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HYDROCARBON PROCESSING®

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Meeting strict government standards for wastewater reuse and improved water quality

China's recent three Five-Year Plans have put clean water in the forefront. For example, new central government requirements for reducing chemical oxidation demand (COD) in refining and petrochemical wastewater effluents and controlling their use of freshwater sources have gotten increasingly strict. As a result, China has driven greater wastewater reuse of these industries and the need for more sophisticated treatment technology to achieve the new effluent and wastewater reuse standards.

The Chinese government's 13th Five-Year Plan (2016–2020) presented the latest in a series of increasingly stringent discharge standards for China's petrochemical industry, including China Petroleum and Chemical Corp.'s (Sinopec's) Anqing refinery.

The standards set out in the current plan require maximum COD concentration in discharged water to be limited to 40 mg/l. By comparison, in the U.S., where discharge standards are measured as biochemical oxygen demand (BOD), the equivalent COD discharge limit would be 150 mg/l–200 mg/l, which are levels much higher and far less stringent than China's new standard.

The current plan also reduces total nitrogen (TN) discharge levels to less than 40 mg/l, requiring an additional biological treatment step to achieve compliance.

Coupled with these technical challenges, another factor that made the new discharge standards particularly pressing for the Sinopec Anqing refinery is the high visibility of its location on the north bank of the Yangtze River in Anhui Province. This location is approximately 500 mi west of Shanghai, where the river flows into the East China Sea. Not only is the Yangtze River China's longest—and the world's third-longest river—but it is also the world's longest river contained completely in one country. This means China has virtually complete control over its water quality.

How important is the water quality of the Yangtze? The Yangtze Basin accounts for more than one-third of both China's total surface water resources and its total population—a population responsible for more than 40% of the country's GDP.[1]

To meet the new wastewater effluent standards in the 13th Five-Year Plan, the Anqing refinery decided to build on the existing design and in-place process equipment of its wastewater treatment plant built to meet the standards of the earlier 12th Five-Year Plan.

How the Anqing refinery met the new, stricter water treatment standards. For the Chinese petroleum and chemical industries, these new standards present challenges such as:

- Defining the appropriate and cost-effective technology that will consistently produce water quality that meets the new effluent standards.
- Maximizing the use of existing infrastructure in the revamp plan that must work in concert with the newly added technology.

A successful approach to adhering to the new standards would involve reconfiguring existing equipment and process units, as well as adding new process treatment trains to achieve the required high levels of treatment efficiency.

The Anqing refinery had just completed construction of a new water treatment plant, so to undertake a complete rebuild of this system was not necessary nor economical. That is why the technical strategy for meeting the government's new, stricter water treatment standards was to repurpose or adapt as much of the existing equipment as possible to a new design and treatment strategy, installing new equipment only where necessary.

This approach solved the challenge of the new Five-Year Plan standards, while making both technical and financial sense. For help, the refinery turned to its water treatment solutions partner[a], which supplied the existing equipment and systems.

FIG. 1. The refinery's wastewater treatment process units include PACT biological treatment systems and a wet air regeneration (WAR) hydrothermal treatment unit.

The existing treatment facilities consisted of powdered activated carbon treatment (PACT) systems (**FIG. 1**), one for each of two separate plants:

- **Oily plant operations,** where the treated wastewater is used for cooling water make-up. This system cost-effectively treats low-salt wastewater from petrochemical, steam stripping and oily wastewater refinery operations.
- **Salty plant operations,** from which the treated water is discharged to the Yangtze River. This system cost-effectively treats high-salt wastewater from the refinery production process, including highly toxic and malodorous spent caustic, as well as alkaline wastewater from petrochemical spinning (acrylic fiber) and polymerization operations.

As previously mentioned, the challenges for the new treatment facilities included the need to meet new, more stringent effluent discharge standards for COD and TN content for both treatment facilities (< 50 mg/l and < 40 mg/l, respectively). In addition, the facility had to handle a 25% increase in designed COD load from the oily plant compared to its original design capacity.

The 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 sludge thickening system.

The required performance limits for the PACT system/sand filter effluent PACT for the oily and salty facilities are shown in **TABLE 1.**

TABLE 1. The required performance limits for the PACT system/sand filter effluent PACT for the oily and salty facilities

Item	Unit	Process performance guarantee value
Oil PACT system/sand filter effluent PACT		
pH	–	6–9
Oil	mg/l	≤ 2
TSS	mg/l	≤ 10
COD_{cr}	mg/l	≤ 40
BOD_5	mg/l	≤ 10
NH_3-N	mg/l	≤ 5
TN	mg/l	≤ 35 (max); ≤ 30 (average)
Sulfide	mg/l	≤ 0.1
Phenol	mg/l	≤ 0.1
Phosphorous	mg/l	≤ 0.5
Salty PACT system/sand filter effluent PACT		
pH	–	6–9
Oil	mg/l	≤ 3
TSS	mg/l	≤ 10
COD_{cr}	mg/l	≤ 50
BOD_5	mg/l	≤ 20
NH_3-N	mg/l	≤ 5
TN	mg/l	≤ 35 (max); ≤ 30 (average)
Sulfide	mg/l	0.5
Volatile phenol	mg/l	≤ 0.1
Phosphorous	mg/l	≤ 0.5

Effluent COD: Test runs demonstrate good news. The refinery's water solutions partner[a] used bench-scale laboratory test results to formulate carbon isotherms that defined the process configuration and changes required to meet the new effluent COD standards.

The PACT biological treatment system relies on powdered activated carbon dosing into the biological system and regeneration of that carbon using the WAR technology. The Anqing refinery's existing WAR system features a defined carbon regeneration capacity, so maximizing its carbon dosing capability was an especially important design criterion in the upgrade plan.

As part of the refinery's upgrade design and engineering phase, its water solutions partner's field services personnel conducted a bench-scale, proof-of-concept study using final effluent samples from the wastewater treatment plant. In addition, samples of the Anqing oily and salty wastewaters and treated effluents were shipped to the partner's headquarters to validate the work performed in the field and confirm the upgrade plan.

The evaluations were performed in a 1,000-m^2 pilot testing plant supported by more than 500 m^2 of analytical testing laboratories—one of the world's best-

FIG. 2. The refinery's WAR is used to reactivate spent powdered activated carbon from its PACT system.

equipped facilities for analyzing industrial, municipal and hazardous wastewaters, waters and sludges.

The validation work consisted of bench-scale PACT system treatability testing and laboratory analyses to screen powdered activated carbon types and dose, as well as process modeling to determine the optimum configuration of process trains needed to achieve the required treatment at the lowest possible cost.

Typically operating at a regenerated carbon recovery rate of up to 95%, high-quality effluents can be produced at a powdered activated carbon cost of 97%–98% lower than the typical cost for granular activated carbon producing the same quality effluent.

Effluent TN: Denitrification process units added. The effluent discharge specification for TN introduced a new challenge to the current wastewater treatment process. Much of the nitrate nitrogen (NO_3-N) created during nitrification would need to be converted to nitrogen gas by a biological process known as *denitrification*.

This new process step required the addition of anoxic (oxygen-limited) biological process units immediately upstream of the PACT aeration tanks. The addition of a readily biodegradable substrate, such as acetate, is normally required to promote high-efficiency TN removal. However, the need for this nutrient was controlled and kept to a minimum by routing the filtrate from regenerated carbon to the anoxic reactors. The regenerated carbon filtrate contains an abundant source of soluble, biodegradable substrates, thereby optimizing the use and cost of this essential nutrient.

Salty wastewater treatment system. Because of its greater COD loading design, the salty PACT system was converted to a true two-stage PACT process to meet the new effluent quality standards. New, larger first-stage PACT system anoxic and aerobic bioreactors and clarifiers were constructed. The first-stage effluent could then be routed to a second-stage PACT system bioreactor, consisting of an existing, but repurposed, oily PACT system bioreactor. The second-stage PACT system effluent is then run through the sand filter and discharged to the Yangtze River.

Oily wastewater treatment system. To meet the new effluent standards, the oily PACT system bioreactor needed to be larger, and the existing salty PACT system bioreactor provided the right volume for this need. The oily PACT system upgrade was accommodated by rerouting oily wastewater flow to a new anoxic tank for TN control and to the existing salty PACT system bioreactor to meet the new effluent COD requirement.

PACT system technology: Synergistic cleaning efficacy. The refinery's PACT system combines powdered activated carbon adsorption and biological treatment synergistically to maximize the cleaning efficacy of each. PACT system treatment also provides the refinery with three key advantages for high-quality effluent water when compared with granular activated carbon column treatments. These advantages include:

1. Powdered activated carbon costs far less than granular carbon used in filtration columns
2. Because powdered activated carbon is powdered instead of granulated, it offers more active surface area per equivalent mass than granular carbon
3. Powdered carbon interacts more efficiently and thoroughly with treated water inside the bioreactor, and the required dose can be tailored to the precise discharge requirement.

WAR to reactivate spent powered activated carbon. Pairing the refinery's WAR system with its PACT biological treatment system enables it to reactivate spent powdered activated carbon (**FIG. 2**). This significantly reduces the amount of fresh carbon required in the PACT system, while destroying the excess biomass and eliminating the need for costly sludge dewatering and disposal. Typically operating at a regenerated carbon recovery rate of up to 95%, high-quality effluents can be produced at a powdered activated carbon cost of 97%–98% lower than the typical cost for granular activated carbon producing the same quality effluent.

Takeaway. China's system of Five-Year plans has guided the nation's development and modernization. With each Five-Year Plan, the government has shown an increasing focus on the reclamation and preservation of the country's natural resources with ever-stricter environmental regulations. In doing its part, Sinopec has stepped up its water treatment capabilities to help minimize the impact its oil and gas refining operations have on the environment, while also maximizing the cost-efficiency of those operations. HP

NOTES

[a] Siemens Water Solutions

LITERATURE CITED

"HKH River Briefs," China WaterRisk, 2018, online: http://www.chinawaterrisk.org/wp-content/uploads/2018/09/HKH-River-Briefs.pdf

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