On the outskirts of Shanghai, one of China’s largest refineries produces extremely toxic and odorous wastewater called “spent caustic” as a byproduct of making ethylene — a primary feedstock for plastics manufacturing. Arguably the world’s dirtiest water, it is fortunately treatable, using a process developed nearly a century ago in Rothschild, Wisconsin, United States. In fact, that process spawned what is today one of the most sophisticated water treatment facilities anywhere for solution development, testing, and pilot facility simulations.

The facility is owned and operated by Siemens Energy’s Water Solutions (Rothschild, Wisconsin) business segment, and it serves global customers in oil and gas production, refining, chemicals, and many other industries. This article looks at the unique development process used within the Rothschild facility and how it has contributed to advances in widely used treatment methodologies over the years — including hydrothermal, separation and filtration, and biological activation processes.

Tailored Treatment

One unique attribute that has contributed to both the reputation and success of the Rothschild facility is the highly collaborative approach...
that it employs for treatment system testing and development. The facility does not focus on providing “off-the-shelf” or “out-of-the-box” treatment systems that can be universally applied. Instead, it creates tailored solutions that address the unique requirements of customer applications.

Although many facilities across the oil and gas, petrochemical, and chemical processing sectors share similar wastewater treatment requirements and challenges, unique factors often come into play when it comes to regulatory compliance, capital, and operating expenses, organizational objectives, safety, and so forth. These factors need to be considered to develop a treatment solution that aligns with the customer’s business.

For this reason, engagements at the Rothschild facility are highly interactive and cooperative — often involving customers’ engineering teams. If an initial evaluation indicates that a treatment solution is technically feasible, groups within the facility proceed to a bench-scale investigation.

Bench-scale testing is used to establish preliminary design criteria for a full-scale design, allowing for evaluation of process economics. This typically takes about 2 months to complete. After obtaining the results of the study, a
A proposal is developed outlining a recommended, commercial-scale treatment solution, along with its associated cost.

**Pilot Testing**

After the customer approves, the water treatment solution proceeds to the pilot testing phase. The Rothschild facility houses its own pilot facility that spans 930 m$^2$ (10,000 ft$^2$). It includes various systems with different configurations made from various construction materials. The facility is permitted to test hazardous waste under the Resource Conservation and Recovery Act Part B, certified by the U.S. Environmental Protection Agency and the Wisconsin Department of Natural Resources.

With these in-house capabilities, facility personnel can perform continuous flow pilot studies under a wide range of operating conditions to optimize the design conditions for custom applications.

The pilot study is a critical step that provides engineers at the facility with data to design and engineer a commercial-scale system. However, it also provides a certain degree of validation — offering customers a chance to see the performance of the system before it is deployed. For hydrothermal treatment solutions, pilot testing can take 2 to 3 weeks. Biological pilot testing can take up to 12 weeks. A full pilot study can last up to 3 months.

In some instances, for example, with hydrothermal solutions, a materials-of-construction study also may be performed. These treatment systems often are used to handle corrosive wastewaters. They require using exotic (and expensive) alloys, such as titanium and high-nickel alloys for pipes and tanks that will be in contact with influent. By testing multiple types of metals, a material can be selected that meets the needs of the application.

Tests are conducted by metallurgists employed at the facility. The goal is to ensure that the metallurgy in customer systems is cost-optimized for their requirements. In this way, over-specification can be avoided, as can unnecessary costs.

**Optimizing Systems**

Studies and testing at the Rothschild facility typically involve wet air oxidation (WAO), biological treatments that can be coupled for effluent polishing like carbon absorption and the treatment of produced water. Solutions tested often entail one or more of the following water treatment technologies:

*Hydrothermal WAO processes.* Hydrothermal WAO systems are often used to treat spent caustic, biorefractory industrial wastewaters, and
solids from biological treatment methods. Often these are used for wastewater pretreatment, before biological polishing or for the destruction of specific compounds, the elimination of toxicity or reactivity, recovery or recycling of specific compounds, or a process liquor treatment for gross reduction in chemical oxygen demand (COD).

Typical industrial applications for the WAO process have a feed flow rate of 1 to 50 m³/h (4 to 220 gal/min) per train, with a COD from 10,000 to 150,000 mg/L (higher CODs with dilution).

One of the most common industrial applications for the WAO process is the treatment of spent caustic wastewater streams generated by ethylene facilities and refineries. The process is used for the oxidation of reduced sulfur species, including sulfides and mercaptides completely. By increasing temperature and pressure, complex organic contaminants such as phenols also can be broken down into either carbon dioxide and water or biodegradable short-chain organics. By applying WAO, odor associated with sulfides and mercaptides can be eliminated, and the treated spent caustic is suitable for discharge to a conventional biological treatment process.

Another widespread application of WAO has been for the treatment of municipal solids. Most of these systems are low temperature, and low-pressure designs commonly referred to as low-pressure oxidation (LPO). An LPO system uses temperatures and pressures of less than 220°C (425°F) and 35 Bar (500 lb/in.²). Under these conditions, solids are broken down to enhance dewaterability. When higher temperatures and pressures are applied, destruction of volatile solids occurs, and WAO can be used for solids destruction, a possible alternative to incineration.

**Biological and water activation processes.**

Biological treatment solutions are typically included as a part of fully integrated water treatment solutions. They often are required when dealing with highly challenging industrial wastewaters and/or where there are very stringent discharge standards in place. These processes can include subsurface applications, anaerobic digestion processes, various aeration methods, such as bubble diffusers, and activated sludge techniques.

The biological treatment system can be enhanced by incorporating powdered activated carbon treatment (PACT) systems. One proprietary specialized WAO design developed at the Rothschild facility is designed to treat solids generated by PACT biological systems. The WAO process simultaneously destroys organic solids and regenerates powdered carbon for reuse in the PACT system. The system has been used for multiple municipal and large industrial PACT systems.

**Separation and filtration processes.**

The Rothschild facility also conducts studies that evaluate the use of physical separation and filtration processes. This includes gravity settling, flotation, media filtration, ultrafiltration, and reverse osmosis for separating oil from water in downstream polishing and facilitating water reuse requirements for customers.

**Practical Application**

The standards set out in China’s current 5-year plan require a maximum COD concentration in discharged water of 40 mg/L. By comparison, the equivalent COD discharge limit in the U.S. is 150 to 200 mg/L. The new plan also requires that total nitrogen (TN) discharge levels be less than 40 mg/L.

These new and more stringent standards are presenting challenges for operators of refineries and petrochemical facilities throughout China. This was the case for the Anqing refinery on the banks of the Yangtze River, 805 km (500 mi) west of Shanghai. The facility had just completed the construction of a new water treatment facility. Undertaking a complete rebuild of the facility to comply with new regulations was not economical. The facility’s operator instead elected to repurpose and modify as much of the existing
treatment equipment as possible. The Rothschild testing facility, located nearly 1,127 km (7,000 mi) away, played a crucial role in making this possible.

The existing treatment facilities consisted of two powdered-activated carbon treatment (PACT) systems (one for oily facility operations and one for salty facility operations). Existing wastewater treatment process units for the original design of each of the oily and salty facilities included PACT biological treatment systems and sand filtration systems, along with a shared common wet air regeneration (WAR) hydrothermal unit and a common solids thickening system. The Anqing refinery’s existing WAR system features a defined carbon regeneration capacity. Maximizing its carbon dosing capability was an important design criterion in the upgrade plan.

As part of the upgrade, a bench-scale, proof-of-concept study was conducted using final effluent samples from the wastewater treatment facility. Also, samples of the Anqing oily and salty wastewaters and treated effluents were shipped to the Rothschild facility to validate the fieldwork and confirm the upgrade plan.

The validation work consisted of bench-scale PACT system treatability testing and laboratory analyses to screen-powdered activated carbon types and dose. Process modeling also was conducted to determine the optimal configuration of process trains that would enable effluent levels to be achieved at the lowest possible cost to the operator.

After extensive testing at the Rothschild facility (along with field testing), the decision was made to convert the salty PACT system into a proper two-stage PACT process to meet the new effluent quality standards.

Additionally, larger first-stage PACT system anoxic and aerobic bioreactors and clarifiers were constructed. This allowed the first-stage effluent to be routed to a second-stage PACT system bioreactor, consisting of a repurposed oily PACT system bioreactor. The second-stage PACT system effluent was then run through the sand filter and discharged into the Yangtze River.

For the oily treatment system, wastewater flow was rerouted to a new anoxic tank for TN control and the existing salty PACT system bioreactor to meet the new effluent COD requirement.

Pairing the refinery’s WAR system with the PACT biological system resulted in a highly cost-effective treatment solution that enables the operator to reactivate spent powdered-activated carbon. This reduces the amount of fresh carbon required in the PACT system and destroys excess biomass, thus eliminating the requirement for sludge dewatering and disposal, which can be cost prohibitive.

The system typically operates at a regenerated carbon recovery rate of up to 95%. This allows for high-quality effluents to be produced at a powdered-activated carbon cost that is ~98% lower than that for granular activated carbon — all without affecting the ability of the operator to meet effluent standards.

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