Wet Air Oxidation Pre-Treatment of Spent Caustic for Discharge to Biological Wastewater Treatment Allowing for Water Recovery and Reuse
Zimpro® wet air oxidation (WAO) is used to treat refinery spent caustic, resulting in an oxidized effluent that can be safely and easily polished using standard biological waste water treatment allowing for water recovery and re-use

The following presentation will discuss:

- Typical characteristics of refinery spent caustic
- Issues related to the treatment of refinery spent caustic
- Overview of the Zimpro® wet air oxidation (WAO) Process
- Test methods for evaluating spent caustic treatment effectiveness
- Case studies of three existing refinery WAO treatment systems
- A novel process currently in R&D for recovering fresh NaOH
# Classification of Spent Caustics

<table>
<thead>
<tr>
<th>Type</th>
<th>Source</th>
<th>Principle Contaminants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfidic</td>
<td>Ethylene or LPG</td>
<td>Sulfides and/or mercaptans</td>
</tr>
<tr>
<td>Cresylic</td>
<td>FCC Gasoline</td>
<td>Phenolic compounds and reduced sulfur</td>
</tr>
<tr>
<td>Naphthenic</td>
<td>Kerosene, Diesel, and Jet Fuel</td>
<td>Naphthenic compounds and reduced sulfur</td>
</tr>
</tbody>
</table>
# Refinery Spent Caustic
## Typical Characteristics

<p>| | |</p>
<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td><strong>Inorganic Sulfides as S %</strong></td>
<td>0 to 4</td>
</tr>
<tr>
<td><strong>Mercaptides %</strong></td>
<td>0 to 4</td>
</tr>
<tr>
<td><strong>Salts of Cresylic Acids %</strong></td>
<td>0 to 20</td>
</tr>
<tr>
<td><strong>Salts of Napthenic Acids %</strong></td>
<td>0 to 10</td>
</tr>
<tr>
<td><strong>NaOH %</strong></td>
<td>1 to 15</td>
</tr>
<tr>
<td><strong>COD mg/l</strong></td>
<td>50,000 to 400,000</td>
</tr>
<tr>
<td><strong>pH</strong></td>
<td>13 to 14</td>
</tr>
</tbody>
</table>
Refinery Spent Caustic Disposal Concerns

Typical Concerns with on-site disposal of spent caustic:

- **Naphthenic** spent caustics
  - High COD (50,000 to 150,000 mg/l)
  - Cause of serious foaming issues when agitated or aerated
  - Limited biodegradability

- **Cresylic** spent caustic
  - Extremely high COD (> 100,000 mg/l)
  - Cresylic compounds are derivatives of phenol
    - Limited biodegradability
    - Can cause operational issues with WWTP (primarily related to sludge settling)

- **Sulfidic** spent caustic
  - Release of potentially dangerous \( \text{H}_2\text{S} \) and Mercaptans
  - Extremely odororous
  - Can cause operational issues with WWTP (pH swings)
Zimpro® Wet Air Oxidation –
Typical Process Flow Diagram
Treatment objectives for Siemens WAO spent caustic treatment systems:

- Pre-treat the spent caustic and make it suitable for polishing by the facilities WWTP.
- Destroy sulfides and mercaptans
- Make refractory or toxic organics biodegradable
- Destroy foaming characteristics
Refinery Spent Caustic
Methods for Testing Biodegradability

Measuring the biodegradability of a high COD / high TDS wastewater

**Standard BOD$_5$ Test**
- Samples are small
- High dilutions are typically required – often leading to exaggerated error and the potential remove toxicity concerns
- Test is a batch system – single data point at end of test

**Continuous Flow Bench Scale Testing**
- Requires large sample amounts
- Requires significant resources
- Requires long operating schedule
Siemens uses closed cell respirometry to measure a high TDS samples ability to be degraded biologically.

Respirometry is based on the rate at which the biomass consumes dissolved oxygen. This rate is measured by monitoring the changes in gaseous oxygen concentration using volumetric techniques.

Siemens respirometry method is based on EPA Method OPPTS 835.3110
Respirometry uses closed cell metabolic rate monitoring to evaluate biological activity.

Respirometry allows:

- Testing of multiple samples simultaneously
- Testing of control samples to assure proper operation
- Monitoring of biological activity over time
Refinery Spent Caustic – Respirometry Testing Method

For high TDS spent caustic samples Siemens uses:

- Challenge Technology AER-208 FlowCell Respirometer
- Controlled temperature bath
- Biological seed acclimated for high TDS wastewaters
- 10 day run period
Respirometry COD Consumption Trend Plot

Example Trendplot

≥60% COD Uptake represents a biologically degradable sample
The following slides present data collected from three refineries using Zimpro® WAO technology to pre-treat their spent caustic:

- Refinery Case A – Spain
- Refinery Case B – China
- Refinery Case C – India
Mixed Sulfidic / Naphthenic Refinery Spent Caustic
Medium Temperature Commercial WAO Treatment System at a Spanish Refinery

60% or greater uptake after 240 hours represents a biodegradable material

Phthalic Acid Standard

200°C WAO Effluent

Brine After Springing With Acid to pH 3

Untreated Naphthenic Spent Caustic

Oxygen Uptake, % of COD

Elapsed Time, hours
Mixed Sulfidic / Cresylic Refinery Spent Caustic
High Temperature Commercial WAO Treatment System at a Chinese Refinery

60% or greater uptake after 240 hours represents a biodegradable material
Refinery Spent Caustic – Case C
Respirometry COD Consumption Trend Plot

Mixed Sulfidic / Napthenic Refinery Spent Caustic
High Temperature Commercial WAO Treatment System at an Indian Refinery

60% or greater uptake after 240 hours represents a biodegradable material

Oxygen Uptake, % of COD

Elapsed Time, hours

Run A Effluent
Run B Effluent
Run C Effluent
Run A Feed
Run B Feed
Run C Feed
Phthalic Acid Standard
Zimpro® wet air oxidation of refinery spent caustic will:

- Destroy Sulfides and Mercaptans
- Eliminate Noxious Odors and H$_2$S Emissions
- Destroy Toxic Constituents
- Destroy Refractory Organics
- Destroy Foaming Characteristics
- Break Apart Large Organic Constituents

Zimpro® wet air oxidation produces a biodegradable effluent suitable for polishing in typical activated sludge treatment systems.
Recovery of NaOH using ED

Purpose and Objective

- Recover NaOH from waste oxidized spent caustic
  - Re-use in caustic tower
  - Useful strength – target 10 wt%
- Cost effective
  - Product should cost less than commodity purchase price
- Eliminate acid neutralization
  - Use the ED process to pH neutralize the oxidized spent caustic
  - Eliminate acid costs
- Reduce TDS to downstream biological treatment

Source: www.purchasingdata.com
Integrated ED System in an Ethylene Refinery

Fresh Caustic → Caustic Tower → WAO

Spent Caustic → WAO

Recovered Caustic

Oxidized Spent Caustic → ED

Neutralized Oxidized Spent Caustic
Laboratory Test Work

Electrolyte Solution

Oxidized Spent Caustic

DI Water

Na⁺ (Neutralized)

Electrolyte Solution

OH⁻

NaOH Product

Oxidized Spent Caustic (Neutralized)

Electrolyte Solution

Electrolyte Solution

Cathode

Anode

Na⁺

H⁺

OH⁻

Na⁺

H⁺

OH⁻

Na⁺

H⁺

OH⁻

Na⁺

H⁺

OH⁻

Na⁺

H⁺

OH⁻

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H⁺

OH⁻
Other Key Laboratory ED Results

- Product acceptable for caustic tower
- Up to 20 wt% NaOH produced
- Power consumption less than chlor-alkali process
- No major obstacles encountered
- No apparent performance or efficiency decline after 320 hours of testing
- No fouling
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