Wet Air Oxidation Treatment of Spent Caustic in Ethylene Plants and Petroleum Refineries

SAWEA

Russell Forbess
Bryan Kumfer
Steven Olsen
Overview

- Description of the Zimpro® WAO process
- Spent Caustic Chemistry
- Autoclave and Full Scale Data
  - Ethylene Spent Caustic
  - Refinery Spent Caustic
- Conclusions
Description of Zimpro® Wet Air Oxidation
What is Wet Air Oxidation?

- Oxidation of Soluble or Suspended Components in an Aqueous Matrix

- Oxygen (Air) is the Oxidizing Species

- Oxidation Reactions Occur at Elevated Temperatures and Pressures

BASF, Port Arthur, Texas
Common Uses

- Destruction of Specific Constituents
- Pretreatment for Biological Polishing
- Gross Reduction in COD Loading

Repsol, Tarragona, Spain
Wet Air Oxidation For High Strength Industrial Wastewaters

Typical Industrial Wet Air Oxidation Feed Characteristics

Flow Range: 1 to 50 m³/h
COD Range: 10,000 to 100,000 mg/L
Temperature Range: 150 to 320°C
Pressure Range: 5 to 225 barg
Wet Air Oxidation – Typical Process Flow Diagram
Wet Air Oxidation

**Process Variables**

- Oxidation Temperature and Pressure
- Hydraulic Detention Time
- Oxidant – Typically Air or Oxygen
- Flow Configuration
- Oxidation Enhancer

Atofina, Rho Italy
Spent Caustic Chemistry
# Classification of Spent Caustics

<table>
<thead>
<tr>
<th>Type</th>
<th>Principle COD Source</th>
<th>Source</th>
<th>Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfidic</td>
<td>Sulfides and/or mercaptans</td>
<td>Ethylene or LPG</td>
<td>130°C / 7 barg to 200°C / 27.5 barg</td>
</tr>
<tr>
<td>Cresylic</td>
<td>Phenolic compounds and reduced sulfur</td>
<td>FCC Gasoline Washes</td>
<td>200°C / 27.5 barg to 260°C / 86 barg</td>
</tr>
<tr>
<td>Naphthenic</td>
<td>Naphthenic compounds and reduced sulfur</td>
<td>Kerosene, Diesel, and Jet Fuel</td>
<td>240°C / 55 barg to 260°C / 86 barg</td>
</tr>
</tbody>
</table>
Issues With Spent Caustic Produced in the Petrochemical Industry

- Odors caused by sulfides, mercaptans and volatile organics
- Potential inhibitory or toxic effects in biological treatment
- Hazards associated with toxicity
- High chemical oxygen demand
- Tendency to foam
- Corrosive

Spent Caustic Before and After WAO Treatment
Sulfidic Reactions During WAO of Spent Caustics

Sulfide - NaHS

\[ \text{NaHS} + \text{O}_2 + \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]
\[ \text{NaHS} + \text{O}_2 \rightarrow \tfrac{1}{2} \text{Na}_2\text{S}_2\text{O}_3 + \tfrac{1}{2} \text{H}_2\text{O} \]

Thiosulfate - Na$_2$S$_2$O$_3$

\[ \text{Na}_2\text{S}_2\text{O}_3 + \text{O}_2 + \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \]

Mercaptan - NaSR

\[ \text{NaSR} + \text{O}_2 \rightarrow \text{RSO}_3\text{-Na} \]
Organic Reactions During WAO of Spent Caustics

Cresylic Acids - C₆H₅O-Na

- C₆H₅O-Na + O₂ + NaOH → Na₂CO₃ + H₂O
- C₆H₅O-Na + O₂ + NaOH → Na₂CO₃ + CH₃COO-Na + H₂O

Naphthenic Acids - Na-C₁₂H₂₂O₂

- Na-C₁₂H₂₂O₂ + O₂ + NaOH → Na₂CO₃ + H₂O
- Na-C₁₂H₂₂O₂ + O₂ + NaOH → Na₂CO₃ + CH₃COO-Na + H₂O
Autoclave and Full Scale Results
Wet Air Oxidation of Various Spent Caustic Types

Autoclave and Full Scale Results

- Oxidation of Sulfidic Components
- Biotreatability of WAO Effluent
- Overall COD Destruction
Ethylene Spent Caustic
Wet Air Oxidation
Ethylene Spent Caustic – Sulfidic Components

<table>
<thead>
<tr>
<th>Oxidation Temperature, °C</th>
<th>Feed</th>
<th>110</th>
<th>125</th>
<th>150</th>
<th>200</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide (NaHS/Na2S as S)</td>
<td>13900</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;10</td>
<td>&lt;1</td>
<td>&lt;1</td>
</tr>
<tr>
<td>Thiosulfate (Na2S2O3 as S)</td>
<td>275</td>
<td>5,503</td>
<td>2,686</td>
<td>949</td>
<td>40</td>
<td>31</td>
</tr>
<tr>
<td>Sulfite (NaSO3 as S)</td>
<td>5</td>
<td>643</td>
<td>435</td>
<td>4</td>
<td>81</td>
<td>85</td>
</tr>
<tr>
<td>Sulfate (Na2SO4 as S)</td>
<td>200</td>
<td>3,940</td>
<td>7,740</td>
<td>11,200</td>
<td>12,500</td>
<td>11,100</td>
</tr>
</tbody>
</table>
Wet Air Oxidation
Ethylene Spent Caustic – Sulfidic / Organic COD

<table>
<thead>
<tr>
<th>Oxidation Temperature, °C</th>
<th>Feed</th>
<th>110</th>
<th>125</th>
<th>150</th>
<th>200</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Carbon, as C</td>
<td>648</td>
<td>747</td>
<td>708</td>
<td>710</td>
<td>641</td>
<td>537</td>
</tr>
<tr>
<td>Sulfidic COD, as O₂</td>
<td>28,085</td>
<td>7,184</td>
<td>3,567</td>
<td>1,185</td>
<td>90</td>
<td>80</td>
</tr>
<tr>
<td>Total COD, as O₂</td>
<td>29,800</td>
<td>10,900</td>
<td>8,040</td>
<td>3,260</td>
<td>1,830</td>
<td>1,410</td>
</tr>
</tbody>
</table>
### Full Scale WAO Case Studies
#### Ethylene Spent Caustic

<table>
<thead>
<tr>
<th></th>
<th>ConocoPhillips, Texas</th>
<th>BASF, Texas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feed</td>
<td>Effluent</td>
</tr>
<tr>
<td><strong>Temperature, °C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Residence Time, minutes</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Analysis</strong></td>
<td>Units</td>
<td></td>
</tr>
<tr>
<td><strong>COD</strong></td>
<td>mg/L</td>
<td>10,500</td>
</tr>
<tr>
<td><strong>Sulfide-S</strong></td>
<td>mg/L</td>
<td>4,031</td>
</tr>
<tr>
<td><strong>Thiosulfate-S</strong></td>
<td>mg/L</td>
<td>&lt;224</td>
</tr>
<tr>
<td><strong>Sulfite-S</strong></td>
<td>mg/L</td>
<td>&lt;64</td>
</tr>
<tr>
<td><strong>Sulfate-S</strong></td>
<td>mg/L</td>
<td>&lt;55</td>
</tr>
<tr>
<td><strong>Mercaptan—CH₃SH</strong></td>
<td>mg/L</td>
<td>---</td>
</tr>
<tr>
<td><strong>Methyl Mercaptan</strong></td>
<td>mg/L</td>
<td>---</td>
</tr>
<tr>
<td><strong>Ethyl Mercaptan</strong></td>
<td>mg/L</td>
<td>--</td>
</tr>
<tr>
<td><strong>Calculated Sulfidic COD</strong></td>
<td>mg/L</td>
<td>8,060</td>
</tr>
<tr>
<td><strong>% Sulfidic COD Destruction</strong></td>
<td>%</td>
<td>---</td>
</tr>
</tbody>
</table>
WAO Ethylene Spent Caustic Biodegradability

- Formosa, Texas
- Westlake P2, Louisianna
- Westlake P1, Louisianna
WAO Ethylene Spent Caustic

- Operation at 200°C
  - Sulfide < 1 mg/l as S
  - Mercaptan < 1 mg/l as Methyl / Ethyl
  - Thiosulfate < 100 mg/l as S

- Remaining Organic COD is Biodegradable
  - BOD to COD Ratio > 0.5
Refinery Spent Caustic
Wet Air Oxidation
Refinery Spent Caustic

- Operating Conditions Dependent on Mixture Composition
- Assure Biological Treatability

- Sulfidic (LPG, etc) - 200°C / 27.5 barg
  - Higher Mercaptan Content

- Cresylic – 200°C / 27.5 barg to 260°C / 86 barg
  - COD Reduction

- Napthenic – 240°C / 55 barg to 260°C / 85 barg
  - Prevent Foaming
Wet Air Oxidation
Organic Refinery Spent Caustic – 260°C

Chemical Oxygen Demand, mg/L O2

- CRESYLIC FEED
- CRESYLIC EFFLUENT
- NAPHTHENIC FEED
- NAPHTHENIC EFFLUENT

- Other Short Chain Organics
- Other Volatile Acids
- Acetic Acid

77%
79%
WAO of Napthenic Spent Caustic – Respirometer Trendplot

- 10 g/L Molasses Standard
- Untreated Spent Caustic
- 250 °C WAO Effluent
- 260 °C WAO Effluent

Oxygen Consumed, % of initial COD

Elapsed Time, hours
Full Scale WAO Study – Refinery Spent Caustic Mixture

Repsol-YPF, La Pampilla, Peru
## Repsol YPF Refinery
### Spent Caustic Composition

<table>
<thead>
<tr>
<th></th>
<th>Sulfidic spent caustics</th>
<th>Naphthenic spent caustics</th>
<th>Cresylic spent caustics</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD as g/l</td>
<td>7 - 110</td>
<td>50 – 100</td>
<td>165 - 230</td>
</tr>
<tr>
<td>TOC, g/l as C</td>
<td>0.02 – 4</td>
<td>11 – 25</td>
<td>23 - 60</td>
</tr>
<tr>
<td>DIC, g/l as C</td>
<td>0.15 – 5</td>
<td>0 – 0.16</td>
<td>0.33 – 0.35</td>
</tr>
<tr>
<td>Sulfide, g/l as S=</td>
<td>2 – 53</td>
<td>&lt; 0.001</td>
<td>0 - 64</td>
</tr>
<tr>
<td>Mercaptans, g/l as S=</td>
<td>0 – 28</td>
<td>&lt; 0.03</td>
<td>0 – 5.4</td>
</tr>
<tr>
<td>Thiosulfate, g/l as S=</td>
<td>0 – 3.7</td>
<td>0.07 – 0.13</td>
<td>10 - 12</td>
</tr>
<tr>
<td>Total Phenols, g/l</td>
<td>0.003 – 002</td>
<td>2 – 10</td>
<td>14 - 20</td>
</tr>
</tbody>
</table>
## Repsol YPF Refinery
### Zimpro® WAO Performance

<table>
<thead>
<tr>
<th></th>
<th>Destruction</th>
<th>Feed</th>
<th>Effluent (measured, after dilution)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD, mg/l as O₂</td>
<td>85%</td>
<td>73,000</td>
<td>6,300</td>
</tr>
<tr>
<td>TOC, mg/l as C</td>
<td>73%</td>
<td>15,000</td>
<td>2,400</td>
</tr>
<tr>
<td>Sodium, mg/l as Na</td>
<td>-</td>
<td>41,000</td>
<td>24,000</td>
</tr>
<tr>
<td>pH</td>
<td>-</td>
<td>13.2</td>
<td>8.9</td>
</tr>
<tr>
<td>Sulfide, mg/l as S⁻</td>
<td>&gt; 99.9</td>
<td>8,500</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Sulfite, mg/l as S</td>
<td>&gt; 99.9</td>
<td>100</td>
<td>&lt; 2</td>
</tr>
<tr>
<td>Mercaptans, mg/l as CH₃SH</td>
<td>&gt; 98.8</td>
<td>1,500</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Thiosulfate, mg/l as S₂O₃</td>
<td>&gt; 98.8</td>
<td>1,500</td>
<td>&lt; 30</td>
</tr>
<tr>
<td>Total phenols, mg/l as C₆H₆O</td>
<td>&gt; 99.6</td>
<td>6,500</td>
<td>36</td>
</tr>
<tr>
<td>Flow rate, m³/h</td>
<td>0.67</td>
<td>1.14</td>
<td></td>
</tr>
</tbody>
</table>
Repsol YPF Refinery  
Zimpro® WAO Performance

- **Biological Treatability**
  - Effluent BOD/COD Ratio: 0.58
  - Volatile Acid COD: 4,150 mg/L
    - 66% of Effluent COD

- **Sulfidic Components Non-Detectable**
  - Including Mercaptans
Conclusions

- Reasons For Treatment
  - Biotreatable Effluent
  - No Sulfide Odors
  - No $\text{H}_2\text{S}$ emissions
  - Minimize Downstream Corrosion
  - Eliminate Foaming Problems
Conclusions

- Ethylene Spent Caustic (Sulfidic)
  - Sulfide <1 mg/l as S
  - Mercaptans <1 mg/l
  - Thiosulfate <100 mg/l as S
Conclusions

- Refinery Spent Caustic (Higher Temperature for Organics)
  - Elimination of Sulfides and Mercaptans
  - High Conversion of Complex Organics to Short Chain Compounds
- Both Sulfidic and Organic COD Reduction