanol, GRO, DRO

### Evaluation of Produced Water

<table>
<thead>
<tr>
<th>Facility</th>
<th>Sample Date</th>
<th>Benzene (mg/l)</th>
<th>Ethylbenzene (mg/l)</th>
<th>Toluene (mg/l)</th>
<th>Xylene (mg/l)</th>
<th>Hexane (mg/l)</th>
<th>TVH 8260 (mg/l)</th>
<th>TEH-DRO (mg/l)</th>
<th>Methanol (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combined Averages</td>
<td>12</td>
<td>0.54</td>
<td>19</td>
<td>7</td>
<td>0.24</td>
<td>43</td>
<td>88</td>
<td>2619</td>
<td></td>
</tr>
</tbody>
</table>

*Methanol = 95% of Total VOCs*
Methanol Is Readily Biodegradable

- Simplest form of alcohol.
- Used as an antifreeze throughout the winter months.
- Miscible
- Henry’s Law Constant $4.55 \times 10^{-6}$ atm-m$^3$/mole
  - Benzene $5.55 \times 10^{-3}$ atm-m$^3$/mole
- Readily metabolized by acidogens and 11 known species of methanogens.
- VOC and a HAP
Determining the Rates of Metabolism
For Covered Bioreactor and Uncovered Evaporation Ponds
## Sampling Program

<table>
<thead>
<tr>
<th>Substance / Method</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkalinity, Total as CaCO₃, COD</td>
<td>SM2320B</td>
</tr>
<tr>
<td>Individual BTEX Compounds</td>
<td>SM 5210B-2011</td>
</tr>
<tr>
<td>Hexane</td>
<td>8260B</td>
</tr>
<tr>
<td>Methane</td>
<td>8260B RSK175</td>
</tr>
<tr>
<td>GRO</td>
<td>MOD</td>
</tr>
<tr>
<td>DRO</td>
<td>8015B</td>
</tr>
<tr>
<td>Methanol</td>
<td>8015B</td>
</tr>
<tr>
<td>HEM Oil and Grease</td>
<td>8015B</td>
</tr>
<tr>
<td>TDS</td>
<td>1664A</td>
</tr>
<tr>
<td>TSS</td>
<td>SM 2540C-2011</td>
</tr>
<tr>
<td>VSS</td>
<td>SM 2540C-2011</td>
</tr>
<tr>
<td>pH</td>
<td>SM 2540E-2011</td>
</tr>
<tr>
<td>VFAs (Microseeps Subcontract)</td>
<td></td>
</tr>
<tr>
<td>Ammonia</td>
<td>AM21G</td>
</tr>
<tr>
<td>Sulfate</td>
<td>SM 4500NH3 D-2011</td>
</tr>
<tr>
<td></td>
<td>EPA 300.0/SW846 9056</td>
</tr>
</tbody>
</table>
Methanol Removal By Metabolism

- 30 Day HRT
- Nutrient and Electron Acceptor Amendment Oct 22, 2013
- Methanol removal significantly increased
- Water Temp °C
- 20 Day HRT

Percent Removal

Degrees C

Pond Emissions
Calculating Methanol Emissions From Uncovered Ponds

Step 1:

\[(\text{mg/m}^2/\text{hr in March}) \times (\text{surface area of pond}) \times (\text{hrs in a month}) = \text{monthly emissions March} = 4.7 \text{ tons}\]

Step 2: Calculate total mass passing through the pond that month.
Conc in water \(\times\) total volume of water = total mass accepted into pond = 59.7 tons

Step 3: Convert emissions to a percent of the total
4.7 tons of emissions / 59.7 tons total = 7.9%

Step 4: Seasonal adjustment in emissions

\[(\text{lake evaporation for a specific month} / \text{lake evaporation for March}) \times \% \text{ emitted in March} = \% \text{ emissions for the specific month}\]
### Example Calculation Pond Emissions

#### Lake Evaporation for Roosevelt Utah

<table>
<thead>
<tr>
<th>Jan in</th>
<th>Feb in</th>
<th>March in</th>
<th>April in</th>
<th>May in</th>
<th>June in</th>
<th>July in</th>
<th>Aug in</th>
<th>Sept in</th>
<th>Oct in</th>
<th>Nov in</th>
<th>Dec in</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.65</td>
<td>0.95</td>
<td>2.17</td>
<td>3.6</td>
<td>5.43</td>
<td>5.6</td>
<td>6.17</td>
<td>5.63</td>
<td>3.97</td>
<td>2.71</td>
<td>1.41</td>
<td>0.79</td>
</tr>
</tbody>
</table>

#### Methanol Flux Estimates Assuming Variations are Roughly Proportional to Lake Evaporation Rates

<table>
<thead>
<tr>
<th>Jan tons</th>
<th>Feb tons</th>
<th>March tons</th>
<th>April tons</th>
<th>May tons</th>
<th>June tons</th>
<th>July tons</th>
<th>Aug tons</th>
<th>Sept tons</th>
<th>Oct tons</th>
<th>Nov tons</th>
<th>Dec tons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>2.1</td>
<td><strong>4.7</strong></td>
<td>7.9</td>
<td>11.9</td>
<td>12.2</td>
<td>13.5</td>
<td>12.3</td>
<td>8.7</td>
<td>5.9</td>
<td>3.1</td>
<td>1.7</td>
</tr>
</tbody>
</table>

#### Flux as a percent of the Measured March Field Measurements

| 30% | 44% | 100% | 166% | 250% | 258% | 284% | 259% | 183% | 125% | 65% | 36% |

March Pond Emissions = 7.9% percent of the total methanol mass accepted into ponds

August Pond Emissions = 7.9% \( \times \frac{5.63}{2.17} \) = 20.5 % of total mass accepted into the ponds.

Additional studies of season effects on pond emissions are planned by Utah State.
Putting It All Together

Bioreactor performance, modeled emissions for covered bioreactor, flux sampling of uncovered ponds
Annual Summary

@ 3000 bbls/day = 20 Day HRT

Emissions vs Metabolism

Received = 502 tpy of Methanol

Primary Bioreactor = 157 tpy = 31.2%

Secondary Reactors = 155 tpy = 31%

Emissions = 199.7 tons = 37.8%
<table>
<thead>
<tr>
<th>Constituents</th>
<th>RN Industries Average Facility Inlet Concentrations</th>
<th>Estimated Total Annual Mass in 3000 bbls/day</th>
<th>Overall Treatment Facility Efficiency</th>
<th>Overall Treatment System Mass Removal</th>
<th>Evaporation Pond Emissions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/L</td>
<td>tons/year</td>
<td>%</td>
<td>tons/year</td>
<td>tons/yr</td>
</tr>
<tr>
<td>GRO</td>
<td>42.50</td>
<td>8.2</td>
<td>34.2%</td>
<td>2.8</td>
<td>5.4</td>
</tr>
<tr>
<td>DRO</td>
<td>88.47</td>
<td>17.0</td>
<td>79.8%</td>
<td>13.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Benzene</td>
<td>12.17</td>
<td>2.3</td>
<td>0.0%</td>
<td>0.0</td>
<td>2.3</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.54</td>
<td>0.1</td>
<td>5.3%</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.83</td>
<td>3.6</td>
<td>8.7%</td>
<td>0.3</td>
<td>3.3</td>
</tr>
<tr>
<td>Xylene</td>
<td>6.82</td>
<td>1.3</td>
<td>7.0%</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td>Hexane</td>
<td>0.24</td>
<td>0.0</td>
<td>0.0%</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Methanol</td>
<td>2619</td>
<td>502.4</td>
<td>0.0%</td>
<td>0.0</td>
<td>502.4</td>
</tr>
<tr>
<td>Total VOCs</td>
<td>2750.0</td>
<td>527.5</td>
<td>16.3</td>
<td>511.2</td>
<td></td>
</tr>
<tr>
<td>Total HAPS</td>
<td>2657.6</td>
<td>509.8</td>
<td>0.4</td>
<td>509.4</td>
<td></td>
</tr>
</tbody>
</table>

Current system

System w/o nutshell and with biotechnology

Biotechnology removes 300 tons more VOCs / year.
Conclusions

Temperature of pond water is critical to the rate of metabolism.

In our case metabolism in the uncovered evaporation ponds was more effective than in the primary bioreactor.

BTEX, GRO, DRO metabolism was low. Only 8% of the GRO and 12% DRO mass received was removed by metabolism.

The performance varies so you need to quantify your metabolism and emissions monthly.

Amendments of select alternate electron acceptors and nutrients may increase performance without producing undesirable bi-products.
Quick Recap - Why It Worked?

It worked because methanol is

miscible,
readily metabolized, and
represented 95% of the dissolved VOCs.

It did not work well for BTEXH, GRO or DRO because of temp / contact time

Lessons learned:

Evaporation ponds were more effective – greater retention time.

Water temperature is the key to success.

15,000 to 20,000 mg/L salinity was not a problem.

Amendments of alternate electron acceptors nitrate, iron, sulfate or manganese may increase performance without producing metabolic byproducts at levels of regulatory concern. Be careful about H$_2$S production.
"I think you should be more explicit here in step two."
Plans For Improving Performance

Nitrate Amendment

• Electron acceptor (something to breath).

$$6\text{NO}_3^- + 6\text{H}^+ + C_6\text{H}_6 ----> 6\text{CO}_2(g) + 6\text{H}_2\text{O} + 3\text{N}_2(g)$$

• $150 of ammonium nitrate amended in fall. Removal rate for 20 day HRT jumped from 5% to 30%. Low cost big benefit.

• Inert nitrogen gas is the primary bi-product of metabolism.
Nitrogen Cycle – Electron Acceptor

- Nitrogen accepts electrons and becomes less positive
- (+5 → 0) Valence
- Nitrate = Something for anaerobic bacteria to breathe when O₂ is absent.
- Consume methanol, GRO, DRO (food)
- Produce inert gas.
- Pseudomonis, and other common bacterial species.
Other Potential Amendments / Improvements

**Ferric Iron (Electron Acceptor)**

\[
60H^+ + 30Fe(OH)_3 + C_6H_6 \rightarrow 6CO_2 + 30Fe^{2+} + 78H_2O
\]

**Sulfate (Electron Acceptor)**

\[
7.5H^+ + 3.75SO_4^{2-} + C_6H_6 \rightarrow 6CO_2(g) + 3.75H_2S + 0.5H_2O
\]

*Be careful to monitor for H_2S!*

**Manganese (Electron Acceptor)**

\[
30H^+ + 15MnO_2 + C_6H_6 \rightarrow 6CO_2 + 15Mn^{2+} + 18H_2O
\]

**Nutrients (ammonium, phosphorous)**

**Micro Nutrients**

(Nickel, Cobalt, Molybdenum, Calcium, Sulfide, Magnesium, Potassium, Zinc, others as needed).

**Heat retention strategies** (insulated covers, hot reservoir water, natural hot springs, deeper ponds)