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A Better Method For Treating Spent Caustic

When refineries generate caustic, they run the risk of hurting the environment or local wastewater treatment plants unless it is treated properly. Of course, doing so is not as easy as it sounds.

While many operations treat caustic through biological methods and run into obstacles, [Siemens](#) offers an alternative method. Oil and Gas Online spoke with Mark Clark about the properties of spent caustic, the problems inherent in biological treatment, and their way forward.

What processes produce spent caustic in the petroleum and petrochemicals industries?

Spent caustic is generated during the final sweetening stages in the production of high-quality refinery and petrochemical products. The caustic removes acidic components such as hydrogen sulfide (H₂S), mercaptans, and naphthenic acids that cause corrosion.

What regulations govern the treatment and disposal of spent caustic?

There are no specific regulations regarding the treatment of spent caustic. However, when spent caustic is sent to a standard biological wastewater treatment plant it can have a significant negative impact on the operation and safety of that treatment plant.

What are the qualities of spent caustic that make it difficult to treat?

Primarily, the difficulties are toxicity to biological activity; health, safety, and environmental (HSE) concerns; and very high concentrations of chemical oxygen demand and total dissolved solids of the spent caustic solution.

Why are conventional biological methods not up to the task of treating and disposing of spent caustic?

Sulfides and mercaptans will strip out of the wastewater when the pH is neutralized and aerated. Both are highly odorous and have low permissible threshold limits, creating direct health risks to plant operators and causing issues with neighboring residents and businesses.



Naphthenic acids are toxic and/or inhibitory to biological treatment processes. Naphthenic acids also produce significant amounts of foam when added to the aeration basin.

The oxygen demand associated with spent caustic is very high and is often greater than 50,000 mg/L. A small amount of this spent caustic can represent a very large part of the overall oxidation capacity of the biological treatment plant. Additionally, the dissolved solids or salts in spent caustic often approaches 10 wt% (weight percent).

Adding a high-salinity wastewater to the biological treatment system can have a significant negative impact for any facility trying to recover water from the biological effluent, trying to

achieve zero liquid discharge, or reusing and recycling the water.

Do many operators try to treat their spent caustic biologically? What can be the consequences of doing so?

That is difficult to say. There are over 600 refineries throughout the world and the quantity of spent caustic produced at each of these facilities is highly dependent on the feedstock being processed.

It is safe to say that some of the refineries using relatively sweet crude are producing a small amount of spent caustic and may be disposing of it via their wastewater treatment plant. Refineries using high-acid or sour crudes will most likely need to dispose of the spent caustic via other means. The cause of many wastewater treatment plant operational problems such as foaming, effluent toxicity, oil emulsification, and impaired bio-flocculation can be linked to just a small amount of refinery spent caustic being added to a wastewater treatment plant, and those operational problems could be eliminated by the removal of the untreated spent caustic.

What alternative method for treating spent caustic do you recommend? Why is this important regarding biological treatment?

We primarily recommend using oxidation technologies. When spent caustic is oxidized, it results in an effluent that is primarily composed of non-reactive inorganic salts and low-molecular-weight carboxylic organics. The resulting effluent has no offensive odor, no HSE concerns related to H₂S or mercaptans, no foaming concerns, and a significantly reduced amount of oxidation demand — which means the effluent can be easily polished using standard biological treatment processes.

These effluent results can be achieved via wet air oxidation and by using advanced oxidants such as hypochlorite, peroxide, or ozone. Siemens recommends using the Zimpro® wet air oxidation method for treating refinery and petrochemical spent caustic streams.

How have you determined that wet air oxidation is a superior method for treating and disposing of spent caustic?

We have decades of experience in the field and in research and pilot testing. Wet air oxidation produces an effluent that, once the pH is neutralized, is neither harmful nor difficult for standard effluent treatment plants to handle. Because the oxidant is air, the operating expenses associated with wet air oxidation are relatively low. Zimpro wet air oxidation systems are designed to be robust and use highly corrosion-resistant materials of construction, resulting in long service life.

Other oxidation treatment technologies, such as incineration or advanced oxidation, are far more expensive to operate and maintain. Treatment technologies other than oxidation methods — such as acid springing — simply reduce the amount of contaminant but do not actually treat or mitigate the problems associated with spent caustic.

How does wet air oxidation work?

Wet air oxidation occurs in the aqueous phase at relatively low temperature conditions. When wastewater, air, and heat are combined, hydroxyl radicals are formed that produce oxidation reactions. The higher the temperature, the higher the oxidation potential. The oxidation reactions convert sulfides into sulfate, mercaptans into sulfonates, and oxidize high-molecular-weight organic compounds into low-molecular-weight carboxylics, such as formate and acetate, and carbon dioxide.

When oxidation occurs in the aqueous phase, oxygen that is dissolved into the water from the air is consumed, allowing for more oxygen to dissolve into the water phase and allowing additional oxidation reactions to occur.

After a specific amount of time has passed during which the wastewater is held at temperature and oxygen is present, the wastewater will have been treated and the liquid effluent and non-condensable gasses — mostly nitrogen — are cooled.

The non-condensable gasses will be separated from the liquid effluent.

What other advantages does wet air oxidation offer over other treatment methods?

The operating costs are low compared to other treatment technologies. The wet air oxidation process' energy demands are relatively low and the spent caustic itself provides much of the energy required to heat the wet air oxidation system. In comparison, a high-temperature incineration system requires substantial amounts of supplementary fuel to achieve treatment.

Acid-springing systems produce extremely corrosive and toxic off-gasses that require disposal. Incineration uses refractory that is subject to the corrosive effects of the high salts and caustic. Both of these systems require frequent maintenance and repair to continue operation. Zimpro wet air oxidation systems are designed to be robust and have a long life, therefore the overall cost of ownership is among the lowest of the available technologies.

Wet air oxidation is performed in a closed system and the oxidation results in the destruction of the highly odorous, reduced sulfur compounds, eliminating concerns related to H₂S and mercaptans. Unlike high-temperature oxidation processes, no nitrogen oxides, sulfur oxides, or dioxins are formed.

Advanced oxidation processes often require extensive pH adjustment and the use of expensive liquid oxidizers that must be stored in tanks on-site. Storage of these highly reactive chemicals introduces significant hazards that need to be addressed at the refinery. Wet air oxidation only uses atmospheric oxygen, electricity, steam, and cooling water, which are already available at every refinery site.

Siemens' Zimpro wet air oxidation systems are custom-designed to meet customers' design and site specifications, assuring that they will be easily integrated into the refinery or chemical plant operations. ■