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PETROCHEMICAL DEVELOPMENTS　　　**SPECIAL**REPORT

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_2S) and carbon dioxide (CO_2) 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.
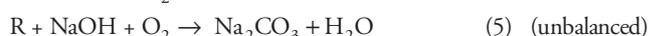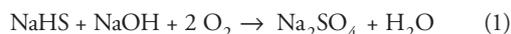
Spent caustic composition and treatment. Table 1 summarizes the composition of typical ethylene plant spent caustic. Sulfides are highly odorous, even at the ppb level. A typical spent caustic stream also has a high chemical oxygen demand (COD), usually in the tens of thousands mg O_2/l. Also, the spent 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. 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_2) must transfer from the gas to the liquid phase to satisfy reaction demands. The process is operated with excess O_2 in the offgas, to maintain sufficient surplus O_2 to protect the metallurgy and satisfy the reactions. Reactions at 200°C (392°F) are shown here:

$$NaHS + NaOH + 2\,O_2 \rightarrow Na_2SO_4 + H_2O \qquad (1)$$
$$NaSR + NaOH + O_2 \rightarrow Na_2SO_4 + RCOONa \qquad (2) \quad \text{(unbalanced)}$$
$$R + NaOH + O_2 \rightarrow CH_3COONa \qquad (3) \quad \text{(unbalanced)}$$
$$R + NaOH + O_2 \rightarrow NaOOCCOONa \qquad (4) \quad \text{(unbalanced)}$$
$$R + NaOH + O_2 \rightarrow Na_2CO_3 + H_2O \qquad (5) \quad \text{(unbalanced)}$$

The dissolved O_2 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
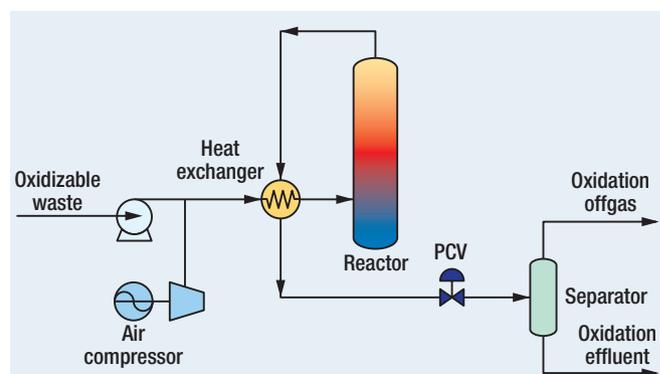
TABLE 1. Compounds commonly present in spent caustic from ethylene plant operations.

Compound	Concentration range, wt%
NaHS	0.5%–6%
Na_2CO_3	1%–5%
NaOH	1%–4%
NaSR	0%–0.2%
Soluble oil	50–150 ppm
TOC	50–1,500 ppm
Benzene	20–100 ppm

FIG. 1 Block flow diagram of WAO system.

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_2 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 metallurgy. 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_2 mass transfer rate increases. Under normal operations, this zone does not corrode because the O_2 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_2 transfer rate is inhibited, and/or the dissolved O_2 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:

$$CH_3COH + Na\,OH \leftrightarrow Na^+(CH_2COH)^-$$

$$Na^+(CH_2COH)^- + CH_3COH \rightarrow\ \rightarrow polymer$$
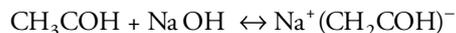
The rate of reaction increases as temperature and acetaldehyde concentration increases. The initial, smaller polymer remains soluble in the caustic. As the polymer grows, it forms a light, insoluble oil that floats on top of the aqueous phase. In this form, it can be separated by a simple skimming step. 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_2, H_2S, 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
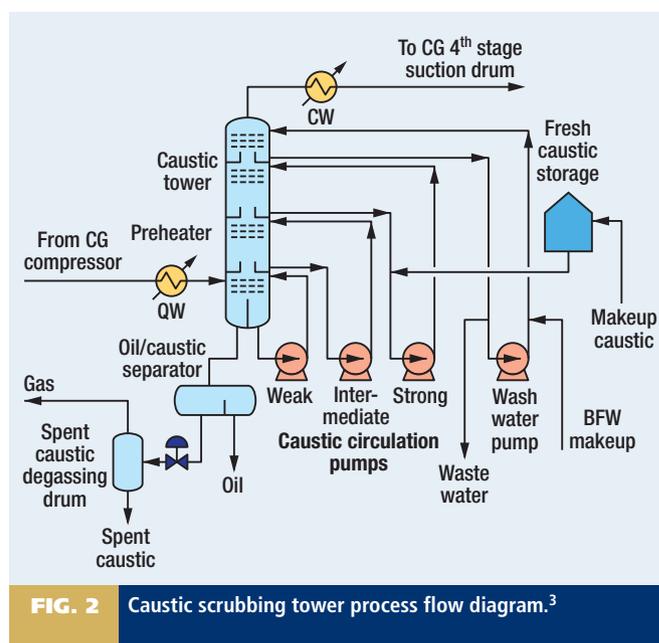

FIG. 2 Caustic scrubbing tower process flow diagram.[3]

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, carbonates and hydrocarbons. A portion of the weak liquor is recirculated in the bottom stage, and the remainder is discharged as spent caustic.

A layer of hydrocarbon oil may float on top of each caustic reservoir. The caustic tower should be designed to avoid retaining this red oil since higher residence time increases polymerization. The intermediate section sumps may 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 dependent, 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 bottom is used to remove the floating red oil layer, so that it does not continue to polymerize. Others may drain the bottom completely on a periodic basis. Most towers also send the mixed spent caustic to a gravity-separation drum to skim the oil.

Spent caustic handling and gasoline washing. As shown in Fig. 2, the discharged spent caustic passes to a separation drum where caustic, entrained gases 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. Fig. 3 shows a gasoline wash configuration, although 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
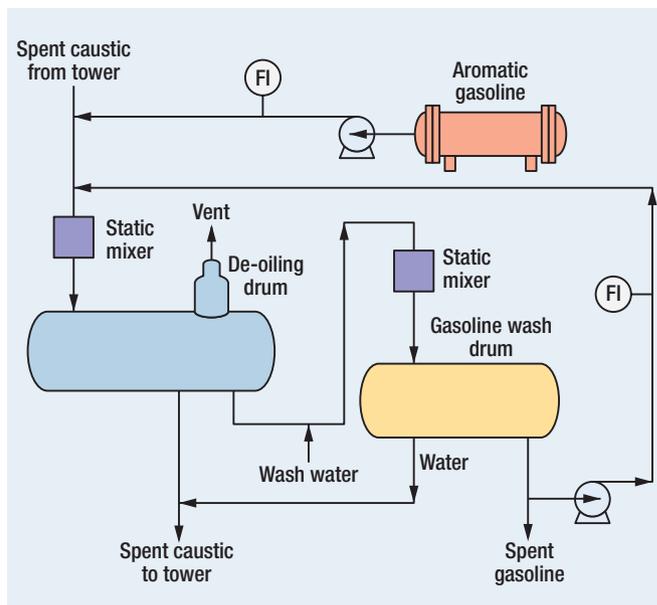

Example gasoline washing step configuration.

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. Pure naphtha is the most effective gasoline wash, as, sometimes, quench tower bottoms or other distillate cuts (pygas) can contain contaminants that will actually accelerate red oil formation.

Spent caustic storage. After the separation step, 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 may contain some red oil precursors. These compounds will continue to polymerize in the storage tank and form more red oil. Oxygen at ambient temperature 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 plant upsets. Red oil slugs entering the feed line pose a definite hazard to WAO operations.

Spent caustic tanks are equipped with a 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 may degrade after years of use, ultimately reducing its flexibility. Eventually, the floating line may be abandoned and fixed side taps on the tank can be used instead. This can be effective but may lead to channeling where red oil is only removed locally and not from the entire tank diameter. "Floating cover" style tanks are thought to be the most effective form of skimming, where a skim line is attached to the bottom of the floating cover.

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**

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