

Sustainability

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Treat toxic, malodorous ethylene spent caustic using WAO technology

As China's largest integrated refinery, Sinopec's Zhenhai Refining & Chemical Co. (ZRCC) plant can process approximately 23 MM metric tpy of crude oil. The plant produces more than 50 fuel and chemical products, including different grades of gasoline, jet and diesel fuels, asphalt and polypropylene plastics, as well as more than 1 MM metric tpy of ethylene. The latter generates spent caustic, one of the world's most toxic wastewaters.

Despite the toxic nature of its industry, the company takes pride in its environmental, health and safety (HSE) record—the Chinese government awarded ZRCC one of the nation's earliest National Environment-Friendly Enterprises awards. This is important because the ZRCC refinery sits across Hangzhou Bay from Shanghai and its 26 MM people, not to mention several residential communities just a few kilometers away.

The largest of Sinopec's four refineries, ZRCC has won many other environmental awards over the past decade. A highly effective wet air oxidation (WAO) technology^a has played a role in these awards since its deployment in 2009. The refinery uses WAO to treat extremely toxic and malodorous sulfidic spent caustic wastewaters from ethylene production.

Treating large volumes of spent caustic wastewater.

Solutions of water and sodium hydroxide are used by the plant to sweeten its ethylene output. The addition of these solutions helps remove sour components, especially sulfides and mercaptans that are malodorous and toxic. The produced spent caustic wastewater resists biological wastewater treatment, so it must be pretreated with WAO.

To understand just how dirty spent caustic wastewater is, it helps to know its constituents: biorefractory, hazardous and inhibitory reduced sulfur compounds; high-dissolved solids; and a salts mass fraction that is nearly 10% by weight. Given these components, using biological treatment processes to treat spent caustic biologically is impractical and can be counterproductive, as it can compromise the health of the biomass used in such a treatment approach.

Worse, when a spent caustic's pH is lowered to levels required for biological treatment, reduced sulfur compounds can become volatile and release hydrogen sulfide (H₂S) and mercaptans. Both are malodorous and hazardous to humans, even in small concentrations.

Also, ethylene spent caustic has an extremely high chemical oxygen demand (COD), ranging from 10,000 mg/l–50,000

mg/l. Given flowrates of spent caustic between 5 m³/hr and 20 m³/hr, the kilogram COD load typically can exceed the combined amount found in a water treatment plant's other waste streams. For these reasons, the ZRCC plant needed a way to pretreat its spent caustic before it entered the facility's biological treatment stream.

Deployment of WAO technology. To find a solution, ZRCC plant engineers selected WAO rather than alternative oxidation treatment approaches, which either try to strip the sulfides out of the spent caustic—resulting in a corrosive and odorous sulfide gas—or incinerate it in a gaseous phase. The latter is also corrosive and energy-intensive. Another reason the ZRCC engineers rejected these approaches was their high operating and maintenance costs, as shown in **FIG. 1**. Incineration needs fuel, while advanced oxidation uses expensive and hazardous liquid oxidizers to oxidize the spent caustic.

In contrast, when oxidized using WAO, spent caustic turns into an effluent consisting of fully oxidized, inorganic salts that are non-reactive, and carboxylic organics with a low molecular weight. This effluent has no unpleasant odors and can be safely

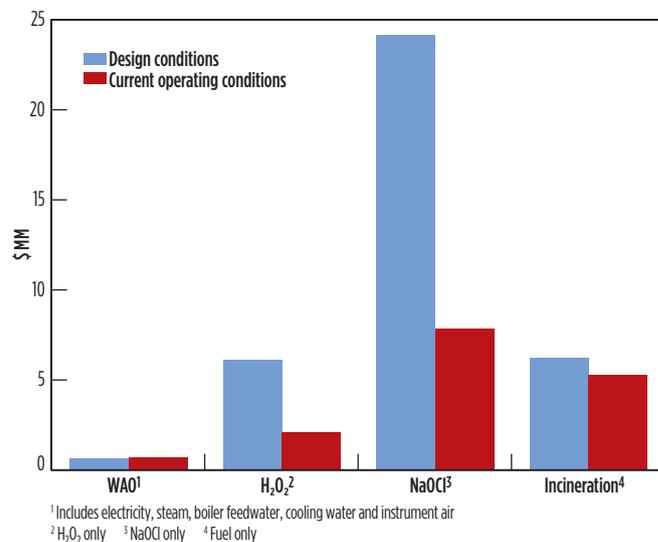


FIG. 1. Annual operational expense comparison of WAO technology^a vs. alternative oxidation treatment approaches for ZRCC's ethylene spent caustic at current operating conditions and design conditions.

neutralized. Since its COD levels have been significantly reduced and the organics oxidized to a biodegradable form, the effluent can be directed into biological treatment for final polishing before disposal.

Ultimately, the ZRCC engineering team combined a pre-treatment solution with a WAO system, as illustrated in FIG. 2. This solution first decants the spent caustic wastewater and then skims free-floating and corrosive red oil from its surface. The WAO technology then processes the aqueous spent caustic.

WAO at the ZRCC refinery. As deployed, the spent caustic processing capacity of the ZRCC plant's WAO system is 18.2 m³/hr. The system operates in an aqueous phase at relatively low temperatures. It combines spent caustic wastewater with oxygen from the ambient air and heat, which forms hydroxyl radicals that drive the oxidation reactions.

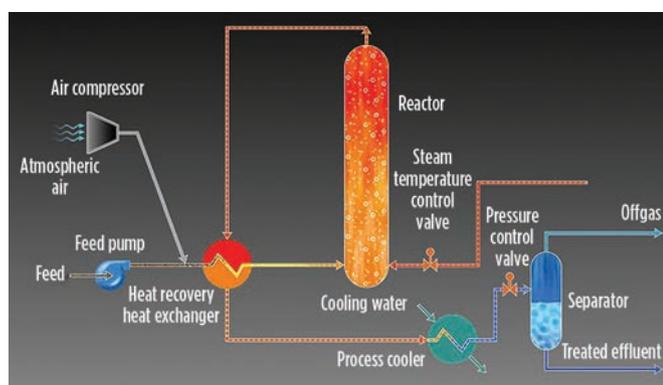


FIG. 2. Diagram of the WAO system deployed by ZRCC, designed to process a spent caustic flow of 18.2 m³/hr.

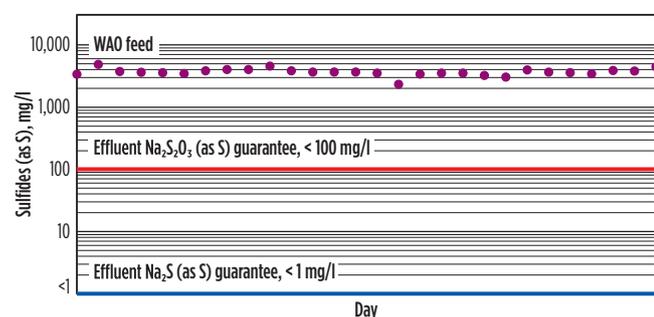


FIG. 3. WAO feed and near-complete oxidation of sulfides over the course of 1 mos (February 2018).

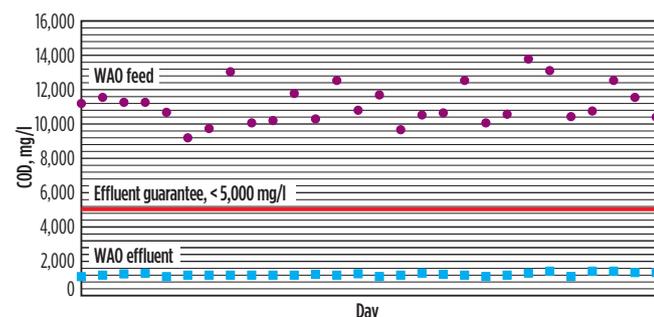


FIG. 4. WAO feed and stable effluent COD over 1 mos (February 2018).

In turn, these reactions convert sulfides to sulfates and mercaptans to sulfonates. They also oxidize high-molecular-weight organic compounds into carboxylic of low molecular weights, such as acetate and formate. The WAO process converts organic contaminants to biodegradable, short-chain organic acids, such as acetic acid, plus carbon dioxide (CO₂) and water. Inorganic constituents, including sulfides and cyanides, can also be oxidized.

The process can typically involve any or all of the following reactions:

- Organics + O₂ → CO₂ + H₂O + RCOOH
- Sulfur species + O₂ → SO₄⁻²
- Organic N + O₂ → NH₃ + CO₂ + RCOOH.

When the oxidized spent caustic is neutralized, the resulting effluent has a smaller COD load than previously achieved. It is then ready for treatment at the ZRCC biological wastewater treatment plant.

Supporting HSE stewardship. Designed to reduce odorous sodium sulfide from approximately 2% by weight to less than the analytical detection limit in the oxidized caustic, the WAO system effectively eliminates odor problems.

It also dramatically reduces total COD in the plant's spent caustic, which can range as high as 21,450 mg/l. FIGS. 3 and 4 display operational data over 1 mos (February 2018) showing that the WAO system is producing a stable effluent with 1,000 mg/l–1,500 mg/l COD, well below the allowable design limit of < 5,000 mg/l. The remaining COD in the effluent is in the form of biodegradable organics.

Despite feeds ranging from 2,300 mg/l–4,900 mg/l sulfides (as S), the WAO system destroyed the sulfides, with < 1 mg/l as S (detection limit) and < 100 mg/l Na₂S₂O₃. Additionally, all daily effluent phenol readings were below 1 mg/l (detection limit), well under the design limit of < 20 mg/l.

In effect, this data shows that the WAO system can achieve complete oxidation of sulfides. At 200°C (392°F), the compounds are almost completely oxidized to sulfate. This conversion to sulfate eliminates the malodorous sulfides and the high COD associated with sulfides or thiosulfates. As a result, the WAO effluent produces a biologically degradable, non-odorous/non-offensive effluent.

According to the ZRCC engineering team, the WAO system is highly reliable and quickly paid for itself, given its lower operating costs vs. other spent caustic oxidation alternatives. **HP**

NOTES

^a Siemens Zimpro® Wet Air Oxidation (WAO) system

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