

# Update: Spent caustic treatment

## Better operating practices and prevention methods reduce problems in handling 'red oil'

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Caustic towers at ethylene plants remove acid gases, hydrogen sulfide (H<sub>2</sub>S) and carbon dioxide (CO<sub>2</sub>) from ethylene gas. The spent caustic from these towers contains mercaptans and sulfides, which are reactive and odorous. Accordingly, the spent caustic requires special handling and treatment before being discharged to a conventional wastewater treatment plant.

Often, the spent caustic is most commonly treated in an oxidation reactor. Also known as wet air oxidation (WAO), this process converts the sulfides into oxidation products such as sulfate ions. Other components and contaminants present in the spent caustic can affect the WAO systems. Field observations conducted at multiple ethylene facilities over the years have helped this industry to identify typical contaminants, discover how they form and affect system operation, and provide mitigation strategies to eliminate negative effects.

**Spent caustic composition and treatment.** Table 1 summarizes the composition of typical ethylene plant spent caustic. Sulfides are highly odorous, even at the ppb level. A typical spent caustic stream also has a high chemical oxygen demand (COD), usually in the tens of thousands mg O<sub>2</sub>/l. Also, the spent caustic is highly alkaline, with a pH near 14. In addition to the composition shown in Table 1, there is sometimes entrained polymer which, at times, can be at very high concentrations. Ethylene plant operations staff often refers to this polymer oil as "red oil." When present, red oil can greatly increase the total organic carbon (TOC) and, thus, the COD of the spent caustic.

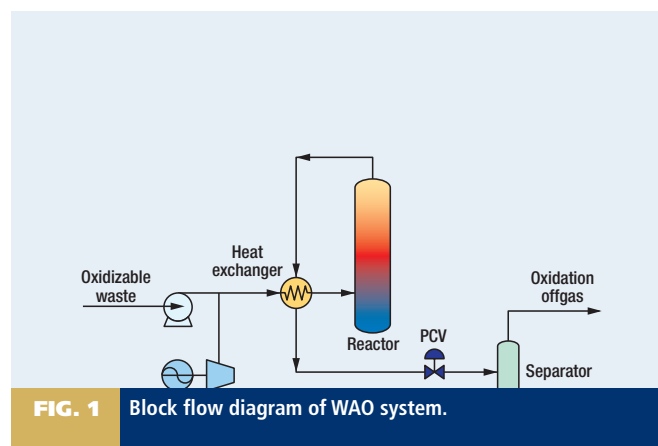
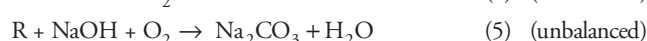
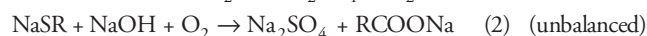
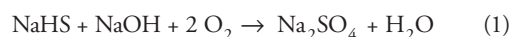
**TABLE 1. Compounds commonly present in spent caustic from ethylene plant operations.**

Compound	Concentration range, wt%
NaHS	0.5%–6%
Na <sub>2</sub> CO <sub>3</sub>	1%–5%
NaOH	1%–4%
NaSR	0%–0.2%
Soluble oil	50–150 ppm
TOC	50–1,500 ppm
Benzene	20–100 ppm

This can create operational issues with the spent caustic treatment system, i.e., the WAO system.

**WAO: Purpose and design.** The WAO system treats the spent caustic by oxidizing the sulfides and mercaptans and most of the COD. Effluent is typically sent to a conventional biological treatment plant for polishing. Fig. 1 shows a typical WAO process flow diagram. A feed pump increases the liquid pressure to about 28 barg (400 psig), and the liquid is combined with compressed air. The fluid is heated in an exchanger or with direct-contact steam. The hot fluid is held in a reactor for a one-hour residence time, at 200°C (392°F).

As the reactions are liquid-phase based, oxygen (O<sub>2</sub>) must transfer from the gas to the liquid phase to satisfy reaction demands. The process is operated with excess O<sub>2</sub> in the offgas, to maintain sufficient surplus O<sub>2</sub> to protect the metallurgy and satisfy the reactions. Reactions at 200°C (392°F) are shown here:



**FIG. 1** Block flow diagram of WAO system.

The dissolved O<sub>2</sub> reacts with the sulfide compounds to produce sodium thiosulfate, which further oxidizes to form sodium sulfate, as shown in Reaction 1. As shown in Table 1, over 1,000 ppm of TOC may be present. At 200°C (392°F), organic compounds are partially oxidized, as shown in Reactions 3 and 4, which lowers the COD loading. TOC concentration is not affected much, with only 0–10% mineralized (Reaction 5). The nature of the TOC is changed, which makes for lower COD, lower fouling rates and improved bio-treatability.

**Effects of red oil on WAO operations.** The composition of the ethylene gas stream, the way the caustic tower is operated and how 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 O<sub>2</sub> deficient. When this happens, the offgas oxygen monitoring safety interlock (located at gas discharge piping from the WAO system separator) should switch the WAO unit from caustic to water, to prevent system damage. Since there is some delay before the trip, frequent oil excursions will result in coking, plugging and possible corrosion of heating equipment, i.e., the feed/effluent heat exchanger.

Sulfides above 120°C (248°F) are highly reactive. Should oxygen-deficient conditions persist, such as by neglecting the oxygen offgas monitoring system or frequent slugs of red oil, then the reactive sulfides will consume oxygen from the metalurgy. In a system with poor oxygen sensor reliability or frequent red oil excursions, corrosion will occur around the middle section of the first heat exchanger, and may extend downstream into the reactor.

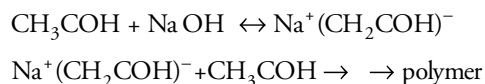
Sometimes the corrosion is isolated to just a small section in the middle of the exchanger, in what is called a “light off” zone. This zone exists in all WAO systems, and is where the temperature is warm enough that the sulfides begin to oxidize at a rapid rate, approaching the mass transfer replenishment rate for oxygen transfer from the entrained gas, into the liquid phase. This is usually well below the 200°C (392°F) operating temperature, and so occurs in the heat transfer equipment prior to the reactor. Transfer from the gas into the liquid can be inhibited when there is a high TOC content (i.e., red oil) present.

After this zone, the sulfides are sufficiently oxidized, and the O<sub>2</sub> mass transfer rate increases. Under normal operations, this zone does not corrode because the O<sub>2</sub> transfer rate is sufficient for the COD loading and reaction rate. However, when high oil content is present, either as a regular stream of small intermittent oil slugs, or by large doses of oil, then it is theorized that the O<sub>2</sub> transfer rate is inhibited, and/or the dissolved O<sub>2</sub> is consumed by the TOC rather than by the sulfides. High organic loads (red oil excursions) can also create saponification conditions and result in foaming in the separator.

**Organic polymer sources and effects on WAO unit.** Polymer formation is the most common cause of fouling in caustic towers. Entrained oils formed from polymerization can upset the WAO operations as well.

**Red oil: Polymerization and fouling.** The polymerization reaction is due to the aldol condensation reaction of acetaldehyde. Acetaldehyde and vinyl acetate (an acetaldehyde-forming compound) are formed in the ethylene process

and are adsorbed into the caustic. Contaminated cracker feedstocks that result in the formation of these compounds have the undesirable side effect of producing more polymer within the tower. The polymerization reaction can generally be written as:



The rate of reaction increases as temperature and acetaldehyde concentration increases. 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 to form heavier polymers, eventually forming solids that may become entrained or suspended within 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 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 can be managed by solid upstream practices to reduce the organic load on the tower, through chemical addition to reduce the reaction rate for aldol formation and/or by effectively isolating the red oil from the spent caustic. Red oil that is not well controlled or 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.

**Ethylene handling.** Ethylene gas contains CO<sub>2</sub>, H<sub>2</sub>S, 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 condense hydrocarbons from the gas. Any hydrocarbons that condense are separated from the vapor. The vapor feed to the caustic tower is then reheated by about 5°C to 10°C (9°F to 18°F), to reduce organic compound condensation in the tower.

Insufficient reheating can result in excessive condensing of organic compounds in the tower, which increases the volume of red oil present in the spent caustic that must be handled. Excessive reheating is inefficient. Indicators of insufficient pre-tower temperature control include high oil purge rates or fouling in the caustic tower, high red oil content in the spent caustic and/or foaming in the separator.

**Caustic tower scrubbing.** The caustic tower is a vertical gas/liquid contactor that is pressurized and operated between 30°C and 50°C (86°F and 122°F). The typical caustic tower (Fig. 2) has three to four stages, starting with the top (water-wash) stage, the second (strong-caustic) stage, and then the bottom (intermediate- and weak-caustic) stages. Each stage has a liquid reservoir at the bottom. Gas/liquid contacting is enhanced by recirculating the caustic from the reservoir to the top of that stage. Part of the reservoir is cascaded 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,



Over several years of operation, a heavy organic sludge that is formed from the aged red oil will build in the bottom of a non-agitated tank and can have a depth of up to one meter (3 feet) or more. As this depth increases, slugs of the oily sludge might be drawn into the WAO feed tap. The location of tank inlet ports can also have an effect, as the risk of drawing an oil slug increases if an inlet stream disturbs the bottom oil sludge. Typically, the spent caustic draw line is located a short distance 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.

**Optimize WAO operations.** WAO systems are both a reliable and effective means of treating spent caustic. 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 with these recommended practices:

- The ethylene gas is cooled and then reheated prior to entering the caustic tower.
- Skim loops and/or antifoulant additives are used in the caustic tower to control red oil formation or manage it once formed.
- A gasoline wash is used with the fresh spent caustic to remove entrained oils and red oil precursors.
- 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 1 meter (3 feet) above the floor of the tank.
- Boiler feedwater or other low-mineral water is used for all dilution and flush streams. **HP**

**ACKNOWLEDGMENT**

Revised and updated from an earlier presentation, titled “The Effects of Caustic Tower Operations and Spent Caustic Handling on the Zimpro Wet Air Oxidation (WAO) System of Ethylene Spent Caustic,” that was presented at the AIChE’s 21st Ethylene Producers Conference, Tampa, Florida, April 2009.

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