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Wet Air Oxidation of Refinery Spent Caustic: A Refinery Case Study

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Tania Mara S. Carlos, Refinaria de Petroleos de Manguinhos,
Rio de Janeiro, Brazil; and
Clayton B. Maugans, USFilter, Zimpro Products,
Rothschild, WI, USA

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**Tania Mara S. Carlos
Refinaria de Petroleos de Manguinhos
Rio de Janeiro, Brazil**

**Clayton B. Maugans
USFilter, Zimpro Products
Rothschild, WI USA**

Abstract

In 1995, a wet air oxidation (WAO) system was put into operation for treatment of refinery spent caustic from gasoline sweetening, gasoline and LPG prewashing and from gasoline and LPG mercaptans extraction at the Refinaria de Petroleos de Manguinhos, S.A. (RPDM) in Rio de Janeiro. RPDM is a producer of liquid fuels and is located near residential property within Rio de Janeiro. Prior to installing a WAO system, the refinery was dependent on off-site disposal of their spent caustic. In considering on-site treatment, there was great concern for odors since the refinery was in a populated area. The refinery concluded that wet air oxidation was the best choice for their scenario, allowing for on-site treatment without the production of odorous off-gas.

After treatment by WAO, the oxidized spent caustic is sent to the refinery's biological treatment system for final treatment. System performance includes complete removal of sulfides, mercaptans, and thiosulfates as well as significant reductions in phenols and overall chemical oxygen demand (COD). The oxidized spent caustic is polished in the on-site biological treatment facility before discharge.

Refinery Introduction and Background

The use of aqueous caustic washing in order to improve the quality of the product and to aid in the refining process is common. The caustic washings are done to remove sulfidic and acidic components from the relevant hydrocarbons stream. The aqueous spent caustic solution from these treatments is laden with various contaminants including sulfides, mercaptans, naphthenates and phenols (cresylates), as well as emulsified hydrocarbons. This stream is hazardous and must be treated before discharge. The odorous and reactive nature of the spent caustic precludes the use of biological treatment as the primary means of treatment, even with reasonable dilution.

A technology gaining popularity in the refining industry for treating this harsh waste stream is WAO. WAO detoxifies the spent caustic by oxidizing the sulfides and mercaptans to sulfate and breaking down the toxic naphthenics and cresylics. RPDM is one of the first refineries to use WAO for the treatment of both sulfidic and organic contaminants in refinery spent caustic. This paper describes the 5 year old system and its operation.

The Refinery

Refinaria de Petroleos de Manguinhos S. A. (RPDM) is a relatively small refinery located in the suburbs of Rio de Janeiro, Brazil. The facility is 45 years old and is a sweet crude refinery. As shown in Figure 1, the RPDM spent caustic comes from gasoline sweetening, gasoline and LPG prewashing, and from gasoline and LPG mercaptans extraction.

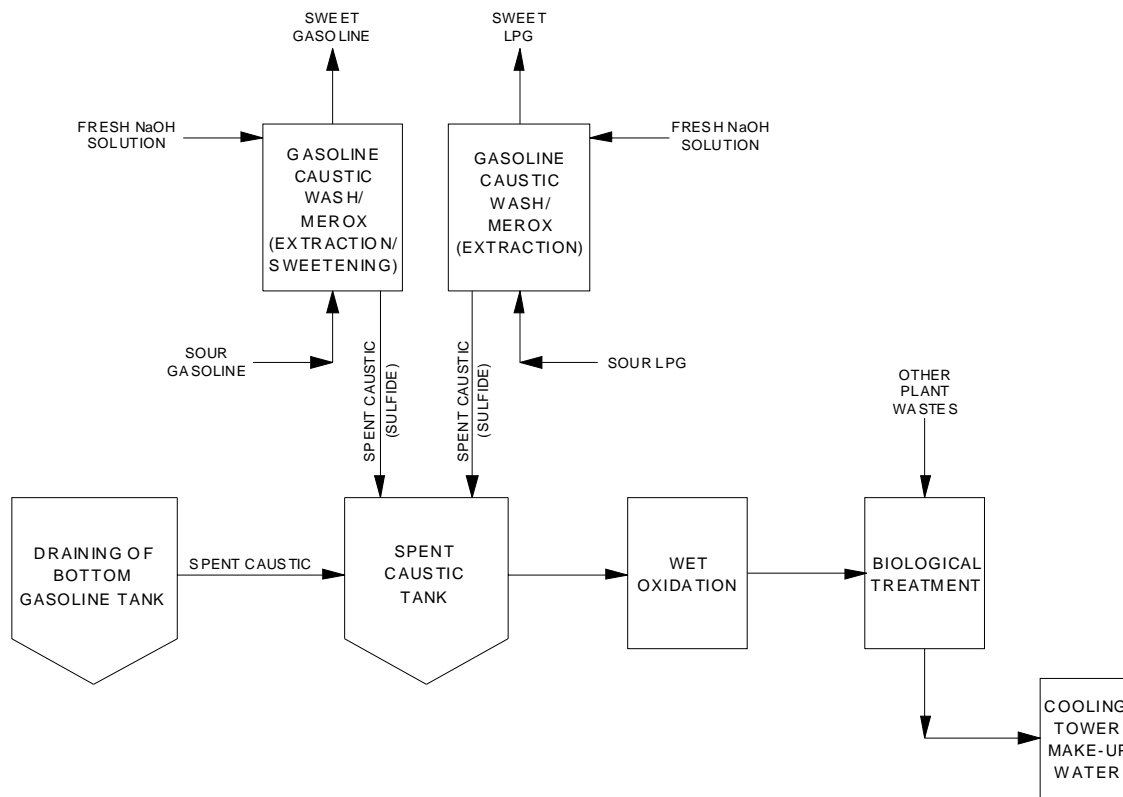


Figure 1. RPDM Spent Caustic Sources

Treatment Selection

In 1995 the refinery installed a WAO unit for the treatment of the spent caustic. WAO was chosen to detoxify the spent caustic prior to treatment in the existing biological treatment facilities. The technologies that were considered for the treatment of the spent caustic included partial oxidation at low temperature/pressure and high temperature/pressure WAO. The overall economic and performance advantages favored high temperature WAO. WAO is commonly used for treatment of sulfidic spent caustic in the ethylene industry¹⁻⁵, but at the time of implementation, no other refinery was employing WAO for cresylic and naphthenic acid salts destruction⁶⁻⁸. While the process is similar to ethylene spent caustic applications, higher temperatures are required to meet treatment objectives for refinery spent caustics containing cresylic and naphthenic compounds, as well as to control foaming in the reactor.

Prior Spent Caustic Disposal

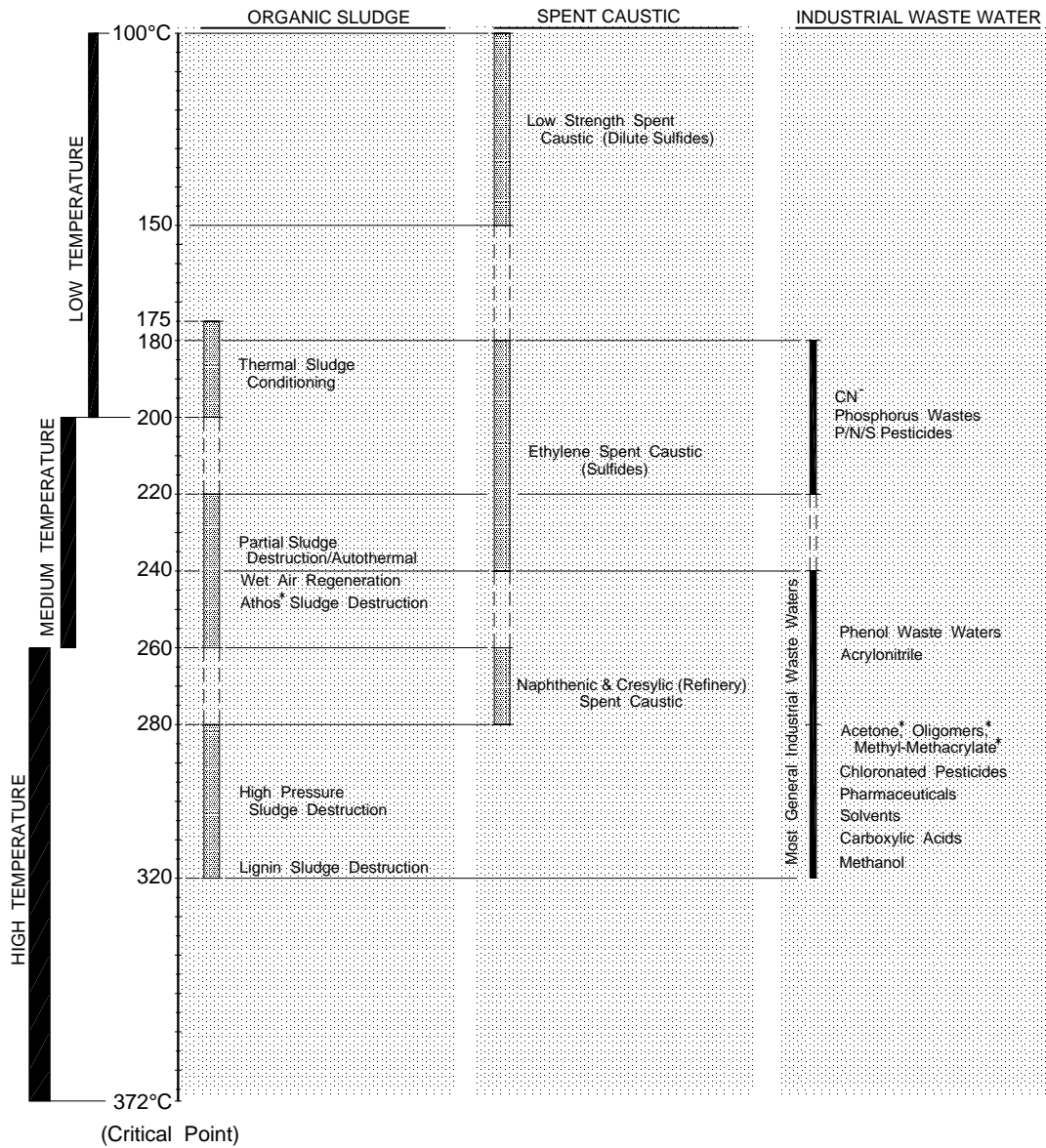
Prior to the installation of the WAO unit, the spent caustic was stored on-site and periodically trucked to a nearby Petrobras refinery for disposal by incineration. However, rising waste disposal costs and the close proximity of residencies caused by urban encroachment from the surrounding community became a growing concern. Odors from the stored spent caustic were becoming a concern upon the encroaching urbanization. To eliminate these concerns on-site treatment of the spent caustic was considered the best option.

Wet Air Oxidation Technology Background*WAO: General Background*

Wet air oxidation (WAO) is the process of oxidizing organic matter in the presence of liquid water. Theoretically, any substance that is capable of burning can be wet oxidized in water. WAO is typically employed as a waste treatment technology when the waste is non-conductive to incineration or biological treatment. It is an ideal process for pretreatment of wastes that are problematic to conventional biological facilities. The WAO process is uniquely suited to the oxidation of concentrated waste liquors, slurries, and sludge's where the oxygen demanding organic matter is only a few percent of the predominantly water stream⁹. For perspective, a general summary showing the traditional applications of this technology can be seen in Figure 2.

WET OXIDATION WASTE TREATMENT SPECTRUM

(A sampling of typical non-catalytic Zimpro Wet Oxidation applications)



* = Catalytic

Figure 2. Wet Air Oxidation Typical Application Spectrum

General WAO Reactions and Chemistry

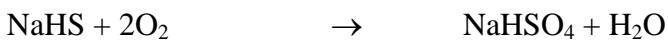
While air (oxygen) is bubbled through the reactor to provide an economical supply of oxidant, WAO is a liquid phase process and should not be confused with submerged combustion or any of the molten metal/molten salt processes. Oxidation reactions take place in the aqueous environment where the water behaves much like a catalyst and is an integral part of the reaction. It is theorized that the chemistry of WAO involves free radical formation with the oxygen and/or water derived radicals attacking the organic compounds and encouraging the formation of organic radicals¹⁰⁻¹¹.

A noteworthy characteristic of WAO chemistry is the formation of carboxylic acids and other partially oxidized short chain organics, in addition to the primary end-products, CO₂ and H₂O. The yield of these compounds varies greatly depending on system design, but typically 5-25% of the TOC from the feed remains as by-products, predominantly acetic acid. Carboxylic acids such as acetic acid are readily degradable in conventional biological treatment facilities. Organic forms of the elements: nitrogen, phosphorous, sulfur, and chlorine which enter the reactor bonded to organic molecules are reacted to NH₃, PO₄³⁻, SO₄²⁻, and Cl⁻ respectively.

The chemistry of WAO has some advantageous properties with regards to the off-gas produced. The off-gas from a WAO reaction has negligible NO_x, and SO_x; and negligible particulates. Volatile Organic Compounds (VOCs), such as aldehydes, ketones, and alcohols may be in the off gas depending on the composition of the original waste.

RPDM WAO System

In this application, WAO is a pretreatment technology, and at the refinery the oxidized effluent is routed to the pre-existing biological treatment facilities before discharge to the environment. A summary of the reactions occurring in the reactor can be expressed as:



where R' is typically CH₃.

A key point which is illustrated in this reaction summary, is that as oxygen is reacted, acids are produced. This is an important consideration as NaOH depletion can lead to acidic conditions, resulting in slower reactions and corrosion in the reactor. In the RPDM reactor, the COD loading is high enough that additional caustic is added to the system to prevent acidic conditions.

The reactor achieves a high COD removal as well as detoxification; with the effluent consisting mostly of sodium sulfate and acetic acid (sodium acetate), which are benign compounds to biological treatment facilities.

Process Description

The reaction conditions of the RPDM wastewater WAO facility are now typical for refinery spent caustic systems containing cresylic and naphthenic salts, at 260°C (500°F), 88 bar (1270 psig), and a 1 hour hydraulic detention time. The flow diagram for the RPDM WAO unit is shown in Figure 3 and a photograph of the unit is shown in Figure 4.

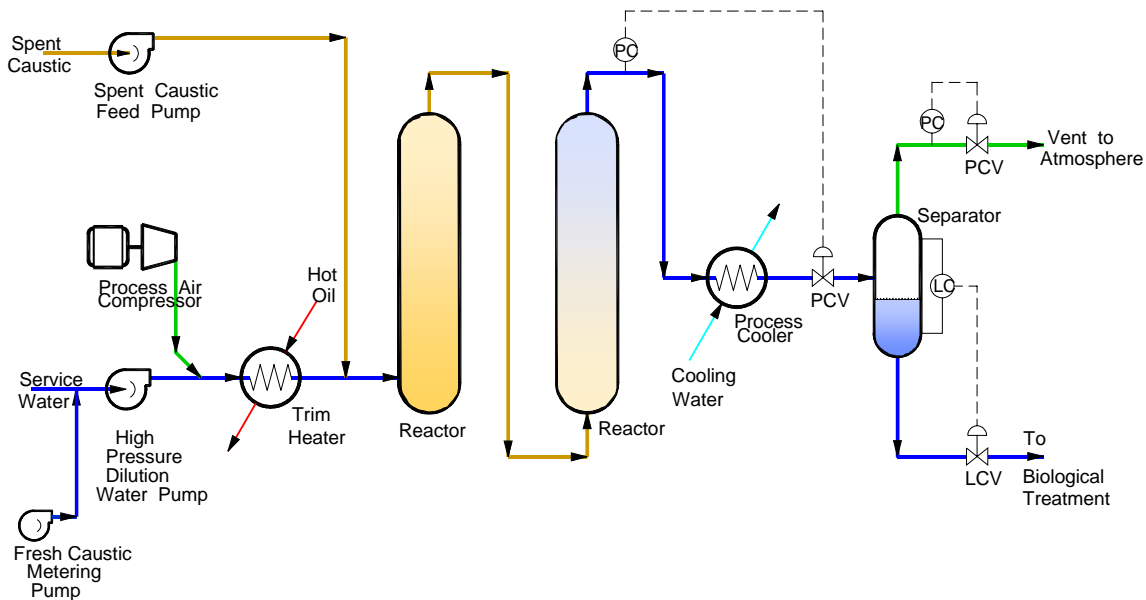


Figure 3. RPDM WAO Flow Diagram



Figure 4. RPDM WAO System

The highly concentrated nature of this spent caustic stream called for the addition of dilution water at a 3:1 ratio. This dilution is performed in order to maintain a controllable exotherm in the reactor. The dilution water is preheated, along with the pressurized air, in a hot oil heat exchanger. The cold spent caustic is then injected directly into the bubble column reactor where the hot inlet water, coupled with the reactor heat from the exothermic reaction, raise the temperature high enough for reaction to commence. The exothermic nature of the reaction causes an increase in reaction temperature as the reactants rise through the vertical bubble reactor.

The operating conditions and flowrates are seen in Table 1.

Table 1. Design conditions of RPDM Spent Caustic Oxidation System.

Spent Caustic Feed Rate	0.20 m ³ /hr (0.88 gpm)
Dilution Feed Water	0.40 m ³ /hr (1.76 gpm)
Reactor Temperature	260°C (500°F)
Reactor Pressure	90 bar (1270 psig)

The hot effluent from the reactor is cooled using a cooling water heat exchanger before it is depressurized. The pressure control valve is a proprietary erosion resistant valve for reducing the pressure from 90 bar inlet to 3 bar. The depressurized effluent is then phase separated in a flash tank with the liquid effluent consisting mainly of sodium sulfate and sodium acetate in water routed to the biological treatment facility. Ultimate discharge is as makeup water for the refinery cooling towers. The off-gas is vented to the atmosphere.

The reactor and process sides of the heat exchangers were manufactured out of alloy 600 in order to withstand the corrosive environment during normal operating conditions, as well as during upsets¹. The WAO system was skid manufactured by Zimpro in their factory and shipped to Brazil, reducing the on-site installation work required. The reactors were field erected and connected to the skid on-site.

Performance

As shown in Table 2, approximately 80% destruction of COD is achieved, with near complete phenols (cresylic) destruction and sulfide levels reduced to below detection limits.

Table 2. RPDM Spent Caustic WAO Performance (T=246 °C)

	Reactor Inlet	Reactor Effluent
COD (mg/L)	72,000	15,000
COD reduction	--	79.2%
BOD/COD	--	0.515
Phenols (mg/L)	1,700	3
Sulfide - S (mg/L)	2,700	<1*
Mercaptans - CH ₃ SH (mg/L)	2,800	2
Thiosulfate - S ₂ O ₃ (mg/L)	640	<26*
pH	13.43	8.24

[* below detection limit]

Performance and overall reliability over the past 5 years has been good. The unit was run continuously for the first years of operation in order to treat production as well as stockpiled spent caustic. Now the unit is operated every other week to treat production spent caustic as it accumulates. No dedicated operators are assigned to the WAO unit, but rather operation is performed as necessary by RPDM refinery staff.

There have been a few maintenance issues, which for the sake of completeness should be mentioned. The cooler for the system air compressor experienced corrosion due to off-spec oil. The corroded radiator was replaced and heat transfer oil quality is now monitored more closely. Compressor performance has been trouble free after these corrections.

The occasional instrumentation breakage has also been experienced. An example would be leakage in the seals of the safety Pressure Release Valve (PRV) on the fresh caustic metering pump, calling for the replacement or repair of the PRV. Another example involved the leak detectors on the diagram feed pumps in which two of the detectors needed repair.

Conclusion

Implementation of WAO at RPDM allows the refinery to treat all spent caustics produced at the refinery on-site. On-site WAO has eliminated odor problems and the need to outsource spent caustic waste management. After 5 years of operation the unit continues to meet design specifications with 80% COD destruction and good detoxification of the waste. Operation of the unit has been relatively trouble free, with the exception of the occasional instrumentation maintenance issue.

Sulfidic and hazardous organic compounds in the wastewater such as mercaptans, naphthenic, and cresylic compounds are destroyed or converted to benign molecules. Additionally, the pH of the effluent is reduced. Reactor effluent is discharged to the on-site biological facilities for final polishing. The elimination of stockpiles of spent caustic and the need to truck those materials through residential areas for off-site disposal has reduced environmental and health risks, improving public relations.

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