A Lower-cost Approach to Treating Low-volume Refinery Spent Caustic Streams

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Electro-oxidation, also called electrochemical advanced oxidation, uses electricity to generate hydroxyl radicals to perform oxidation in wastewater treatment. A new commercially available electro-oxidation process—Zimpro® Electro-oxidation (ZEO)—is especially effective for treating the highly problematic spent caustic streams produced by sweetening operations in petroleum refineries and ethylene plants, particularly at volumes below the economically feasible threshold for existing established treatment technologies. The new electro-oxidation process overcomes the practical limitations of earlier technology by employing a robust, freestanding, substrate-less, electrically conductive electrode fabricated from synthetic diamonds. This allows the electrodes to handle high current densities while providing a long life in this difficult waste stream. It also allows for on-site treatment while avoiding the potential liability of handling hazardous spent caustic material and shipping it off-site. In addition to providing background on the technology, its applications and its predecessors, this paper presents data from a treatability study using the new Zimpro® electro-oxidation technology on a variety of refinery spent caustic streams. The spent caustic waste streams studied contained a mixture of organic and reduced-sulfur compounds. Following treatment, the odorous sulfides and mercaptans were consistently eliminated and the majority of the COD was removed, producing an effluent that allows final polishing in a biological wastewater treatment facility.
Keywords

Spent caustic, refinery wastewater, COD, chemical oxygen demand, oxidation, electro-oxidation, electrochemical oxidation, advanced oxidation processes, sulfides, mercaptans, naphthenic acid, phenol, cresylic acid, wet air oxidation, acid springing, deep neutralization

Introduction

Among wastewaters, the spent caustic streams produced as a result of sweetening operations in petroleum refineries and ethylene plants are in a class by themselves. They possess high chemical oxygen demand (COD)—in the range of 20 g/L–300 g/L—contain hazardous, inhibitory and/or biorefractory chemicals, not to mention very high dissolved solids with a salts mass fraction greater than 5% (>5 wt%). The most challenging constituents include highly odorous reduced-sulfur compounds, such as sulfides and mercaptans, as well as corrosive organic species, such as the sodium salts of naphthenic and cresylic acids.

Standard biological wastewater treatment technologies simply cannot effectively treat these compounds. This has forced refineries and petrochemical plants to consider and implement more advanced treatment technologies to pretreat their spent caustic streams. These treatment technologies generally fall into two categories: 1) oxidation and 2) physical separation, with oxidation being the primary candidate. Many traditional spent caustic treatment processes have proven to be unattractive due to difficult operation and high maintenance costs and/or the noxious products that require disposal. The best and most popular modern treatment technologies involve wet air oxidation (WAO), which produces a high quality biodegradable effluent. However, WAO technology can have a high capital cost that may not be economically feasible if the facility only produces a small amount of spent caustic.

Now there is a new, commercially available treatment process developed especially to treat spent caustic streams that are generated in volumes or concentrations that may be below the economically feasible threshold for WAO. The Zimpro® Electro-oxidation (ZEO) process uses electricity to directly produce hydroxyl radicals in the spent caustic to perform oxidation. While the electro-oxidation technology has been researched and tested for years, it has been largely unavailable to industry due to the lack of a commercially feasible electrode material that could demonstrate a viable, industrial-scale lifetime. ZEO uses electrically conductive, freestanding, substrate-less, synthetic diamond electrodes to reliably produce hydroxyl radicals over an effective industrial lifetime.

In addition to providing background on the ZEO technology, its applications and its predecessors, this paper presents data from a treatability study using the ZEO process on a variety of refinery spent caustic streams. The spent caustic streams studied contained a mixture of organic and reduced-sulfur compounds typical of refinery spent caustics used for sweetening petroleum products. Following treatment, the odorous sulfides and mercaptans were eliminated and the majority of the COD was removed, allowing final polishing of the effluent in a biological treatment facility.
Background

Spent caustic is a term applied to solutions of sodium hydroxide and water that have been used to sweeten hydrocarbon products in the petroleum and petrochemical industries. The typical sources of spent caustic are presented in Table 1. Caustic is very effective at removing sulfides and mercaptans from products such as ethylene, LPG or other light petroleum products. Removing the sour components from these products is important because they often become the raw materials for making more complex organics that may be generated using a precious metal catalyst or other sophisticated chemical processes—processes that are negatively affected by the presence of sulfides or mercaptans.

Table 1. Sources of Spent Caustic

<table>
<thead>
<tr>
<th>Type</th>
<th>Principle COD Source</th>
<th>Source</th>
<th>Primary Treatment Issues</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfidic</td>
<td>Sulfides and/or mercaptans</td>
<td>Ethylene or LPG scrubbers</td>
<td>Odor, high COD, HSE concerns</td>
</tr>
<tr>
<td>Cresylic</td>
<td>Phenolic compounds and reduced sulfur</td>
<td>Scrubbing of FCC gasoline washes</td>
<td>Very high COD, toxicity to microbes</td>
</tr>
<tr>
<td>Naphthenic</td>
<td>Naphthenic compounds and reduced sulfur</td>
<td>Scrubbing kerosene, diesel, and jet fuel</td>
<td>High COD, foaming, limited biodegradability</td>
</tr>
<tr>
<td>Chloridic</td>
<td>Low concentration of sulfides</td>
<td>Isomerization and FCC</td>
<td>Odor</td>
</tr>
</tbody>
</table>

The production of heavier products such as gasoline, diesel and kerosene may also generate spent caustic. Caustic solutions in these processes are used to remove corrosive acid oils from the heavy products. The acid oils are removed so they burn cleaner and are less corrosive to the engines or turbines burning these fuels. Crude oil with high TAN (total acid number) will require more cleaning and produce more spent caustic than low TAN crude oils.

The spent caustic produced from these sweetening processes can be very difficult to dispose of through conventional treatment processes (Suarez 1996). Sulfides and mercaptans are highly and offensively odorous and can be dangerous to operating personnel if released to the atmosphere. In the spent caustic stream, sulfides are present primarily as sodium bisulfide (NaH2S). However, once neutralized, the equilibrium shifts the bisulfide to hydrogen sulfide (H2S) and the hydrogen sulfide will quickly vaporize into the air. A similar effect happens when solutions containing mercaptans are neutralized. The acid oils absorbed in the spent caustic from treating heavier products include naphthenic and cresylic acids—high molecular weight organic acid compounds that are soluble in water at high pH. Cresylates are phenolic compounds and are essentially the same as cresols.
Naphthenic acids are a group of high boiling point organic acids that are also soluble in water at high pH. Cresylates and naphthenates exhibit their own difficulties when treated using standard biological treatment processes (Galil et al. 1988, Clemente et al. 2005). Neither of these families of chemicals are easily biodegraded. Additionally cresylates—even in small concentrations)—can cause operational problems with the biological treatment process, for example, sludge settling (Galil, 1998). Naphthenates, as well, can cause biological effluent toxicity and have significant foaming tendencies—even at low concentrations—that will quickly produce a great deal of foam when agitated and/or aerated (Ford, 1992). Another issue with treating acid oils is related to pH. When the caustic is neutralized so that it may be biologically treated, a portion of the acid oils will come out of solution and form a separate phase. Any additional change in pH can produce or “spring” additional free acid oil.

Compounding the previously mentioned difficulties in attempting to treat spent caustic with conventional wastewater treatment technology, both sulfidic and organic (naphthenic and cresylic) spent caustic streams have very high chemical oxygen demand (COD) values. The typical constituents contained in spent caustic that contribute to the high COD are presented in Table 2. Sulfidic spent caustic typically has a COD from 10,000 mg/L to 60,000 mg/L. Organic spent caustic COD can range from 50,000 mg/L to 250,000 mg/L, or even higher. While spent caustic is generally produced in small quantities (0.25 m³/h to 10 m³/h) the COD load, measured in kilograms, can often be much higher than the rest of a facility’s wastewater streams combined.

### Table 2. Spent Caustic Typical Constituents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>1-5 wt%</td>
</tr>
<tr>
<td>Carbonates</td>
<td>1-5 wt%</td>
</tr>
<tr>
<td>Sulfides</td>
<td>0.5-5 wt%</td>
</tr>
<tr>
<td>Mercaptans</td>
<td>0.1-1 wt%</td>
</tr>
<tr>
<td>Total Phenols</td>
<td>0-3 wt%</td>
</tr>
<tr>
<td>Naphthenics</td>
<td>0-5 wt%</td>
</tr>
<tr>
<td>Chemical Oxygen Demand (COD)</td>
<td>10-250 g/L</td>
</tr>
</tbody>
</table>
Overview of Spent Caustic Disposal and Treatment Methods

Traditional disposal options have included both off-site disposal and on-site disposal options. Off-site disposal can be expensive and involve liability as spent caustic itself is considered a hazardous waste. On-site spent caustic treatment options generally fall into two categories: 1) oxidation technologies and 2) physical separation. The oxidation process converts sulfides to harmless sulfate salts and mercaptans to sulfonic acids. Both sulfates and sulfonic acids are not odorous and do not pose Health, Safety and Environmental (HSE) concerns. Oxidation also breaks apart the organic acid molecules essentially converting them to either carbon dioxide and water or small molecular weight, easily biodegradable organic acids. Oxidation technologies include chemical or advanced oxidation, incineration, direct discharge to an on-site wastewater treatment plant (WWTP), wet air oxidation (WAO), and now electro-oxidation. Physical separation is primarily associated with acid springing or stripping, in which pH adjustment is used to separate the contaminants of concern from the bulk of the aqueous phase. When considering spent caustic treatment options, both wet air oxidation and electro-oxidation have distinct advantages over other on-site treatment methods, with the deciding factor between the two being the amount of spent caustic to be treated.

**Acid springing** is probably one of the oldest on-site treatment methods used in refineries to dispose of spent caustic. Acid springing works by adding a strong acid (e.g., sulfuric acid) to the spent caustic until the pH is around 3. At this low pH, the acid oil tends to dissociate from the aqueous phase to form a separate floating "oil" layer. The acid oils will float and be skimmed off and collected for off-site disposal or blending into low-grade products. At low pH, the sulfides and mercaptans will tend to gas-off from the low pH brine. While this treatment method does remove a significant amount of COD, several issues remain. At low pH, the wet H₂S off-gas is extremely corrosive, resulting in high maintenance, odor and HSE concerns. Such gases need to be disposed of in a flare, thermal oxidizer or some form of sulfur recovery unit (SRU). In addition, since almost all water-based chemistry is subject to equilibriums, the acid springing does not complete the treatment process, but instead only reduces the amount of sulfidic and organic components in the aqueous brine effluent. Sulfidic, cresylic and naphthenic compounds will still be present in the acidified brine after springing. These constituents remain difficult to degrade biologically and pose significant operating challenges to the WWTP, including odor and foaming in the aeration basin.

**Direct discharge** of spent caustic into a biological WWTP creates issues during treatment. Facilities using this method for disposal need to have a very large WWTP with only a small amount of spent caustic, providing for significant dilution. Even in such cases, the operation of the WWTP needs to be closely monitored to prevent odors, corrosion and other negative effects to the WWTP. Most commonly the risks associated with direct discharge to a WWTP—H₂S release, toxicity, oil springing, strong odor and foaming—are considered too high to warrant this practice.
**Chemical advanced oxidation** is a technology that is widely used and commonly found in WWTPs. Advanced oxidation typically uses hydrogen peroxide with a catalyst such as Fe+ (known as Fenton’s Reagent), however, the low pH required springs acid oils and liberates the sulfides and mercaptans. This results in the same concerns associated with acid springing. Additionally, the process raises safety concerns related to peroxide potentially coming into contact with undissolved oil. Ozone or chlorine can also be used to perform the oxidation and can be used at the high pH naturally associated with spent caustic. Naturally, the more oxidant used, the better the results. Typically, though, the amount used can quickly make this process economically unattractive—even when only a small amount of spent caustic needs to be treated. Safety is also a significant concern related to storing large amounts of strong oxidizers inside a refinery.

**Incineration** can also be effective for disposing of spent caustic, however this option tends to require a significant amount of fuel because the water-based waste does not have enough fuel value to allow the incineration process to operate ‘auto-thermally’ or self-sustaining. In addition, the incinerator needs to be specially designed to handle the high concentration of salt and will require frequent replacement of refractory.

**Wet air oxidation** uses air (oxygen) under elevated temperature and pressure to perform oxidation in the aqueous phase. These reactions oxidize reduced sulfur species to forms such as Na₂SO₄. Complex organic compounds are oxidized to carbon dioxide and simple short-chain organic compounds that are biodegradable (Maugans, 2002). Following pretreatment with WAO, the oxidized spent caustic can be treated in a conventional on-site WWTP. The temperature at which the WAO operates determines its oxidation potential.

- **Low Temperature WAO (110°C–150°C at 2 bar–10 bar):** Best used to convert sulfide to thiosulfate, but does not destroy organics. Nor does it have the oxidation potential to achieve complete sulfide oxidation: typically 2 mg/L–10 mg/L sulfide and mercaptans remain in effluent. A substantial amount of thiosulfate in effluent will require special attention in both design and operation of the downstream WWTP.

- **Medium Temperature WAO (200°C–220°C at 20 bar–45 bar):** This process has the oxidation potential to completely destroy sulfides, thiosulfate and mercaptans, with partial oxidation of organics and acid oil. The effluent is biodegradable, with phenols destroyed and very little naphthenic acid remaining.

- **High Temperature WAO (240°C–260°C at 45 bar–100 bar):** Completely destroys sulfides, thiosulfate and mercaptans. Oxidizes the majority of organics to low molecular weight carboxylic compounds that are highly biodegradable. Completely destroys phenols and naphthenic acids. The biodegradable effluent is safe for polishing in an on-site WWTP.
Zimpro® Electro-oxidation (ZEO) generates hydroxyl radicals directly in the spent caustic using electricity. Similar to other oxidation technologies, it completely destroys sulfides, thiosulfate and mercaptans, and the process also will oxidize the organic compounds. The resulting effluent is suitable for polishing in a standard WWTP or can potentially achieve enough oxidation to allow direct discharge into a sea or ocean. The degree of COD reduction corresponds directly to the current density and the amount of time the ZEO system is operated. Operating expenses (mainly electricity) are stoichiometrically related to the amount of COD destroyed.

The hydroxyl radicals (oxidant) are produced by splitting water into an OH radical and an H+ ion, using electricity and a special electrode. Mineralization of the spent caustic is possible. However, the efficiency of the process begins to decrease—though not rapidly—at COD <10,000 mg/L. Compared to WAO, ZEO is practical for small COD loads. As the amount of COD increases so do the number of oxidation reactors required and the amount of electricity used. Higher COD destruction loads can economically justify the capital cost of modular expansion with much lower operating cost than other AOPs.

See Table 3 for a summary of on-site spent caustic treatment options and Table 4 for an operational comparison of treatment processes.
### Table 3. Spent Caustic Treatment – On-site Options

<table>
<thead>
<tr>
<th>Technology</th>
<th>Eliminates Odor</th>
<th>Reduces COD</th>
<th>Destroys Acid Oils</th>
<th>Produces Biodegradable Effluent</th>
<th>Produces Byproducts Requiring Disposal</th>
<th>Capital Cost</th>
<th>Operating Cost</th>
<th>Maintenance Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid Springing</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>Yes</td>
<td>Medium</td>
<td>Medium</td>
<td>Medium</td>
</tr>
<tr>
<td>Chemical Advanced Oxidation</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes / No</td>
<td>Low</td>
<td>Very High</td>
<td>Medium</td>
</tr>
<tr>
<td>Low Temp WAO</td>
<td>Mostly</td>
<td>Yes</td>
<td>No</td>
<td>Dependent upon Load &amp; WWTP</td>
<td>No</td>
<td>Medium /High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Medium Temp WAO</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Medium /High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>High Temp WAO</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>High</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>ZEO</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
<td>Medium</td>
<td>Medium</td>
<td>Low</td>
</tr>
</tbody>
</table>
Table 4. Operational Comparison of Treatment Processes

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Medium / High Temp WAO</th>
<th>ZEO</th>
<th>Advanced Oxidation</th>
<th>Acid Springing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfide</td>
<td>&lt;1 mg/L</td>
<td>&lt;1 mg/L (no odor)</td>
<td>&lt;1 mg/L (no odor)</td>
<td>Up to 2,000 mg/L</td>
</tr>
<tr>
<td>Mercaptan</td>
<td>&lt;1 mg/L</td>
<td>&lt;1 mg/L (no odor)</td>
<td>&lt;1 mg/L (no odor)</td>
<td>Up to 2,000 mg/L</td>
</tr>
<tr>
<td>Foaming</td>
<td>Eliminate / Reduce</td>
<td>Eliminate / Reduce</td>
<td>Eliminate / Reduce</td>
<td>No effect</td>
</tr>
<tr>
<td>COD Reduction</td>
<td>&gt;99+% Sulfidic</td>
<td>Near complete; Most efficiently operated with COD &gt;10,000 mg/L</td>
<td>&gt;99+% Sulfidic</td>
<td>&gt;10,000 mg/L COD plus phenols remain in effluent</td>
</tr>
<tr>
<td>Ideal Capacity</td>
<td>&gt;20 kg/h COD Uptake</td>
<td>&lt;20 kg/h COD Uptake</td>
<td>&lt;10 kg/h COD Uptake</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Ideal COD Uptake</td>
<td>&gt;10,000 mg/L uptake</td>
<td>&gt;250 mg/L</td>
<td>&gt;250 mg/L</td>
<td>Not applicable</td>
</tr>
<tr>
<td>Destination</td>
<td>Effluent Treatment Plant</td>
<td>Effluent Treatment Plant, Outfall, Crystallizer</td>
<td>Effluent Treatment Plant</td>
<td>Effluent – ETP Acid oils – off-site or blending Off-gas – SRU</td>
</tr>
<tr>
<td>Cost</td>
<td>Higher CapEx Lower OpEx</td>
<td>Mid CapEx Mid OpEx</td>
<td>Low CapEx Very High OpEx</td>
<td>Mid CapEx High OpEx</td>
</tr>
</tbody>
</table>
Zimpro® Electro-oxidation – How It Works

By the creation of hydroxyl radicals (-OH), advanced oxidation processes have the ability to mineralize recalcitrant organic and inorganic contaminants in toxic and biocidal wastewater streams that are difficult to treat by other means. Most practical AOPs employ a strong oxidizing reagent such as hydrogen peroxide or hypochlorite. But because electrochemical-based AOPs do not require the purchase, storage and handling of such reactive reagents, they are attractive and also are effective even on relatively small-scale effluent streams.

Although the technology has shown positive results, electrochemical-based AOPs have been largely unavailable and thus far ineffective because they lacked a commercially feasible electrode capable of withstanding the harsh environment of spent caustic electrochemical oxidation. Diamond has an inert chemical surface that resists fouling and is not damaged by the electrolysis of water. And though electrochemical oxidation electrodes based on boron doped diamond (BDD) had been researched for more than 20 years, it is only recently that practical BDD materials have emerged with the oxidation capacity, corrosion resistance and lifetime required for cost-effective industrial scale electrochemical AOPs.

The Zimpro® Electro-oxidation (ZEO) process incorporates this latest BDD electrode technology (see Figure 1). Electrochemical AOPs use DC power to generate -OH radicals directly from the water in solution. Highly reactive and very short-lived, the hydroxyl ions mineralize dissolved organic pollutants in water. With ohmic losses minimized, the specific energy consumption of BDD electrochemical AOPs is around ~75 kWh / Kg-1 COD.

Figure 1. Zimpro® Electro-oxidation - Simplified Flow Diagram
BDD is not a typical electrode material and research by material scientists, chemists, physicists and engineers has been required to harness its exceptional properties. BDD is produced using a form of chemical vapor deposition (CVD) in which wafers of polycrystalline diamond are grown outside the normal high temperature and pressure region of the phase diagram for diamond. The extreme over potential at both the anode and the cathode surface required the development of a grade of bulk free-standing—not attached to a substrate—BDD, that is robust enough to survive the extreme electrochemical conditions. To fully exploit these robust BDD materials, an electrochemical cell of stacked BDD electrodes has been developed. These new BDD electrodes have been incorporated into a non-conductive containment housing resulting in the full-scale electrochemical AOP reactor.

The standard ZEO configuration (Figure 2) is modular, consisting of six reactor modules. Up to another six reactor modules can be added to accommodate higher COD loads. It is conceivable that a refinery site needing to discharge into the ocean—or having few or no utilities available other than electricity—could possibly justify larger COD uptake loads and the capital expense for a 12-reactor module ZEO system.

**Figure 2. Zimpro® Electro-oxidation – Conceptual Commercial System**
Study Results: Treatability of Spent Caustic Streams by a Zimpro® Electro-oxidation Pilot System

To prove the effectiveness of the Zimpro® Electro-oxidation technology, Siemens conducted a Treatability Study on spent caustic samples using a ZEO pilot system at our Rothschild, Wisconsin, site. The Treatability Study consisted of:

1. Sulfidic Only
2. Mixed Organic and Sulfidic
3. Organic Only

1. **Sulfidic Only**: The treatment goal was to eliminate odor by reducing sulfides and mercaptans to non-detectable concentrations.

   **Results (Figure 3)**: The test was performed to evaluate the oxidation of a sulfidic spent caustic that contained sulfides and mercaptans with very little organic compound content. The ZEO treatment process reduced the sulfides and mercaptans to non-detectable concentrations. There was a slight increase in thiosulfate as the oxidation of sulfides progressed, but it was not significant. In bulk oxidation processes like AOP or WAO sulfide normally has a reaction path that leads to thiosulfate and then to the fully oxidized sulfate form. In order to treat sulfides and mercaptans to low concentrations in a sulfidic spent caustic, nearly complete COD removal would be required.

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**Zimpro® Electro-oxidation - Advantages**

- Ideal for smaller COD Loads
- Produces an effluent with no noxious odors
- Uses electricity to treat wastewater (~75 kW / kg COD)
  - Operates at low pressure and temperatures (<5 bar & <60°C)
  - No pH limitations, but needs dissolved salts for conductivity (salt can be added if dissolved salts are not sufficient)
  - Price and operating expense proportional to kg/h of COD destroyed

**Conceptual Design**

- Modular system (capacity can be added)
- Modular system consisting of
  - Electric / Reactor House
  - Process Skid
  - Off-gas Skid
2. **Mixed Organic and Sulfidic**: The goal was to confirm that complete sulfides treatment could be accomplished without complete COD removal.

**Results (Figure 4):** The test used a mixture of organic spent caustic with sodium sulfide added. The ZEO treatment reduced the sulfide concentration to a non-detectable level much more quickly than it affected the total organic carbon (TOC) concentration. A complete oxidation of sulfides in a mixed spent caustic can be accomplished without having to completely oxidize all of the COD in the spent caustic.
3. **Organic Only**: The goal of this test was to determine the effectiveness of ZEO treatment at destroying both COD and TOC in the sample. The concentration of reduced sulfur compounds was low in this untreated organic spent caustic.

**Results (Figures 5-6)**: The ZEO treatment reduced the COD level of the spent caustic to very low concentrations of <100 mg/L and the TOC level to <20 mg/L. However, it should be noted that there is a decrease in efficiency of the treatment process when the COD is lower than 10,000 mg/L. The most efficient treatment range is from high COD (30,000 mg/L – 100,000 mg/L) to an effluent concentration of around 10,000 mg/L, which could then be polished in a conventional biological treatment facility.

The percent reduction of naphthenic acids and total phenols during testing was proportional to the amount of COD reduction achieved over the same time period.

**Figure 5. Treatability Study Results – Bulk COD/TOC Destruction**

![Graph showing treatment of refinery spent caustic](image)

**Figure 6. Treatability Study Results – COD Reduction with TOC, Phenols, Naphthenics Destruction**

![Graph showing COD reduction](image)
Conclusion: ZEO – Right-sized for Low COD Load Spent Caustic Streams

Testing on spent caustic and operation of smaller industrial applications have proven that the Zimpro® Electro-oxidation system can significantly reduce or completely eliminate chemical oxygen demand in a variety of spent caustic streams. The technology also eliminates odors and HSE concerns stemming from the presence of sulfides and mercaptans in the streams, as well as removing toxic compounds from effluent destined for an on-site WWTP.

ZEO technology fills a distinct niche need—it is ideally suited for treating lower flow rate (low COD load) spent caustic waste streams. Many refineries generate relatively inexpensive power at their own site. This helps the ZEO process achieve lower operational costs than AOPs dependent on the costly purchase, storage and handling of large quantities of oxidizers. When ZEO is used for low COD loads, its capital costs are lower than those of the typical wet air oxidation system intended for larger volumes of spent caustic. Yet, because of the ZEO system’s modular concept and configuration, it can be expanded as needed or as a site’s demands might dictate. Testing shows that it is possible to use the ZEO process to produce an effluent with low COD and TOC that could be directly discharged instead of having to be treated (polished) in the WWTP. This is advantageous in situations where water recovery is being implemented at the WWTP. Not having to put the spent caustic in the WWTP eliminates a significant amount of salt that would need to be removed by the recovery/reuse system.
References


Young, J.; Cowan, R. Respirometry for Environmental Science and Engineering, SJ Enterprises: Springdale, Arkansas, 2004; Chapter 1.