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Wastewater eHandbook

## ADDRESS WASTEWATER CHALLENGES



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# Refinery Tackles Water Issues

Skid-mounted treatment unit improves water quality and cuts costs

By Mike Jenkins, Progressive Water Treatment

**THE OIL** and gas (O&G) industry requires massive amounts of water — the water/oil ratio averages 8:1. Currently, American O&G operations consume 82 billion bbl of water (1,300 times San Francisco's annual use) and produce more than 2.5 billion bbl of wastewater each year. Now, as in industry more broadly, O&G companies are placing increasing priority on water management and are beginning to look for advanced wastewater-treatment technology to address operational and economic challenges.

Across the U.S., several key factors impact upgrades:

*Aging infrastructure and tougher regulations.* Without proper infrastructure, industries can't perform efficiently at scale. The U.S. Environmental Protection Agency (EPA) estimates the country requires an additional \$500-billion investment in water infrastructure. Also, environmental concerns are spurring stricter water-disposal regulations to protect natural resources — and, consequently, intensifying the stress on already complicated water-treatment protocols. EPA standards now place the burden of wastewater treatment on businesses rather than local utilities. Numerous facilities now find their existing wastewater-treatment systems can't keep pace with today's regulations. As water use is more heavily tracked and increasingly strict wastewater

regulations are imposed on O&G facilities, many operators are looking to update treatment systems.

*Regional water shortages.* Extreme drought also is affecting industrial (and residential) water use in a variety of areas across the country, especially California, where new standards are cropping up to better manage water across the value chain. For example, California Senate Bill 1281, passed in 2015, requires all O&G operators to provide a monthly water-use statement to the state board for approval. As legislation continues to tighten, operators, still dealing with trimmed budgets because of recent low oil prices, are seeking an environmentally friendly water-treatment alternative that won't break the bank.

*Lack of in-house resources.* Purchasing a water-treatment facility or equipment requires a substantial investment of time and resources. Yet, in general, refineries now lack dedicated in-house water managers. Nevertheless, the companies must find the resources to complete water analyses, technology evaluation, scope development, vendor assessment, capital budgeting, and proposal requests and evaluation. In addition, they must perform final design work, equipment fabrication, environmental permitting, field installation and process optimization. By partnering with external experts who engineer, install and operate water equipment and

services, facility personnel can better focus their resources on their core business. Outsourcing can help take care of all the tasks related to water treatment in a comparatively short time span. Moreover, the specialists can pinpoint how to maximize on-site treatment, minimizing logistics costs associated with central treatment and disposal.

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#### TREATMENT SYSTEM



Figure 1: A large, compact skid with reverse osmosis (RO) technology meets regulations, reduces chemical costs and requires less overall maintenance.

#### ONE REFINERY'S RESPONSE

A leading oil refinery in East Texas exemplifies an industrial facility that needed a water infrastructure upgrade. Its aging ion-exchange system had become inefficient and costly to maintain. The system generated waste every two days, and chemical and treatment costs were high. The plant also desired higher-quality water to feed its high-pressure boilers. Besides addressing these concerns, the refinery had to comply with Texas' strict suspended- and dissolved-solids quality requirements for boiler feed water. So, in December 2015, the refinery decided it was time to update the site's water treatment.

The municipal water fed into the refinery didn't meet regulations for maximum contaminant levels and, thus, required pretreatment for use in the boiler system. This refinery's boiler-feed ion-exchange system required regular regeneration, causing a significant drain on revenue. Not only that, operators had to constantly manage the waste generated from the boiler feed system. The wastewater had to be treated with heavy chemicals before it could be disposed of with the rest of the plant waste. According to analysts at Jefferies & Co., the cost to a site of an industrial water-management process averages \$9–\$26/bbl of water.

To address these three key concerns, refinery managers

outsourced the facility's new boiler-feed system to Progressive Water Treatment (PWT), a McKinney, Texas-based water services company. To replace the outdated system, PWT designed and installed a large yet compact skid with its reverse osmosis (RO) technology that is engineered to comply with regulations, reduce chemical costs and require less overall maintenance (Figure 1).

#### ENGINEERING CHALLENGES

The site posed space constraints. Installing the treatment system in a hazardous area would double or triple the \$1-million+ capital cost for the project. So, instead, PWT designed a system consisting of three complete 250-gpm reverse-osmosis units mounted on one 8- × 23- × 13.5-ft painted steel skid. This enabled the unit to fit in a non-hazardous location in the heart of the plant, thus saving on capital costs for a new building and associated engineering and design labor. Additional process equipment included ion exchange water softeners, multimedia filtration, RO chemical feed systems, and a membrane clean-in-place skid to clean the RO membranes in situ. Thanks to creative engineering, the system has the ability to reuse 100% of the RO wastewater onsite, and offers the option of utilizing the reverse-osmosis reject water as feed for the cooling towers and the reverse-osmosis product as boiler feed water, to improve efficiency and reduce boiler-feed-water costs. PWT manufactured all the equipment involved in the upgrade. To save on capital cost, PWT took advantage of some existing equipment, such as tanks and chemical pumps. The safe and user-friendly system features a programmable logic controller and human machine interface for completely automated control. The skids are easy to access for any necessary repairs and require little manpower to operate, further reducing maintenance and operational costs for the refinery.

Installed in December 2015, the system should enable the refinery to reduce supply costs, improve operating efficiency, decrease maintenance costs, as well as supply consistent high-quality boiler feed water. ●

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# Really Get Bugged

Biological treatment can handle many industrial wastewater streams

By Dirk Willard, Contributing Editor

**BP MANAGEMENT** had its doubts. John Eastman's proposal was to eliminate  $\text{NH}_3$  from wastewater at the firm's chemical plant in Lima, Ohio, using a two-stage bioreactor. It started with aerobic nitrosomonas bacteria converting  $\text{NH}_3$  to nitrites in filter substrates, and then used anaerobic denitrifying bacteria to convert the nitrites to  $\text{N}_2$ . In the second stage, these bacteria were to be grown in large ponds. The pilot plant worked flawlessly and we developed a front-end loading (FEL-3) scope and budget for the process. (Adequate front-end loading is crucial for any project; see "Don't Flub Front-End Loading," <http://goo.gl/cuGZc5>.)

Think of what this means! Instead of an elaborate staged process requiring maintenance staff, bugs are your unit operation. There's a word to describe this: nifty.

Let's consider the pros and cons of biological wastewater treatment for heavy metal removal and elimination of hydrocarbons. First, most all the heavy metal winds up as a solid; this, in itself, is highly useful because the metal is removed from the wastewater. Aerobic treatment excels at converting compounds of carbon, oxygen, nitrogen and phosphorus into  $\text{N}_2$ ,  $\text{CO}_2$ , phosphates and  $\text{H}_2\text{O}$ . Anaerobic digestion of materials produces methane, enabling food-processing and similar wastes to become a source of fuel gas.

The waste composition and type of reactor determine the most-appropriate organism. Aerobic reactors use algae and bacteria. Anaerobic reactors rely on sulfur-reducing bacteria (SRB) and fungi. Anaerobic reactors minimize sludge and loss of chemicals to the atmosphere but tend to require processing in batch because of slow reaction times.

Aerobic fluidized bed bioreactors frequently offer the best economics — but require skilled operators. Often, anaerobic and aerobic reactors are paired in series, as in the  $\text{NH}_3$  cleanup process at Lima. Some research has shown that an anaerobic treatment stabilized and provided nutrients to the bugs in an aerobic process that followed. This research tends to be project-specific — so it's sensible to conduct a pilot study before full implementation.

Studies in Poland, Italy and elsewhere concluded that heavy metals are effectively, but slowly, removed from wastewater in an anaerobic environment using SRB or fungus. The resultant heavy-metals-laden sludge, of course, then requires careful disposal. A fast aerobic reaction involving algae has

successfully treated wastewater containing copper and cadmium — removing 98% of the Cu and 100% of the Cd.

Waste removal efficiencies generally depend upon the relative proportion of different bugs as well as feed stability. Promoting the growth of the best species may require trace nutrients — e.g.,  $\text{Fe}^{III}$  is added to enhance anaerobic disposal of toluene. The heavy metal or organic present also impacts efficiency. Parameters controlling digestion include: pH, which usually is low — SRB raise the pH to neutral; temperature, which generally should stay between 60° and 100°F — the water can't be frozen or boiling; initial concentration of the metal or organic — low concentration discourages bug growth while extremely high concentration kills bugs; and nutrients and their transportation. Consistency is crucial to growing and maintaining the bugs you want.

With hydrocarbons, biological reactions are highly efficient in destroying oxygen and nitrogen components. However, chlorinated compounds, like dioxins, merely are converted to materials such as vinyl chlorides or dichloroacetate that may be nearly as bad or perhaps even worse than the original waste. This is strong argument for anaerobic processing.

One refinery study showed the best results with a carbon/nitrogen/phosphorus mole ratio of 100:5:1. The actual ratio may be less important than the ratio's stability.

Heavy metals like mercury that are mixed in organics often inhibit biological growth of the best organisms. An additional problem is that the heavy metal is converted to an organo-metal that animals and plants can readily absorb. ("Consider the Consequences of Chemistry," <http://goo.gl/cvKWXA>, looks at one unfortunate example — people suffering health effects caused by wallpaper dyed with Prussian Green.)

For additional information, check:

- "Enhanced Remediation of Chlorinated Solvents from Contaminated Solvents Using a Bioreactor System," <http://goo.gl/tfqjJI>; and
- "Trichloroethylene (TCE) Pathway Map," <http://goo.gl/fI3m21>. ●

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# On-Site Tests Verify Equipment Performance

Two-stage water treatment pilot study established an effective chemical coagulation protocol

By Tim Jaglinski, Anguil Aqua Systems LLC

**ANGUIL ENVIRONMENTAL** Systems received a request to quote an oxidizer and packed tower air stripper to treat a 65-gallon-per-minute (gpm) water stream containing significant concentrations of diesel range organics (DROs), volatile organic compounds (VOCs) and some total suspended solids (TSSs). The customer's overall project goals were to reduce facility emissions, ideally to zero, and reduce maintenance activities on its cooling tower heat exchangers that resulted from fouling.

Air pollution control engineers determined that a regenerative thermal oxidizer (RTO) would meet the customer's needs but were skeptical that the air stripper would function properly given the water characteristics. So, it engaged Anguil Aqua to evaluate the water stream. After reviewing the customer-supplied water analysis, it was clear that the concentrations of the heavier organics (naphthalene and higher) were beyond their solubility limits.

Because free product was present in this water stream, any air stripper would foul quickly, impacting performance detrimentally and potentially creating a safety hazard. Anguil Aqua recommended that the customer evaluate an oil-water separation process using emulsion-breaking chemicals to remove and

potentially recover the free product before entering the air stripper.

## SEPARATION STUDY

Anguil Aqua requested water samples for an initial bench evaluation for oil-water separation. Upon receiving the samples, Anguil realized that either the chemical analysis had been done incorrectly or that the water samples received were not characteristic because free product was not detected. Anguil performed the emulsion-breaking tests anyway, expectedly meeting with little success. In addition to the emulsion-breaking tests, Anguil attempted to coagulate the water using some traditional coagulants to determine whether this approach would be suitable. It met with limited success.

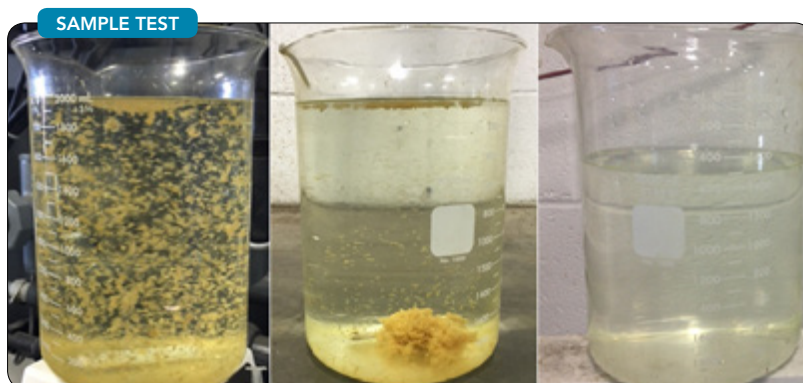


Figure 1: Coagulation and filtration reduced the amount of solids found in the wastewater samples.



Figure 2. Once the customized pilot system was set up, the operator filled the tank with process water and began treatment using the chemical formula determined in stage 1.

Based on results from the initial separation study, Anguil recommended two courses of action. First, it advised the customer to redo its analytical analysis using suggested U.S. Environmental Protection Agency (EPA) test methods to improve confidence in the baseline analysis.

Second, it suggested that a two-stage pilot study be conducted. For Stage 1, Anguil representatives would perform treatability studies on-site via jar testing. Based on the results obtained from Stage 1, Anguil would perform a full-scale, on-site pilot with the appropriate equipment for Stage 2.

**Stage 1.** Anguil representatives traveled to the site and performed jar tests (Figure 1) directly with the process water in question. Because the process water is at a temperature of 110–120 °F, Anguil was able to work with it directly rather than working with potentially compromised samples at the lab.

After a number of trials, Anguil determined that the water could be coagulated by raising the pH from 4 to 8.5, using a coagulant blend and a standard polymer. After coagulation and filtration, color, turbidity and solids content were reduced. Anguil then sent out the untreated

and treated water for analysis to determine the process' overall effectiveness. The results were promising, and the customer elected to move forward with Stage 2 of the pilot study.

**Stage 2.** Based on the site constraints and treatment goals, Anguil modified its custom pilot clarification system to perform the second stage of the study. Equipment arrived on-site and was unloaded and placed within the facility. A generator also was rented because the facility could not supply the required power easily. Anguil then unpacked and plumbed the pilot system into the existing process piping.

After the equipment was set up, pumps primed and running, the operator filled the tank with process water and began processing using the chemical formula determined in Stage 1: Raise pH > 8.5 using caustic solution, add 300 ppm coagulant and add 1 ppm polymer (Figure 2). As expected, the clarifier influent demonstrated a good floc, which began to settle quickly to the bottom of the clarification tank. With continued processing, clarity improvements were obvious as submerged parts of the tank became visible. Water samples pulled from the clarifier effluent were cleaner than the raw process water and





#### CLARIFIED WATER PROCESS



Figure 3: With continued processing, clarity improvements were obvious as sludge (left) fell to the bottom and raw water (middle) clarified (right).

reached equilibrium with continued processing (Figure 3).

After demonstrating the clarification process successfully, treated samples were tested using the same test protocol as used in Stage 1 (Table 1). In addition, a sludge sample was sent for benzene analysis to determine whether it would be considered hazardous. Sludge production rates were quantified by coagulating, flocculating and filtering specific volumes of process water. Filtered samples were wrung dry and air-dried for several days. Wet and dried samples were weighed.

#### TEST PROTOCOLS

ANALYTE	EPA METHOD
TPH-DRO, Diesel Range Organics	8015B
TPH-GRO, Gasoline Range Organics	8015B
VOC, Volatile Organics	8260B
Total Suspended Solids (TSS)	2540D

Table 1. Tests followed established methodologies.

#### PROMISING RESULTS

The qualitative and quantitative results met the customer's expectations and treatment goals. The chemical coagulation protocol and clarifier in this pilot work achieved a DRO reduction of 85% or greater and a TSS reduction of 80%. Because Anguil was proposing a ballasted floc system for the final treatment system to handle the design flow rate of 65 gpm, another set of samples was

taken for ballasted floc testing. These samples achieved similar DRO removal rates but improved on the TSS reduction to less than 1 NTU. After reviewing the sludge production rates and potential hazardous classification for the sludge, the customer asked Anguil to recommend a sludge dewatering system.

Anguil guided the customer through the equipment design and selection process by identifying and rectifying short comings in the analytical data. The final filtration installation differed from the original request as on-site jar and pilot tests allowed the customer to become educated and familiar with the treatment process while understanding the benefits, capabilities and trade-offs of the proposed system. Further, being on site allowed Anguil to understand the customer's needs and process, finding process variables that would could affect treatment system performance and allowing seamless integration of a new treatment system into the existing process. ●

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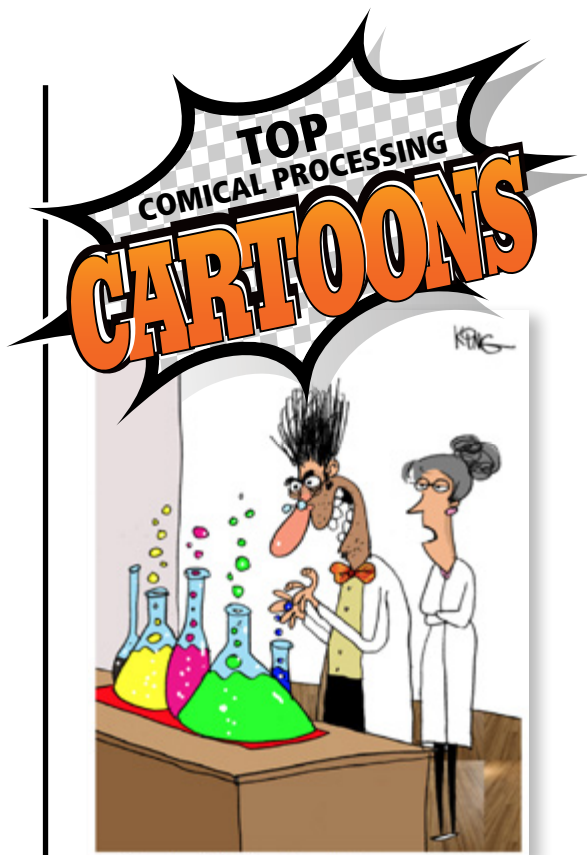
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