

RO Petrochemicals

By Flora Tong & Peter Aerts

Industrial growth in China over the past 15 years has dramatically increased the discharge volumes of wastewater from all industrial sectors. The petroleum/petrochemical industry, which produces chemicals using oil and natural gas as major raw materials, occupies an important position in the world's manufacturing and consuming sectors. According to the China Environmental Statistic Report, the petroleum and petrochemical industry discharged 4.071 billion tons of wastewater in 2007, or 18% of the total industrial wastewater discharge volume, ranked second among all the industries in China. The chemical oxygen demand (COD) discharge volume ranked third among the industries.

Combined UF and RO for refinery wastewater reuse

The Chinese government is imposing increasingly stringent restrictions to encourage companies to treat and reuse wastewater. Refinery and petrochemical wastewater, however, is complex and contains both high levels of toxic substances (e.g., oil, phenolic, amine, ether, cyanogen and sulfide) as well as nonbiodegradable contaminants (e.g., toluene, xylene, alkyl/ aromatic hydrocarbon and their derivatives).

Wastewater in the refinery/petrochemical industry is currently treated by an activated sludge process with pretreatment of oil-water separation. Tightening effluent regulations and the increasing need for reuse of treated water have generated interest in the treatment of wastewater with advanced technologies such as those being developed by leading components manufacturers.

The following case study outlines the application of a combination of ultrafiltration (UF) and reverse osmosis (RO) at a petrochemical operation, illustrating one of the potential solutions to reusing challenging petrochemical industry feedwater in China.

Yanshan Refinery Wastewater Reuse

The refinery wastewater reuse system of Sinopec Yanshan Plant in Beijing, China, has been in operation for more than four years. The feedwater is secondary effluent from conventional biological treatment units, characterized with the presence of some residual oil (1.2 mg/L) and high COD (20 to 50 mg/L). The conductivity (1,400 to 1,900 uS/cm) and hardness (300 to 500 mg/L) was too high for direct reuse purpose. The water reuse system includes biological treatment, media filtration and a combination of UF and RO to decrease oil/COD level, remove suspended solids and for demineralization.

The integrated membrane solution for this water

reuse opportunity is a combination of outside-in pressurized hollow-fiber UF and spiral-wound fouling-resistant brackish water membranes. In total, 600 SFP-2660 elements are used in the UF systems, with a total capacity of 560 cu meters/hr. One-train capacity of the UF system is 56 cu meters/hr.

FILMTEC RO elements are used in the three RO trains, with 270 elements in the first stage and 144 elements in the second stage. The capacity of one train of the RO system is 103 cu meters/hr. A summary of the UF and RO systems is shown in Table 1. The UF permeate water is pumped directly into the RO system by high-pressure pumping after dosing scaling inhibitors, reducing agents and biocides.

Membrane System Performance

The DOW UF SFP-2660 membrane elements were used as a pretreatment to protect the RO elements from suspended solids, colloids and some large-molecular-weight organics. The SDI of the UF permeate was always below three (SDI unit). The turbidities of UF feed and permeate water were about five and 0.3 NTU, respectively.

The average trans-membrane pressure (TMP) was around 0.6 bar in 10 recent months, which indicated that the UF fouling was well managed. The UF system has had five clean-in-places in the reported period. In these 10 months of operation, the highest TMP was about 1.6 bar and far away from the design limit of 2.5 bar. The permeate flow was around 60 cu meters/hr, which was slightly higher than the design flow of 56 cu meters/hr.

Over a period of four months, the operation performance of the RO trains in the refinery wastewater treatment plant, including permeate flow and system



A Chinese petrochemical plant uses a combination of UF and RO to treat and reuse its wastewater. Even with this integrated solution, aggressive pretreatment and chemical cleaning is necessary due to the complex and toxic elements in the water.

Table 1. UF and RO Systems Summary

| Module Model | Ultrafiltration SFP-2660 | FILMTEC BW30-365 FR |
|--|--------------------------|---------------------|
| Capacity (m ³ /hr) | 560 | 309 |
| Number of Skids | 10(8R/2S) | 3 |
| Number of Modules per Skid | 60 | 138 |
| Total Number of Modules | 600 | 414 |
| Capacity per Skid (m ³ /hr) | 70 | 103 |
| Recovery | >95% | 80% |
| Design Flux (L/m ² hr) | 37.2 | 22 |

PRODUCT EMPHASIS

recovery, showed that the system recoveries of the three trains were all stable at 80%. The permeate flows of the three trains were all kept at about 100 cu meters/hr. The normalized salt passages of the three RO trains were close to 1.5% and all less than 2%.

After more than 30 instances of chemical cleaning, the RO system salt rejection was still above 97% and at 80% system recovery. The normalized permeate flow of the three RO trains varied with the operation time, but after chemical cleaning, they recovered back to above the design flow of 100 cu meters/hr.

There were pressure drop variations in the RO train that indicated the fouling nature of the RO feedwater on the first-stage RO. The periodical pressure drop

increase of the first-stage RO suggested biofouling. This could be induced by the secondary contamination of the pipes or water storage tanks.

This problem can be solved by dosing NaClO in the UF permeate pipes and keeping a 0.5-ppm free chloride in the UF permeate tank. A precaution should be taken to add the appropriate amount of reducing agent (NaHSO₃) before the RO operation to protect RO membranes from damage by oxidation. Alternatively, nonoxidized biocides could be dosed prior to the RO operation to reduce the biofouling on the RO elements and increase their life span.

Technology Gaps & Future Needs

In this case study, integrated use of UF and RO technology met the current need for reuse. The output water quality satisfied the requirements as boiler makeup, though advanced physicochemical and biological processes were required to further break down hazardous substances. Some operational concerns such as fouling of the membrane separation systems required the use of more stringent or alternative pretreatment, requiring a more complex system and investment.

For petrochemical plants, the complexity of the waste stream induces tremendous instability to the reuse system. Petrochemical waste streams may contain phenolic compounds or aromatic amines at high concentrations that are highly toxic. A membrane aromatic recovery system is a relatively new process for recovery of aromatic acids and bases.

Other challenges for reuse approaches include:

- Concentration of contaminants in recycled water for cooling towers, the chlorides that will cause corrosion if NF/RO is not adopted;

- Organics causing membrane fouling or interfering with processes;
- The creation of concentrated waste streams that are unsuitable for surface water discharge; and
- Unfavorable economics. Though technology can solve many problems, it is important to use components that perform reliably over a long period of time.

Intense research and development efforts are being applied to these issues by leading components manufacturers and system designers in the water industry. Technological advancements made today will increase performance levels and efficiency in reuse applications. [www](#)

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