Mobile Wastewater Treatment Helps Remediate Concentrated Acidic Process Water at Fertilizer Plant

Bill Perpich Jr., Chris Soule, Sam Zamani, Louis Timchak,
Gary Uebelhoer, Lnsp Nagghappan, and Robert Helwick

Bill Perpich Jr. is with USFilter in Tampa; Chris Soule is with USFilter in Schaumburg, Illinois; Sam Zamani, P.E., is program administrator for phosphate management with the Florida Department of Environmental Protection in Tampa; Louis Timchak is an attorney in Lutz and receiver for the Piney Point site; Gary Uebelhoer is with Environmental Consulting & Technology in Tampa; Lnsp Nagghappan and Robert Helwick are with Veolia Water Systems in Pittsburgh.

One of the most publicized environmental cleanup projects and potentially one of the greatest threats to the Florida environment over the past four years is now making significant progress toward final closure. Part of the success in reducing the initial inventory of 1.2 billion gallons of acidic, ammonia-laden process water can be attributed to a mobile reverse osmosis system.

The former Mulberry Corporation Piney Point Phosphates Inc. plant in Palmetto has been inactive since 1999 and has been managed by the state of Florida since 2001, shortly after the owner filed for bankruptcy. To manage the site and prevent a spill of acidic, nutrient-rich process water, the Florida Department of Environmental Protection (FDEP) petitioned the court to appoint a receiver.

The court appointed Louis J. Timchak Jr., a Tampa attorney and workout specialist who immediately organized a team consisting of an onsite program manager to manage the site on a day-to-day basis, an engineering consultant to design and oversee the closure plan, and an environmental consultant to collectively take over and manage the site. Timchak and his team are funded by and work cooperatively with the FDEP to manage and close the site in accordance with federal and Florida environmental regulations.

It is important to understand how an active phosphogypsum plant operates to fully comprehend the problem. In the production of liquid and granular phosphate-based fertilizers, millions of gallons of water are required to produce water-soluble phosphate and ammonium phosphate fertilizers from phosphate rock mined from nearby reserves. All the water used in production is managed on the facility property through a series of large ponds and canals that act as plant process makeup water and a heat sink for plant operations.

In an active facility, the quantity of heat absorbed in the pond system is sufficient to keep the facility in a negative water balance mode, meaning that water evaporates and must be added as makeup water for production. When plant operations cease, the entire water balance is reversed and more water from rainfall accumulates than is evaporated, so the water balance turns positive. When operations cease permanently, as was the case at Piney Point, it is only a matter of time before the process water must be treated and discharged or transferred offsite to prevent the process water system from overflowing.

Considering that Piney Point is located along the east coast of Tampa Bay approximately 1.5 miles from a shallow water estuary, it was imperative to expeditiously gain control of the water balance in the ponds.

Industry & Facility Background

Florida Phosphate Industry

Phosphate mining in Florida began in the late 1800s, giving rise to numerous companies operating mining and processing facilities. Since then, the number of companies has consolidated to a total of five operating companies today. Operations are generally classified as those that mine the phosphate rock and separate it from its impurities, and those that process the phosphate rock to make fertilizer.

Due to its extraordinary purity (up to 70 percent $Ca_3(PO_4)_2$) and its shallow-lying phosphate ore deposits, Central Florida is one of the world's major phosphate rock mining areas and phosphoric acid producers, generating about 8 million metric tons of phosphoric acid each year. Approximately 7 billion tons of material was excavated from Central Florida from 1910 to 1981, and reserves are expected to allow fertilizer production at least through 2030.

The abandoned Piney Point facility, as seen from U.S. Highway 41 in Palmetto.

Phosphogypsum Generation

During the manufacturing of phosphoric acid, phosphate rock is reacted with sulfuric acid, resulting in the precipitation of calcium sulfate or gypsum as a waste byproduct. This waste gypsum is known as phosphogypsum.

For each ton of phosphoric acid produced, approximately 4.5 tons of phosphogypsum is generated. It is slurried with hot acidic process water and pumped to a disposal area on site, where it is deposited, creating a phosphogypsum stack, known locally as "gyp stacks."

Phosphogypsum is required to be stored onsite in a "stack" in accordance with the U.S. Environmental Protection Agency (EPA) Code of Federal Regulations, Title 40, Chapter I, Subchapter C, Subpart R, Section 61.202, due to its radioactive content. The rule authorizes limited use, subject to additional provisions; therefore, the gypsum is rendered unsuitable for use in construction materials such as wallboard.

The process water is ponded for cooling on top of the phosphogypsum stack, as well as in ponds and ditches next to it. Due to impurities in the phosphate rock deposits and its low pH, process water contains high concentrations of metals. Finally, it is returned to the facility for reuse and for the recovery of as much phosphate as possible.

Normally an active chemical processing plant operates in a negative water balance mode due to an exothermic reaction of phosphate rock with sulfuric acid and subsequent large heat input into the process water that induces evaporation. In the event of excessive rainfall, or if the processing plant is not operating, excess process water that can not be recycled or contained within the phosphogypsum stack system may be authorized for appropriate treatment prior to discharge.

The phosphogypsum stack, together with all pumps, piping, ditches, drainage conveyances, water control structures, collection pools, cooling ponds, surge ponds, and any other collection or conveyance systems associated with transporting phosphogypsum from the plant to the phosphogypsum stack, along with the process water returned to production, is known as the "phosphogypsum stack system."

Most of the existing phosphogypsum stacks in Florida were not constructed over a liner and were subsequently found to cause groundwater contamination. In recognition of this issue, in 1993 the FDEP promulgated Rule 62-673, Florida Administrative Code (F.A.C.), which specifically addressed the permitting of phosphogypsum stacks and required installation of High Density Polyethylene (HDPE) liner.

The rule included criteria for the construction, operation, closure, and long-term care of phosphogypsum stack systems, as well as the financial responsibilies for owners of such systems. This regulation was further strengthened by the amendment of Rule 62-672, F.A.C., which established critical safety standards in areas of construction, operation, inspection, and water management.

Phosphogypsum stacks are typically constructed at natural grade, range in height from 50 feet to 300 feet, and can be as large as 900 acres. Process water is contained in a pond, or ponds, on top of the gypsum stack as free water and in the pores of phosphogypsum crystals as interstitial water. Currently in Florida, there are 24 phosphogypsum stacks spread over nearly 8,000 acres of land that contain an estimated 1.2 billion tons of phosphogypsum and hold more than 50 billion gallons of nutrient-rich, acidic process water.

All the process water within the active phosphogypsum stack systems yet to be closed must some day be treated and purged before these sites may be deemed secure (closed). Typical of industrial wastewater, every site has unique water characteristics. In the case of phosphate fertilizer plant process water treatment, there is no universal solution since the characteristics of the water are dependent on the type of product being produced and the degree to which the process water has been recycled. Most existing phosphogypsum stack systems in Florida have process water concentrations three to four times greater than that of Piney Point.

Each year, based on the actual rainfall registered, many sites operate a delicate balance of managing process water from pond to pond to prevent a spill from occurring. Given that Central Florida experiences an average annual rainfall of 54 inches, primarily from June through November, summer becomes a challenging time for phosphate plant managers.

Four ponds are located on top of the Piney Point gypsum stacks with a series of smaller ponds located on the west side.

Facility

The Piney Point facility, located in Manatee County, began operations in 1966 under the name Borden Chemicals and went through several owners before Mulberry Corporation purchased it in 1993. Piney Point Phosphates Inc. was a subsidiary of Mulberry Corporation. The facility was built to manufacture sulfuric acid, phosphoric acid, and ammoniated phosphate fertilizers.

On February 1, 2001, Mulberry Corporation notified the FDEP that it lacked the funds to maintain the operation at Piney Point Phosphates in Palmetto and Mulberry Phosphates in Bartow and requested state intervention. The FDEP discussed the matter with the EPA and solicited emergency federal assistance to prevent an environmental catastrophe. Six days later, the EPA assumed responsibility for environmental security at the facility until transferring that role to the FDEP on February 21.

On February 8, Mulberry Corporation filed for bankruptcy protection. In April, the state courts ruled twice in favor of the FDEP and appointed Mr. Timchak as the receiver for both facilities, assigned the responsibility of managing the environmental issues at these sites.

Why Piney Point is a Problem

When the Piney Point facility was abandoned, its phosphogypsum stack system contained approximately 1.2 billion gallons of acidic process water, about half of which was ponded on top of the stacks or contained in adjacent above-grade cooling ponds. The water contains a variety of contaminants, such as ammonia nitrogen, phosphates, fluoride, radioactive compounds, trace metals, and other compounds in concentrations that exceed the FDEP water-quality standards for discharge.

Because of the low pH of process water, many of the constituents are at saturation levels. The presence of most constituents is a function of their naturally occurring state, except for ammonia and sulfate, which are introduced in production in the form of sulfuric acid and anhydrous ammonia.

Piney Point consists of approximately 700 acres, of which 478 acres are within the boundaries of the former process water management system watershed. This means that for every inch of rainfall, over 12 million gallons of process water are produced. As rainwater comes into contact with process water or contaminated parts of the plant, it becomes part of total volume of water requiring treatment.

The same year that Mulberry Phosphate filed for bankruptcy, heavy rains and a tropical storm prompted the receiver's team and the FDEP to take immediate action to mitigate the potential of a dike breach and catastrophic environmental damage, as the storage capacity of the system had been consumed.

From the FDEP's perspective, the principal environmental risks posed by Piney Point consisted of: 1) a catastrophic failure of the 30-plus-years-old gypsum stack dikes, releasing the acidic process water into an estuary along Tampa Bay; and 2) adverse impacts on sea grasses and marine organisms in the estuary from insufficiently treating and discharging the process water.

With respect to the second risk, decades of research had concluded that releases of nitrogen to Tampa Bay must be strictly controlled; therefore, the lime precipitation wastewater treatment system installed at

Continued on page 26

WATER MANAGEMENT STRATEGIES

Alternative	Daily Capacity (gallons)	Limitations
Re-use at CF Fertilizer Plant	250,000	Dry weather only
Re-use at Cargill Fertilizer Plant	50,000	None
Land apply through Manatee WWTP	110,000	Dry weather only
Treat at Tampa WWTP	130,000	None
Total No Discharge Alternatives	540,000	

Table 1

Continued from page 25

Piney Point during the 1980s was not sufficient to remove excess nitrogen and meet the Tampa Bay National Estuary Program Water Quality Goal, so it could not be relied upon as a sole treatment option.

The first principal risk, that of a failure of one of the above-grade dikes, was managed by employing a set of trained inspectors to monitor each dike three times per day; equipping the site with personnel, supplies, and machinery to repair boils, sloughs, and collapses immediately upon any such occurrences and, under the supervision of the geotechnical engineer, repairing and upgrading the dikes to the extent practical. Of course, these steps were simply procedures to manage the risk. Reduction or elimination of the risk could occur only by closing the site so that rainfall onto the site would not be contaminated and could drain offsite without adverse impacts.

The Piney Point facility is equipped with a two-stage lime precipitation or double lime treatment, aeration, and sedimentation wastewater treatment system. This system meets the definition of Best Available Technology (BAT) as specified in Title 40 of the Code of the Federal Regulations Part 418.13. The system reacts slaked lime with process wastewater in two stages, using above-ground reactors and in-ground, concrete-bottom clarifiers operated in series.

In the first clarifier, the pH of the process water is raised to 4.4-5.5 pH. During this reaction, fluorine, present as dissolved hydrofluorosilicic acid, is precipitated as calcium fluoride. In the second clarifier, additional slaked lime is added to raise the pH above 11.5, precipitating the remaining fluorine, metals, phosphorus, and radium.

Importantly, at this elevated pH, most of the ammonia nitrogen in the wastewater is converted to dissolved, un-ionized ammonia gas, which can be stripped using spray aeration, a process patented at Piney Point about 20 years ago.

The major disadvantages of the two-stage lime precipitation process were the chemical neutralization cost (6,000 mg/l of lime), the high sludge disposal cost, and the inability to consistently meet the site NPDES discharge standards for ammonia. Treated process water using this process meets all of the EPA's technology-based effluent limitations and Florida's water quality standards; however, the discharge flow path is along several rail and roadside ditches and then into the Bishop Harbor estuary portion of Tampa Bay.

Bishop Harbor is a shallow embayment with very limited tidal flushing due to its narrow mouth. Even though the Piney Point treatment system could achieve over 97 percent removal of ammonia, discharge rates of one million gallons per day would result in excessive ammonia loading to Bishop Harbor.

Historical point and non-point discharges by prior operators of the plant had been monitored extensively and found to be the cause of significant algae blooms. A Level II Water Quality Based Effluent Limitation (WQBEL) study formed the basis for a nitrogen limit in the former operator's NPDES permit that was only 93 pounds per day for the majority of the year. Thus, with the technology that existed at Piney Point in 2001, the maximum discharge rate achievable based on the WQBEL analysis was only 300,000 gallons per day.

Beyond Bishop Harbor in Tampa Bay, nitrogen-driven algae growth and eutrophication has been the focus of governmental action for over 30 years. Algae growth in the bay had reduced sunlight penetration in shallow waters, resulting in the die-off of seagrass beds that form the base of the marine food chain, and some fish kills caused by low levels of dissolved oxygen.

To address these problems, advanced domestic wastewater treatment plants incorporating denitrification were constructed, and numerous other point and non-point source nitrogen control initiatives were implemented—most recently under the direction of the Tampa Bay National Estuary Program and the Total Mass Daily Load (TMDL) Program. Thus, independent of the WQBEL based limits to protect Bishop Harbor, nitrogen loading from Piney Point had to be as low as possible to achieve the Estuary Program objectives.

In the absence of unusual weather, it may have been possible to manage the closure of Piney Point using the existing wastewater treatment circuit at a low flow rate during warm months and a higher flow rate in the winter; however, such plans were washed away in September 2001, some six months after formation of the receiver's team, when Tropical Storm Gabrielle passed directly over Piney Point, depositing over 19 inches of rain. This left widespread flooding and consumed all but 31 million gallons of onsite storage capacity, which equated to only 2.5 inches of additional rainfall, with the wet subtropical season not yet over.

Treatment/Disposal Alternatives

After Tropical Storm Gabrielle, the receiver's team was operating under an "emergency response" mode in order to increase process water storage capacity. A team of experts consisting of local engineers with a variety of disciplines (geotechnical, process, environmental, and regulatory) were gathered by the receiver to develop a list of alternatives to reduce the quantity of process water quickly.

In order to move the site from emergency response status to closure mode, the receiver's team and the FDEP implemented a list (Table 1) of water management alternatives. Table 1 lists only the viable implemented alternatives, understanding that many other options had been presented to the FDEP. Short-term and long-term solutions were needed that could be employed in conjunction with existing infrastructure and processes or as stand-alone technology.

The data in this table illustrate that the offsite transfer alternatives for beneficial reuse (e.g., CF, Cargill, Manatee, and Hillsborough Counties) or for further treatment (e.g., City of Tampa) were clearly insufficient to address the magnitude of the problem. Thus, discharge options had to be developed, both for the short-term recovery from Gabrielle and the long-term closure of the site.

The short-term recovery from Gabrielle and additional excess rainfall conditions caused by an El Niño occurrence during the winter of 2002/2003 was accomplished by the EPA's issuance of a Marine Protection Research and Sanctuaries Act permit to disperse fully treated wastewater in the Gulf of Mexico 100 miles offshore, using two 10-million-gallon tankers during 2003. Approximately 248 million gallons were dispersed offshore during July-November 2003.

The long-term closure effort required development of reliable, sustainable options to remove 1.0-1.5 million gallons per day (MGD) from the site over a three-year peri-

FEED WATER CHARACTERISTICS

Constituent	Typical Concentration	Contract Specification
Calcium, mg/l	551	NA
Magnesium, mg/l	229	NA
Sodium, mg/l	1,290	NA
Potassium, mg/l	196	NA
Aluminum, mg/l	8.4	NA
Barium, mg/l	0.02	NA
Bicarbonates, mg/l	0.78	NA
Sulfates, mg/l	5,200	NA
Chlorides, mg/l	100	NA
Phosphates, mg/l	1,600	< 0.5 mg/l as P
Nitrates, mg/l	0.26	NA
Fluorides, mg/l	150	< 5 mg/l as ion
pH	2.8	6.0 -8.5
Silica, mg/l	200	NA
Iron, mg/l	5.6	NA
Manganese, mg/l	2.9	NA
TDS, mg/l	11,500	< 50 mg/l
Turbidity, NTU	15	NA
TSS, mg/l	24	NA
Color, PCU	110	NA
BOD, mg/l	17	NA
TOC, mg/l	66	NA
TKN, mg/l	650	< 2 mg/l
NH_3-N, mg/l	600	< 1 mg/l

NA = Not Applicable

Table 2

od. In order to meet the expectations of the Estuary Program's scientists and the public, a nitrogen limitation of less than 100 pounds per day has been imposed by FDEP. Without advances in technology, this limitation could not have been met at the required 1.0-1.5 MGD discharge rates.

How Reverse Osmosis (RO) Became a Viable Option

Based on this scenario, the FDEP considered RO technology. RO proved to be the most promising treatment means available to produce a high-quality effluent with low concentrations of ammonia, while avoiding the neutralization and disposal costs that characterized the two-stage lime process.

The choice of RO raised two concerns. First was the absence of historical data on the performance of RO under acidic conditions. Second, the disposal of RO reject could feasibly be addressed only by sending it back to the gypsum stack. This would eventually lead to the cycling-up effect of constituents in the ponds, raising uncertainty about the quality and volume of the remaining waste for treatment before the site could be closed.

Never before had RO technology been used to treat process water for direct discharge from a phosphate plant over any appreciable length of time. Several earlier trials, some at Piney Point, proved the efficiency of RO, but the long-term impact on operation, maintenance, and materials of construction were unknown. The FDEP, however, was very enthusiastic about the use of RO technology for Piney Point, even considering the limited experience applying RO technology to phosphate process water.

The Piney Point Receiver assessed wastewater treatment proposals from several companies. Proposals were evaluated on the basis of expected cost, likelihood of technical feasibility, and assessment of the likelihood of timeliness of execution.

Recognizing the impending rainy season and the need to begin discharging treated water as quickly as possible, the receiver and RO contractor agreed to a phased approach to implement production in an effort to minimize the financial risk for both parties should the process fail. The three-phased approach was structured to treat water 24 hours per day, seven days per week, and would largely employ mobile equipment to execute a performance-based contract for water produced. Feed water characterization and effluent quality specifications are listed in Table 2.

The objective of Phase I was to produce 90 gallons per minute (gpm) of effluent continuously, to demonstrate feasibility and to reliably meet the discharge specification limits identified in Table 2. Phase I was to be completed within three months, or after 5.2 million gallons of water was produced—whichever came first. Phase II was expected to be a "ramp up" to 450 gpm of treated water, based on the knowledge and experience gained during Phase I. Phase III was optional and proposed as a lower cost extension, assuming the contractor could capitalize on economies of scale at possibly higher flow rates in the future.

System Design & Performance

In order to meet the fast-track timetable, the use of all mobile equipment was agreed upon and mobilization of equipment began immediately after the contract was executed.

Within five weeks of the contract award, startup commenced and Phase I was underway. Phase I equipment included filtration, followed by two-pass RO. Filtration consisted of dual media roughing filters, followed by multimedia polishing filters. All phases of the project and associated treatment scheme are shown in Figure 1.

The system was designed to operate at the low pH conditions in the feed water, making no adjustments. The RO system was designed for a double-pass configuration, with the first pass being operated at a very low pH (< 3.0), and the second pass being operated at a close-to-neutral pH.

The primary reason for operating the first pass RO at a low pH is to prevent the

Continued on page 28

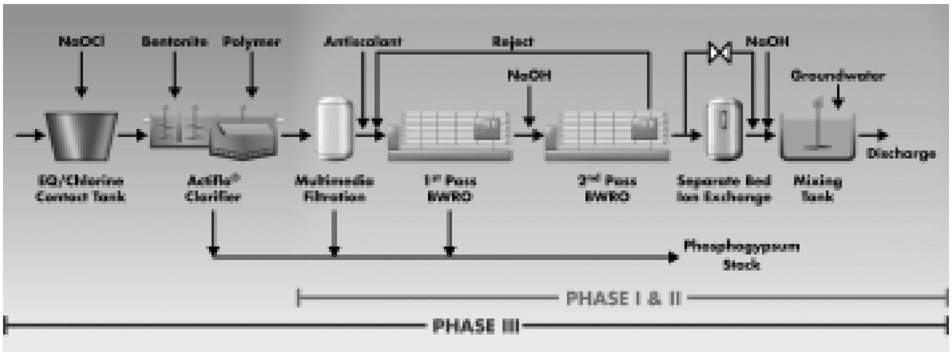


Figure 1 "LowpHRO" Process from Veolia Water Systems for Phosphogypsum Pond Water Treatment

Note: The ACTIFLO" process is a Kruger, Inc. technology.

PROCESS WATER INFLUENT SPECIFICATIONS vs. RO EFFLUENT

Parameter	Units	2002 Process Water Values	RO Effluent Quality	Contract Specifications
Color	PCU	70	NA	NA
Fluoride	Mg/l	170	<2	<5
Calcium	Mg/l	591	<0.5	NA
Phosphorous as P	Mg/l	1600	<0.2	<0.5
Ammonia	Mg/l	700	<1.0	<1.0
pH	Units	2.85	6.0-8.5	6.0-8.5
Silica	Mg/l	210	<0.5	NA
Sulfate	Mg/l	4600	<1.0	NA
Conductivity	µs/cm	10,500	<25	<50
Total Nitrogen	Mg/l	730	<1.0	<2.0
TOC	Mg/l	72	<1.0	NA
Turbidity	NTU	15	<1.0	NA

NA = Not Applicable

Table 3

Continued from page 27

scaling due to silica, fluoride, sulfates, and phosphates present in the feed water at saturated concentrations and to improve the rejection of ammonia present in the feed water. The low pH operation of the first pass RO helped in the promotion of hydrofluorosilicic acid, bisulfate, and phosphoric acid equilibrium and prevented any potential scale formation.

The primary reason for operating the second pass RO at a close-to-neutral pH is to improve the rejection of fluorides, silica, phosphate, organics, and other weakly ionized compounds present in the feed water.

Shortly after Phase I commenced, it was recognized that ammonia levels below the specification of <1.0 mg/l could not be achieved consistently because of the neutral pH operation of the second pass RO. To ensure consistent effluent quality within stringent contract specifications, ion exchange polishers were incorporated as a preventive measure.

Using standard mobile equipment, the contractor added ion exchange trailers consisting of cation and anion vessels. To reduce the ion exchange regeneration frequency, a bypass line was installed around the ion exchange trailers and a blend of 80-percent polished, 20-percent RO effluent proved to meet the specification consistently.

Polishing RO effluent produced another unanticipated challenge. Prior to actual discharge, whole effluent toxicity testing was performed to determine if the polished effluent could be discharged directly to Bishop Harbor. Because of the high purity of the polished RO effluent water, a small amount of groundwater (~5 percent of total effluent produced) had to be blended to meet the toxicity requirement before discharge. The raw process water characteristics vs. RO effluent quality during Phase I are shown in Table 3.

Progress toward the 90-gpm objective was shown during Phase I; however, the contractor was unable to average 90 gpm, even at its conclusion, because of a variety of unforeseen problems that plagued the operation. Phase II revealed problems as well, which collectively are discussed herein.

Phase II consisted of the same unit operations as in Phase I, only additional equipment was added to meet the higher flow rate. Phase II operations revealed significant deficiency in the two-stage filtration process in removing suspended solids prior to the ROs.

Membrane Fouling

Turbidity levels immediately proved to be problematic as suspended solids from the pond water passed completely through the roughing and polishing media filters, as well as the 5 µm cartridge prefilters designed to protect the RO membranes. Considering the fact that the feed water source was not screened ahead of filtration, it was not uncommon to observe grass and sticks in the filter backwash.

Turbidity due to inorganic solids from the ponds and ditches leading up to the system were manageable, but the algae population proved to be a major challenge. Seasonal fluctuations in the water temperature and the amount and intensity of daylight affected algae concentrations in the pond to an extent not anticipated before taking on the project. In fact, because of the low pH environment, nobody expected that algae could survive in the pond water.

ASTM D-4189, Silt Density Index Test Method, is used to predict the fouling potential in RO feed water. As a rule, Silt Density Index (SDI) levels < 3 are desired for RO feed waters; however, the 0.45 micron membrane filter pad used on filtered process water plugged in less than five minutes, resulting in an unmeasurable SDI.

Another source of feed water was found along the edge of the gypsum stack, where algae levels—as measured by chlorophyll-A testing—were determined to be much lower than the algae concentration in the water that was previously feeding the system. Interstitial pond water that collected in the seepage ditch along the outside toe of the gypsum stack was not subject to sunlight and contained 65 ug/L chlorophyll-A. This water also yielded much lower turbidity than the pond water. Table 4 summarizes the test results of alternative feed water sources.

Modifications to the feed piping and ditches were made, and the system began operation using feed water from the seepage ditch. In the laboratory, jar testing showed that the feed water could be more effectively filtered and backwashed if chlorine were added to kill some or all of the particulate algae.

Since the ammonia concentration of the feed water was elevated, there was concern as to how effective chlorine would be as an algaecide, knowing it would convert to chloramine. From an RO performance standpoint, chloramines were expected to be rejected by the membranes, so final effluent ammonia concentration would not be jeopardized.

To test the chlorination idea, a 2,000-gallon chemical feed tank was located at the start of the seepage ditch, and liquid sodium

ALTERNATIVE FEED WATER SOURCES

Sampling Point	pH	Conductivity (_s/cm)	Turbidity (NTU)	Total Suspended Solids (mg/L)	Chlorophyll-A (µg/L)
North Gypsum Stack					
Shallow 1 ft	3.00	12,299	5.60	6.56	3.05
Deep 6 ft	3.00	12,163	5.82	23.00	8.31
South Gypsum Stack					
Shallow 1 ft	3.07	11,461	6.02	13.40	11.40
Deep 9 ft	3.07	11,416	4.38	11.60	1.14
Seepage Ditch	**3.05**	**11,523**	**6.97**	**12.40**	**0.65**
North Cooling Pond	4.98	10,095	70.00	80.00	8.58
South Cooling Pond	3.09	12,025	12.90	21.50	10.20
Feed To RO System	3.06	11,685	28.78	20.00	8.10

Table 4

ALGAL POPULATION IN FEED WATER

Process Water to Media Filters Phase I	Algal (units/ml)
Sample 1	27,421
Sample 2	17,958
Sample 3	17,747

Table 5

hypochlorite was added at various concentrations in an attempt to kill the algae. It quickly became apparent that this approach would not work because total chlorine levels could not be maintained through the length of the seepage ditch and algae still proliferated prior to reaching the RO system. The seepage ditch water would not prove to be a viable solution to the filtration problem.

A closer look at the algae fluctuations, as measured by turbidity and chlorophyll "A" testing, determined that diurnal changes substantially affected algae populations. As such, during the summer season, turbidity levels averaged 20 NTU in the late evening and early morning, and by mid-afternoon would increase to 40 to 60 NTU.

Samples were collected and analyzed by the FDEP and found to be predominantly a euglenophyte (Lepocinclis sp.) a green flagellate and Chlamydomonas sp. Consistent with textbook description, the flagellates were <0.5 µm and could not be filtered via conventional media. The density of algae in pond water samples is summarized in Table 5.

As an interim measure to address the sub-micron-sized algae fouling, RO prefilters were switched from 5.0 µm to 1.0 µm cartridges, reducing RO cleaning frequencies; however, frequent cartridge filter change-outs and the associated labor did little to resolve the high cost of operation.

Several pretreatment technologies were evaluated and two were selected for placement ahead of the multimedia filters: continuous microfiltration (CMF) and ballasted flocculation clarification. The advantages of CMF as pretreatment for RO are well documented and were expected to be the preferred solution:

- high-quality effluent (SDI < 3) based on nominal 0.1 micron filtration rating
- extended RO membrane life
- reduced cleaning frequency of the downstream RO membranes
- reduced biofouling of RO membrane

A CMF pilot study commenced to address performance in the highly organic environment. A 30-gpm pilot unit was run for three weeks. Two membranes were tested: polypropylene (PP) and polyvinylidene difluoride (PvdF).

The first run using PP membranes was very promising in that the unit ran for four days before exceeding the transmembrane pressure (TMP) setpoint, indicating a clean in place (CIP) was required. Unfortunately, after the first clean, the CIP interval shortened to one to two days, a cleaning frequency impractical for operating a full-scale system. Coincidentally, the same CIP interval was observed with the PvdF membranes.

After the first CIP, filtrate flow rate was set to 15 gpm (~ 20 gfd); after the second, it was set to 12 gpm (~ 16 gfd); see Graph 1. CIP cleanings were performed first with citric acid, which was very effective, and then with caustic, which surprisingly was not effective at all.

Considering the source of suspended solids being organic in nature, a cleaning regimen with chlorine was tried with high expectations. A set of CIPs performed with chlorine was the most effective of all the membrane cleanings performed during the PVdF portion of the trial.

Unfortunately, the initial results could not be duplicated the very next day under the same conditions. This suggested that the membranes probably experienced permanent fouling to some degree after operating for just seven days. Each CIP became more labor-intensive, and it was concluded that organic fouling prevented a run time long enough to sustain continuous production.

Testing next focused on clarification technology in the form of ballasted flocculation using polymer and microsand Actiflo Jar test results proved effective using hypochlorite at dosing rates between 2.5 – 4.0 mg/l (total chlorine) to kill the algae. Bentonite was added to adsorb/destabilize the suspended particles, microsand for ballast, and polymer to bind the destabilized floc and enhance the settling and clarification process.

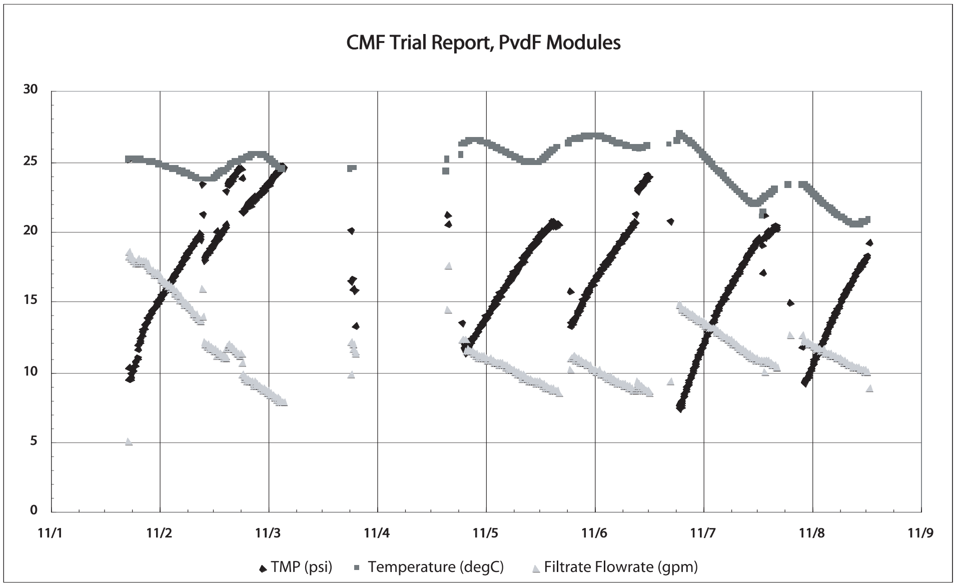
To minimize the hypochlorite dosing, more contact time would be needed prior to coagulation, flocculation, and settling. The site offered the use of an existing 300,000-gallon storage tank that provided adequate hydraulic retention time. The process chemistry devised for Actiflo yielded valuable results. At last, there seemed to be a real solution to the fouling problem associated with sub-micron algae removal.

Membrane Scaling

As indicated in Table 2, the feed water is virtually saturated with silica, fluoride, calcium, sulfate, and phosphate. Operation of a reverse-osmosis system with the above feed-water quality at elevated pH conditions was discounted due to the extreme potential for chemical scaling of the RO membranes. It would also require extensive cost for pH adjustment due to high mineral acidity of the water.

If the system were to operate at the ambient, low pH (< 3.5 pH) of the process water, it was hypothesized that scaling of the RO membranes in the first pass could possibly be minimized as a result of the following factors:

Continued on page 30



Graph 1

2004 INFLUENT AND EFFLUENT WATER QUALITY

Parameter	Units	2004 Process Water Values	RO Effluent	Contract Specifications
Color	PCU	NA	NA	NA
Fluoride	Mg/l	60	<2	<5
Calcium	Mg/l	600	<0.5	NA
Phosphorous as P	Mg/l	4200	<0.2	<0.5
Ammonia	Mg/l	800	<1.0	<0.9
pH	Units	4.6-6.5	6.0-8.5	6.0-8.5
Silica	Mg/l	40	<0.5	NA
Sulfate	Mg/l	7200	<1.0	NA
Conductivity	µs/cm	17,000	<25	<50
Total Nitrogen	Mg/l	800	<1.0	<2.0
TOC	Mg/l	91	<1.0	NA
Turbidity	NTU	180	<1.0	NA

NA = Not Applicable

Table 6

Continued from page 29

- At low pH conditions, silica and fluoride are likely present as combined soluble hydrofluorosilicic acid and thus do not contribute to solubility product species.
- At low pH conditions, sulfates present in water exist in both the sulfate and the bisulfate form and thus reduce the concentration of sulfate available, contributing to the solubility product of calcium sulfate.
- The solubility of calcium phosphate is sufficiently high at pH 3 to 3.5 to prevent scale formation.

Despite the favorable sulfate:bisulfate equilibria, at 50 percent recovery, scaling in the last-stage membranes and reject piping became an issue early in Phase I of the project. Several antiscalants specific for calcium sulfate ($CaSO_4$) were tried, but it became apparent that the maximum recovery rate in the first pass of the system could not exceed 43 percent without scaling the membranes in the final stage. The second-pass RO was operated at 85 percent recovery without adverse effect on the membranes.

Corrosion

One characteristic of the pond water that was anticipated prior to placing equipment on site was the extreme corrosiveness of the water. At pH 2.5 and high specific conductance, corrosion rates were expected to be unusually aggressive. Every effort was made to ensure that all materials of construction were either lined with protective materials vinyl ester or 80 mil polyurethane, or that the components were composed of corrosion-resistant materials, such as 316 stainless steel, PVC, HDPE, or other plastic and/or rubber compounds.

Coupon testing determined that process water corrosion rates on carbon steel were measured at 250 mils per year. Despite efforts to employ corrosion-resistant materials, some components were overlooked and experienced premature failure, and isolated instances of "holidays" in lined equipment required field repair at the first scheduled outage for inspection and preventive maintenance. No significant interruptions in performance were experienced, since all failures were quickly repaired.

Over time, the constant operating pressure of the RO around 300 psig, and quite possibly the acid conditions of the feed water, caused several RO vessels to crack and leak, requiring replacement.

With the extreme ambient temperature fluctuations experienced in Florida, the water temperature would change by as much as 10°F overnight. Accordingly, recovery rates on the system would vary continuously and required close monitoring. Given the continuous presence of three to four operators per shift, the added responsibility was manageable.

Although technical issues proved to be a significant challenge, environmental conditions made it difficult for the plant operators to do their job. Working outside on the northern edge of subtropics, with limited overhead cover, meant that much of the work was performed in the rain and direct sunlight. Pestilence proved to be an ongoing issue.

Phase III of the project followed on the heels of phase II, addressing all the issues that arose in the first two phases. About one full year of operating experience was needed before steady-state operations could be achieved.

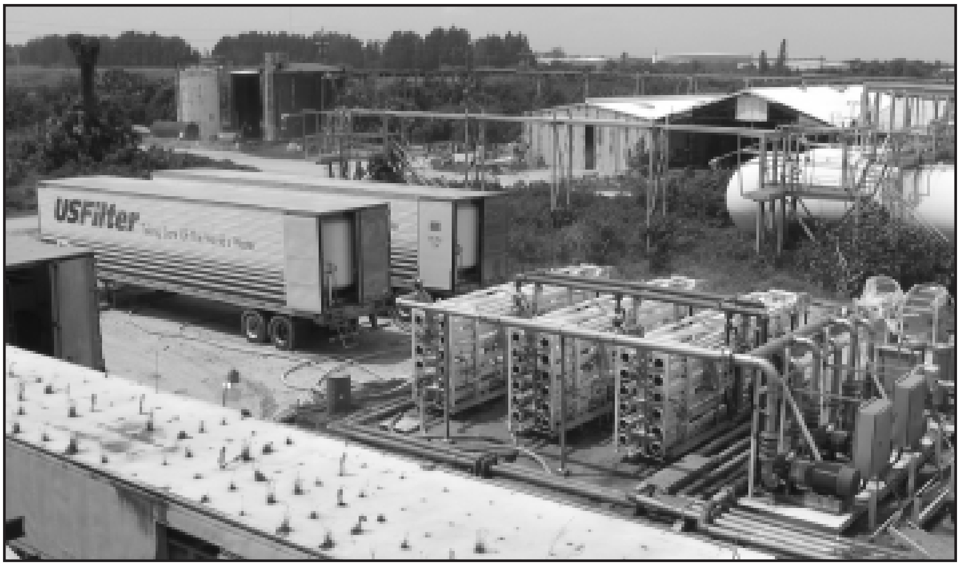
Upon the realization that precipitation/clarification would work and following the installation of two clarifiers, the contractor patched, relined, and re-bedded the media filters, added additional RO capacity, and prepared for a revised startup designed to produce 550 gpm. From July 2003 to May 2004 the contractor produced, on average, more than 490 gpm continuously.

During the later months of Phase III, as the volume of free water in the ponds decreased and the RO concentrate began to impact the ponds, the pH and TDS of the water began to change. Two years prior, the average pH and specific conductance were 3.0 and 10,500 µs/cm, respectively. Then the pH increased rapidly to 6.0 while specific conductance exceeded 17,000 µs/cm. Turbidity levels increased substantially from 15 NTU in 2002 to 180 NTU in 2004.

These changes in feed water quality were a result of the volume reduction and associated shallow water depth in the pond. As sunlight was able to penetrate the entire depth of the water column, algae growth increased significantly. Controlling algae became the limiting factor in producing good-quality effluent.

The increase in pH became a challenge in that the flocculent polymers were no longer effective at the higher pH. It was determined that daily jar testing would be essential to make corrections, as needed, to the pretreatment of the ballasted flocculation clarifiers. Table 6 shows the average process water conditions for 2004 and RO performance.

Continued on page 36



About half the Piney Point treatment system that includes media filtration, 2-pass RO, and off-site ion exchange regeneration.

Continued from page 30

RO performance demonstrated conclusively that effluent could reliably meet contract specifications. RO effluent was blended with double lime, precipitated effluent, to remain below the site discharge limit of 100-lb/day un-ionized ammonia.

Shaw Environmental Inc., the program manager for the receiver, was responsible for balancing double lime treatment with RO effluent. This made site management of the treatment systems very challenging. Shaw is under contract with the receiver to manage the entire site and to prevent a spill from occurring, while remediating and ultimately closing the site.

In November 2003, the site was moved from an "emergency response" mode to "closure" mode and the next step was to begin closing the individual ponds or cells by lining them with an 80 mil HDPE liner. The plan called for lining three of the four ponds that occupy the gypsum stack by August 2004 and the last stack in early 2005. At the time this article was completed, the gyp stack closure was on schedule.

Conclusions

The benefits recognized from RO treatment compared to the other technologies are:

- Timeliness in installation, start-up, and water production.
- Modular equipment that enables flexibility to expand or add unit operation(s).
- High-quality RO effluent can be discharged and thus reduce the threat of an unplanned or uncontrolled release.
- Concentrate that remains results in smaller volume to "double lime" treat for final solution.

To date, RO technology has treated more than 350 million gallons of process water, ultimately discharged to Tampa Bay. Site closure activities are scheduled to complete lining of the existing ponds during 2005. Final treatment and disposal of the remaining free and interstitial water will be accomplished using both RO and the lime precipitation circuits.

In the end, the Piney Point site will be used to help solve the Tampa Bay area's water supply shortages, as the lined ponds eventually collect rainwater for disposition as a source of supply water. A site that once posed potential disaster for a coastal estuary soon will become a reservoir and water source with the capacity to hold 1.2 billion gallons of fresh water.

NOTE: This article was presented as a technical paper at the 65th annual International Water Conference® in Pittsburgh, Pa., October 17-21, 2004.