

THE EFFECTS OF CAUSTIC TOWER OPERATIONS AND SPENT CAUSTIC HANDLING ON THE ZIMPRO® WET AIR OXIDATION (WAO) OF ETHYLENE SPENT CAUSTIC

Clayton Maugans, Ph.D.
Siemens Water Technologies

Mike Howdeshell, Ph.D.
Siemens Water Technologies

Steve De Haan
Lummus Technology

Abstract: Ethylene plant spent caustic is frequently treated using a Spent Caustic Oxidation Unit (SCOU). Commonly, this is a medium pressure (~400 psig) Wet Air Oxidation (WAO) system. There is spent caustic storage for feeding the system. Events that cause excessive downtime in the WAO unit are not acceptable because the spent caustic storage capacity is limited. The hazardous and malodorous nature of the spent caustic makes large inventory unappealing; and ad-hoc storage difficult.

WAO system operations are affected by the composition of the spent caustic. Off-spec feed can cause disruptions or even damage to the WAO system. The design and operations of the caustic tower, gasoline wash, and spent caustic storage affect the spent caustic composition, which ultimately affects WAO operations. While such disruptions are rare, when they do occur the most common cause is excessive organic contamination (red oil) in the spent caustic.

This paper describes the WAO system and the spent caustic parameters that affect WAO operations. Red oil in particular affects WAO operations and the upstream handling, and techniques to best manage this material are discussed.

Introduction

This paper discusses the effects of caustic tower operations and spent caustic handling on the reliability and performance of a wet air oxidation (WAO) system. A description is given of the WAO system and the feed parameters that affect its operation; the caustic scrubbing tower design and operations; and spent caustic storage and handling. The paper closes with recommendations for operating techniques for best reliability of the WAO system.

Wet Air Oxidation: purpose and designs

Spent caustic is intensely malodorous, toxic, and highly alkaline. It contains high chemical oxygen demand (COD), some total organic carbon (TOC), and high total dissolved solids (TDS).

These properties make it difficult to treat by conventional biological treatment. Ethylene plants often have a spent caustic oxidation unit, which is a wet air oxidation (WAO) system to treat the wastewater by oxidizing sulfides, mercaptans, and a majority of the COD. This allows the oxidized spent caustic to be further treated by conventional biological treatment prior to discharge.

There are three design temperature ranges for spent caustic oxidation.

Low temperature WAO: (100 - 150 °C)

This WAO design is more common in older ethylene plants. This is a relatively low cost system and is fabricated from inexpensive alloys such as carbon steel. The design achieves some bulk COD destruction and destroys much of the sulfide content, but sulfide and mercaptan destruction is incomplete. Overall performance and reliability are relatively poor. Effluent is typically high in COD and reduced sulfur (mostly as thiosulfate) and may still be malodorous. Fouling, caused by organic molecule polymerization, creates an organic scale and fouling rates in these older designs are high.

Medium temperature WAO: (200 - 230 °C)

This WAO design is more typical for new ethylene plants. These units achieve high gross COD reduction with complete sulfide and mercaptan oxidation. TOC concentration is not affected much, but the nature of the TOC is changed, which makes for low fouling rates and better bio-treatability. Effluent is low in COD, contains low levels of thiosulfate, and is no longer malodorous.

High temperature WAO: (>250 °C)

This is the most effective (and expensive) form of WAO. Performance is similar to medium temperature WAO, with the addition that TOC is also greatly reduced. High temperature WAO is unnecessary and not used for ethylene plants because the TOC of ethylene spent caustic is rarely greater than a few thousand ppm. This design is commonly used for refinery spent caustics that have a high TOC content.

WAO plant description

Medium temperature (200 – 230 °C) WAO systems are the most commonly built today and this paper will focus on that application. Figure 1 is a block flow diagram for a typical medium temperature WAO system. Typical spent caustic composition is shown in Table 1.

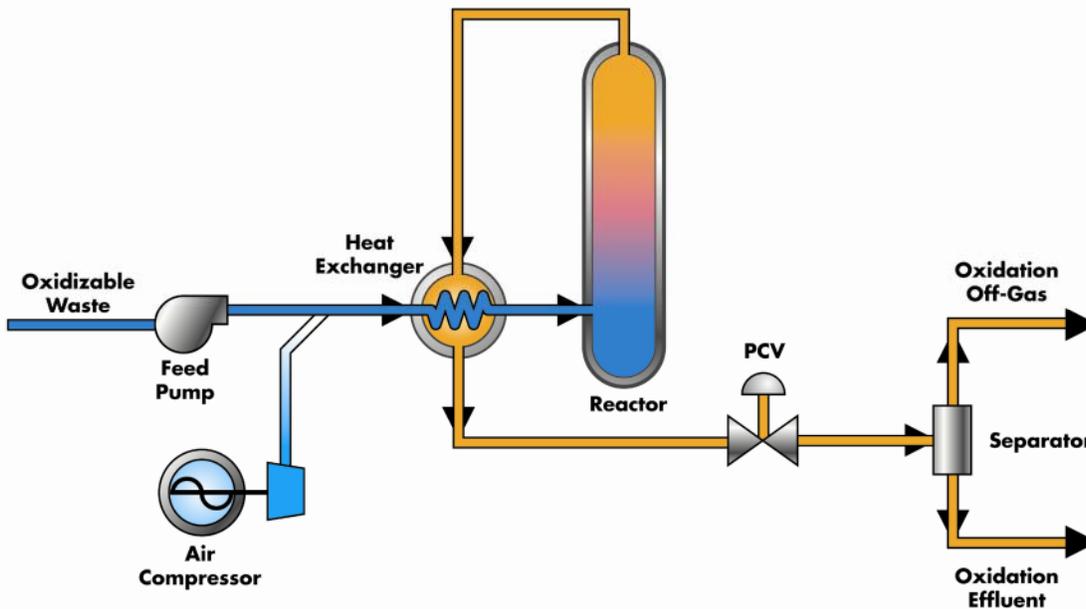


Figure 1. Typical Zimpro® WAO Block Flow Diagram.

Table 1
Typical Ethylene Plant Spent Caustic Composition (1)

Compound	Concentration Range (wt%)
NaHS	0.5%-6%
Na ₂ CO ₃	1%-5%
NaOH	1%-4%
NaSR	0%-0.2%
Soluble oil	50-150 ppm
TOC	50-1500 ppm
Benzene	20-100 ppm

In this design, a high pressure pump is used to pressurize the spent caustic. Compressed air is combined with the pressurized spent caustic and the fluid passes through the feed/effluent heat exchanger (F/E HX). The F/E HX heats the fluid and initiates the oxidation reaction. The feed passes into the WAO reactor, where the oxidation takes place. The hot liquor and off-gas pass out the top of the reactor and back to the F/E HX, where the fluid is cooled. The effluent is depressured across a control valve and the off-gas is separated from the oxidized liquor in a separator. The liquid effluent is discharged or passes to the plant biological facility for final polishing. The off-gas is typically sent to an afterburner.

The reactor is a bubble column. Oxygen transfers from the gas to the liquid phase as bubbles rise through the liquid full reactor to satisfy the oxygen demand of the reaction. WAO reactions at 200 °C are shown below (2):

1. $\text{NaHS} + \text{NaOH} + 2 \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{H}_2\text{O}$
2. $\text{NaSR} + \text{NaOH} + \text{O}_2 \rightarrow \text{Na}_2\text{SO}_4 + \text{RCOONa}$ (unbalanced)
3. $\text{R} + \text{NaOH} + \text{O}_2 \rightarrow \text{CH}_3\text{COONa}$ (unbalanced)
4. $\text{R} + \text{NaOH} + \text{O}_2 \rightarrow \text{NaOCCOONa}$ (unbalanced)
5. $\text{R} + \text{NaOH} + \text{O}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ (unbalanced)

The dissolved oxygen reacts with the sulfide compounds to produce sodium thiosulfate, which further oxidizes to form sodium sulfate (reaction 1). As shown in Table 1, over a thousand ppm of TOC may be present. At 200 °C organic compounds undergo only partial oxidation (reactions 3 and 4). The COD load is lowered and approximately 0-10% of the TOC content is completely mineralized (reaction 5).

Normally the equipment can operate for several years between cleanings or other maintenance. The process is operated with sufficient air to maintain about 5% residual oxygen in the off-gas, assuring an oxidative environment throughout. Metallurgy is selected to withstand this environment.

Parameters that affect WAO operations

Feed COD and sulfides

The COD concentration in the spent caustic is affected by the caustic tower operations and the furnace sulfide and carbonyl production rates. Sulfides make up the bulk of the spent caustic COD content. The WAO system is designed to utilize the exothermic heat release from the oxidation reaction. Low COD spent caustic (<20,000 ppm) will require more utility (steam) consumption in the WAO system, but otherwise will not have any negative impact. High COD spent caustic must be diluted or processed at a reduced flow rate in order to avoid exceeding the oxygen capacity of the air compressor. Otherwise, high COD will cause the off-gas oxygen concentration to become low. The off-gas is continuously monitored and safety interlocks shut down the unit when the oxygen is too low.

Without the interlocks, the WAO system could operate with insufficient oxygen for sulfide oxidation, creating poor quality effluent. With insufficient oxygen, the TOC will not be oxidized and polymerization/coking can occur, which will cause fouling. In addition, the metallurgy is selected to withstand an oxidizing environment, so rapid corrosion can occur under anoxic conditions.

TOC/red oil

In ethylene plants, WAO systems are designed to process a certain maximum content of TOC – usually just a few thousand ppm. The composition of the ethylene gas stream, the way the caustic tower is operated, and the way the spent caustic is stored can result in oil contamination of the spent caustic. This can cause pockets of pure oil (oil slugs) to enter the WAO system – greatly exceeding the design maximum. Oil slugs have high COD and a slug will quickly exceed the capacity of the air compressor, causing the system to become oxygen deficient. When this happens, the off-gas oxygen monitoring safety interlock should trip the WAO unit, to prevent damage to the system. Since there is some delay before the trip, frequent oil excursions will result in coking and plugging of the F/E HX.

Caustic

The metallurgy of the WAO system is selected to withstand oxidative conditions at high pH. Caustic is consumed in the above reactions. Typically there is sufficient surplus caustic in the feed to maintain alkaline conditions in the effluent.

Sodium carbonate

Sodium carbonate is a pH buffer and results from CO₂ gas adsorbed in the caustic tower. Some carbonate is also formed from the TOC oxidation reaction (reaction 5), though only a small portion of the TOC is oxidized fully to CO₂. Carbonate helps regulate the pH in the WAO system and is beneficial to the operation of a WAO unit. Essentially all of the CO₂ and H₂S in the ethylene gas stream are captured in the caustic tower – so there is little that can be done at the caustic tower to affect carbonate mass flow in the spent caustic.

Chlorides

High chloride concentration often comes from using poor quality caustic in the tower. High chloride concentration is corrosive to the standard WAO metallurgy. WAO systems are typically designed for a maximum chloride concentration of 1,500 ppm.

Iron

Spent caustic may have iron present as iron sulfides. This is oxidized in the WAO system to iron oxide and sulfate. Usually the concentration is only a few ppm, - a low enough level that the iron oxides are soluble enough to pass through the system or form only a trivial amount of precipitation. When the iron content in the feed is high, the iron will form an insoluble scale and mechanical or chemical cleaning will be needed. High iron contamination can come from using poor quality caustic, acid, or water or from systems that are experiencing high corrosion in the upstream carbon steel components (e.g. in the caustic tower).

Hardness

Because the pH is high, spent caustic typically has little hardness. Most hardness scaling issues come from the use of poor quality service water for dilution and start-up/shut-down. Any hardness in dilution or start-up water that is fed to the unit will come out on the

heat transfer surfaces as scale. Ideally, the hardness of feed service water should be well under 25 ppm as CaCO₃, though even that will eventually cause scale.

Caustic tower additives

Special chemicals are sometimes added to improve operations of the caustic tower (e.g. antifouling agents to prevent organic fouling). These chemicals and reaction products will pass with the spent caustic. In general this appears to maintain, if not improve, the operability of the WAO system as well. In rare cases, a new additive could be tested in an older caustic tower to solubilize or otherwise remove existing fouling. This can cause a large increase in the TOC and COD content of the spent caustic, which could affect WAO operations.

Upstream operations and their affects on the WAO plant

Ethylene handling

Ethylene gas contains CO₂, H₂S, mercaptans, and other organic molecules. The caustic scrubbing tower is used to adsorb and remove these contaminants. Before entering the tower, the ethylene gas is compressed and cooled to a temperature approach to cooling water. The liquid water and condensed hydrocarbons are separated from the vapor in a drum. The vapor feed to the caustic tower is then reheated by about 5 to 10 °C, to control organic compound condensation in the tower.

Insufficient reheating results in excessive condensing of organic compounds in the tower, which could increase the volume of red oil in the spent caustic that must be handled. Excessive reheating is inefficient.

Caustic tower scrubbing – overview

The caustic tower is a vertical gas/liquid contactor that is pressurized and operated between 30 and 50 °C. The typical caustic tower (Figure 2) has 3 to 4 stages, with the top stage the water-wash stage, the second stage the strong-caustic stage, and the bottom stages the intermediate- and weak-caustic stages. The caustic from each stage cascades down to the next stage. In the bottom stage, most of the free caustic has been consumed and the weak caustic is loaded with sulfides, carbonates, and hydrocarbons. A portion of the weak liquor is recirculated in the bottom stage and the remainder is discharged as spent caustic.

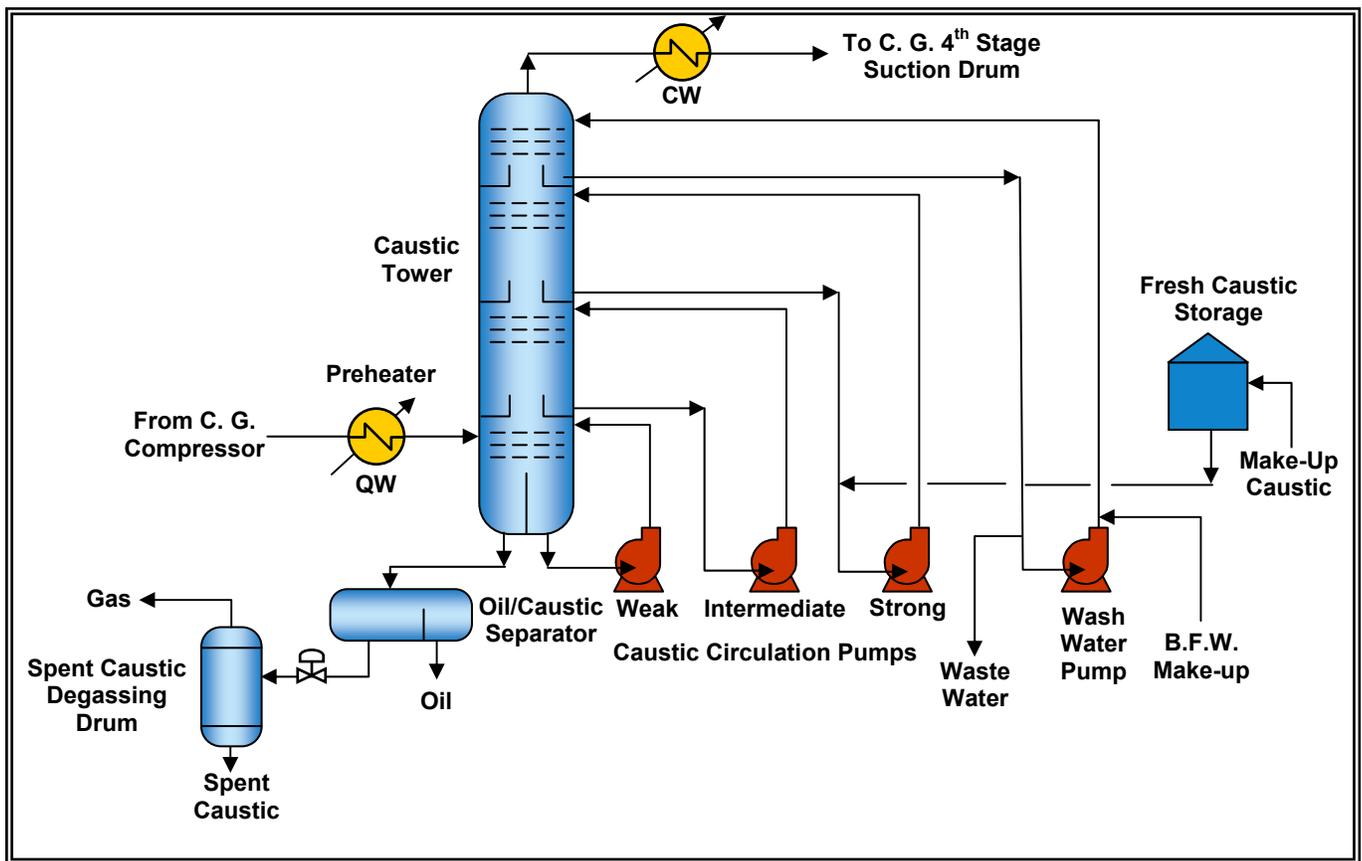


Figure 2. Caustic scrubbing tower process flow diagram (3)

Caustic tower design and operation

Most caustic towers are segregated into stages, with each stage having a liquid reservoir at the bottom. Gas/liquid contacting is enhanced by recirculating the caustic from the reservoir to the top of that stage. A portion of the reservoir is cascaded down to the next stage.

Floating on top of each caustic reservoir may be a layer of hydrocarbon oil, sometimes called "red oil". The tower should be designed to avoid retaining oil since excessive residence time worsens polymerization. The intermediate section sumps should therefore be designed with a standpipe for down flow to the next section. The standpipe allows the oil floating on the caustic to exit to the next stage, thus minimizing residence time. The bottom section sump is designed to allow skimming of the oil by the operators. Oil removed on a routine and frequent basis is typically light, easy to separate, and less prone to fouling than aged oil. The polymerization reaction is temperature dependant, so the warmer the tower, the faster the red oil formation rate. This is another reason that excessive reheating of the feed should be avoided.

Some towers do not have reservoirs with circulation pumps between the stages. Without the reservoirs, the red oil cannot be removed from within the tower. This can lead to a heavier hydrocarbon load on the tower and in the spent caustic.

After the lowest stage, the spent caustic collects in the bottom of the tower. In some towers, a separate tap in the bottoms is used to remove the floating red oil layer, so that it does not continue to polymerize. Others may drain the bottoms completely on a periodic basis. Most towers also send the mixed spent caustic to a gravity-separation drum to skim the oil.

Red oil: polymerization and fouling

Polymer formation is the most common cause of fouling in caustic towers. The entrained oils formed from the polymerization can upset the WAO operations as well.

The polymerization reaction results from the aldol condensation of acetaldehyde. Acetaldehyde and vinyl acetate (an acetaldehyde forming compound) are formed in the ethylene process and adsorbed into the caustic. Contaminated cracker feedstocks that result in the formation of these compounds have the undesirable side effect of more polymer formation in the tower.

The polymerization reaction can generally be written as:

- 1) $\text{CH}_3\text{COH} + \text{NaOH} \leftrightarrow \text{Na}^+ \text{C}^-\text{H}_2\text{COH}$
- 2) $\text{Na}^+ \text{C}^-\text{H}_2\text{COH} + \text{CH}_3\text{COH} \rightarrow \rightarrow \text{polymer}$

The rate of reaction increases with temperature and acetaldehyde concentration. The initial, smaller polymer remains soluble in the caustic. As the polymer grows, it forms a light insoluble oil that floats on top of the aqueous phase. In this form, it can be separated by a simple skimming step. Some residual will remain and that portion will continue to react and form heavier polymers, eventually forming solids that may become entrained or suspended in the caustic. The larger polymers are more difficult to remove because they do not float and may adhere to metal surfaces.

Depending on the extent of polymerization, dehydration, and other contaminants, the polymer can appear to be red, yellow, green, or other colors. Typically it is red, and so the oil layer is usually referred to as "red oil". The red oil will absorb other organics from the cracked gas as well as corrosion products from the tower, and thus increase in volume. Some heavy organic compounds in the cracked gas will condense and remain in the tower. These compounds also make up the total composition of red oil.

Red oil that is not well managed in the tower will exit with the spent caustic. If not removed, this oil can ultimately pass to the WAO system as high COD slugs.

Spent caustic handling and gasoline washing

As shown in Figure 2, the discharged spent caustic passes to a separation drum where caustic, entrained gasses and entrained oils are separated by gravity. The spent caustic then passes through a depressurization valve and into a degassing drum where the evolved gases from depressurization are removed. The spent caustic is then routed to a gasoline washing step or to a storage tank.

The "gasoline" wash is usually pygas (from the quench water tower), steam cracked naphtha (SCN, from the primary fractionator), or some other stream or combination. Figure 3 shows a gasoline wash configuration, though the location and configuration of gasoline washes can vary.

The gasoline wash removes entrained oils as well as some dissolved organic compounds. The loaded gasoline from the wash may also be contaminated with some caustic, which is removed by a separate water-wash step. The used gasoline can be disposed by burning for fuel value or blending into one of the liquid streams from the primary fractionator or quench tower.

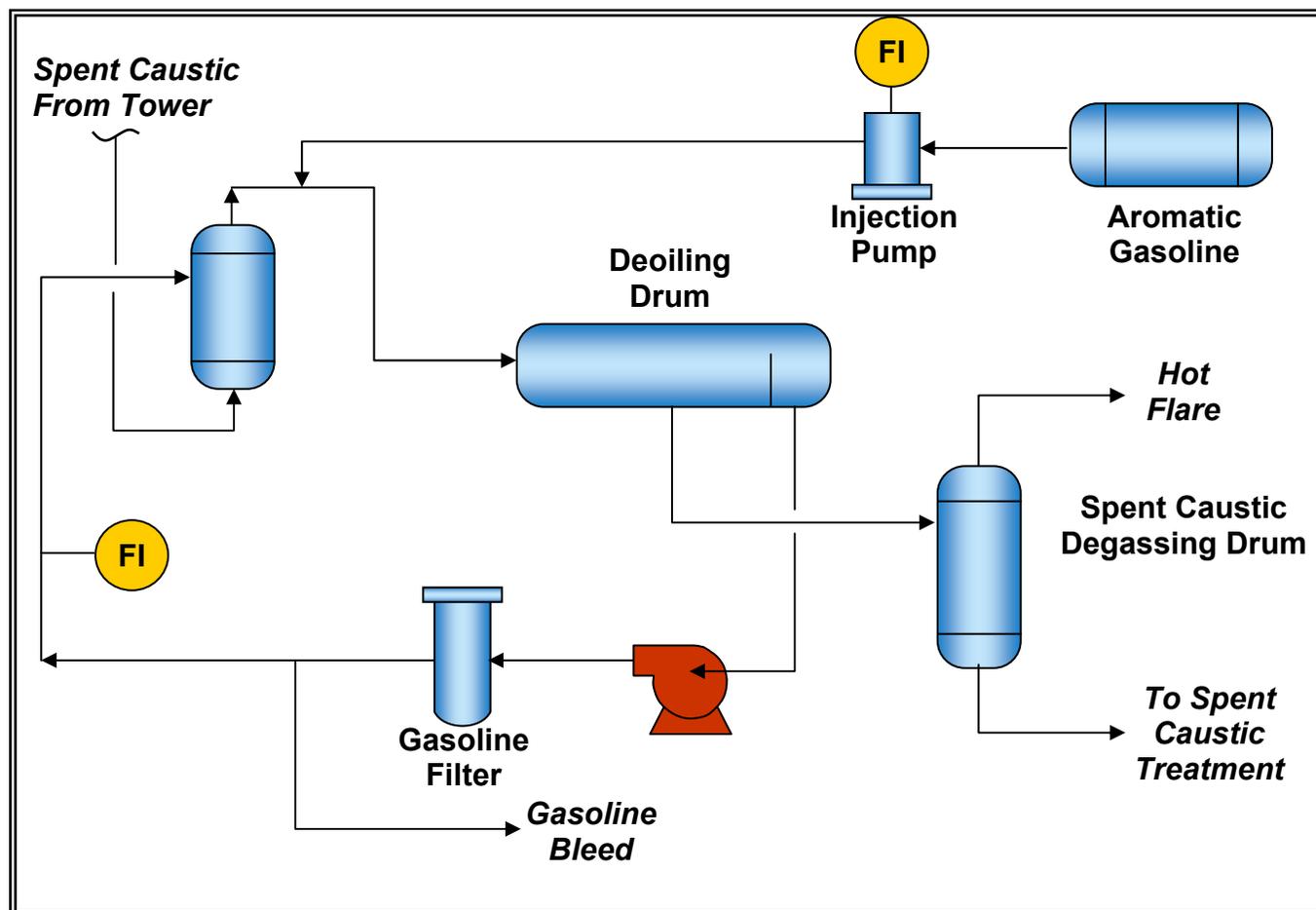


Figure 3. Example gasoline washing step configuration (4)

Spent caustic storage

The spent caustic is transferred to a storage tank. Residence time in the storage tank is typically 24 hours or longer. This tank serves as an equalization tank and is the feed tank for the WAO system. The configuration and operation of this tank can have an impact on the WAO system operations.

Even after a gasoline wash, the spent caustic will contain some red oil precursors. These compounds will continue to polymerize in the storage tank and form more red oil. Oxygen can promote these reactions, so the storage tank should be kept under an inert gas atmosphere. If the oil layer is not removed, it will continue to polymerize and form denser layers that may become entrained in the spent caustic. This will cause oil slugs to enter the

WAO system and result in WAO plant upsets. The hazard is concentrated slugs of red oil entering the feed line.

Spent caustic tanks are equipped with provision for removing the floating oil layer. Most common is a floating skim line, which floats on top of the caustic phase to skim the oil, but floating skimmers are not always reliable. The flexible piping becomes less flexible after years of use. Eventually the floating line may be abandoned and fixed side taps on the tank can be used instead. This can be effective; however, it is not certain if channeling (i.e. "rat-holing") is occurring, where the local red oil is removed, but the floating layer across the entire diameter of the tank may not be. The most effective form of skimming is thought to be "floating cover" style tanks, with a skim line attached to the bottom of the floating cover.

Over several years of operation, a heavy organic sludge will build in the bottom of a non-agitated tank - formed from the aged red oil - and can have a depth of 3 feet or more. As this depth increases, it is possible for slugs of the oil sludge to be drawn into the WAO feed tap. The location of tank inlet lines can also have an affect, as the risk of drawing an oil slug is increased if an inlet stream disturbs the bottom oil sludge. Typically the spent caustic draw line is located several feet from the bottom of the tank. Periodically cleaning the tank to remove the sludge build-up will reduce the risk of heavy oil slugs entering the WAO system.

Conclusions

WAO systems are used for spent caustic treatment and are both reliable and effective. However, WAO reliability can be hampered by off-spec feed, which is affected by the upstream processing and handling of the spent caustic. For maximum up-time, spent caustic management should be done in accordance to the following recommendations:

1. The ethylene gas is cooled and then reheated prior to entering the caustic tower.
2. Low chloride (<500 ppm Cl⁻) caustic is used in the caustic tower.
3. Skim loops and/or antifoulant additives are used in the caustic tower to manage the red oil as it forms.
4. A gasoline wash is used with the fresh spent caustic to remove entrained oils and red oil precursors.
5. The spent caustic is stored in a nitrogen blanketed storage tank; the liquor is skimmed daily to remove freshly formed oils; the tank is periodically drained and the accumulated sludge is removed from the bottom; and the feed tap to the WAO system is at least 3 feet above the floor of the tank.
6. Boiler feed water or other low-mineral water is used for all dilution and flush streams.

References

1. Ellis, C.; Lawson, R.; Brandenburg, B. (1994) "Wet Air Oxidation of Ethylene Plant Spent Caustic", *6th Annual Ethylene Producers Conference*

2. Grover, R.; Goma, H. (1993) "Proven Technologies Manage Olefin Plant's Spent Caustic", *Hydrocarbon Processing*, September, pp 61-69.
3. Reid, J. (1998) "Introduction to Sulfur Compounds and Sulfur Removal as Applied to Olefin Unit Design and Operation", *10th Ethylene Producers' Conference*, pp 713-755.
4. Matthews, R. (1997) "Performance update : Low Pressure Wet Air Oxidation unit at Grangemouth, Scotland", *Environmental progress*, vol. 16, no1, pp. 9-12.