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Chemical Makers Transform Their Water Sourcing

Minimizing potable water intake is becoming more important as are conservation efforts

By Seán Ottewell, Editor at Large

IN THEIR ongoing efforts to optimize water use, large chemical manufacturers including Dow, Solvay, DuPont and BP are adopting a variety of strategies. These range from establishing partnerships with local water treatment companies and municipal water suppliers to getting involved in European Union (EU) research projects to investing in emerging technologies.

Dow, as one of the world's largest chemical companies as well as a leading provider of separation and purification technologies, takes a very broad view of the issues associated with water use, stresses Snehal Desai, global business director for Dow Water & Process Solutions, Edina, Minn.

As an example, he cites the Terneuzen site in the Netherlands (Figure 1), Dow's biggest in Europe: "The nearby city and important surrounding agriculture sector also make big demands on supplies of fresh water there. At one point the city was bringing in all its fresh water from over 120 km away," he says.

So, Dow and two local organizations — Evides water company and the Scheldestromen municipal water board — established a public/private partnership to develop an integrated water use strategy.

Following installation of Dow's own reverse osmosis (RO), fouling-resistant membrane and ion exchange resin technology at Evides' water treatment plant, the flow and quality of permeate now is said to be ideal for use at the chemical site. Currently about 30,000 m^3/d of the city's wastewater is purified and used for steam and various process streams. "So that amount of water is now available for other uses by the city or agricultural sector. On top of that, Dow reuses the water again in cooling towers," notes Desai. [For more details on efforts at Terneuzen, see: http://goo.gl/g6lkU0.]

By 2020, the company hopes to eliminate entirely its reliance on remotely sourced fresh water at Terneuzen and to exclusively use water sourced from the regional water-recycling program.

A similar project is underway at the company's Tarragona site in southern Spain. Here, the local wastewater treatment plant uses Dow's fouling-resistant membranes in the first pass and its low energy membranes in the second pass to supply 40% of the water used by the site's cooling towers.

"This project is important because Tarragona is a very water stressed region. By using reclaimed water for industrial purposes, more water becomes available for municipal uses and the Ebro River Basin, which is a natural area protected by the UNESCO [United Nations Educational, Scientific and Cultural Organization]," adds Desai.

The goal is to be able to use up to 90% of reclaimed water at the site in the coming years — a strategy that also will involve the Tarragona plant installing filtration, ultrafiltration and RO treatment technologies to reuse its own wastewater more efficiently.

Figure 1. Large chemical complex at Terneuzen is in an area with many demands on fresh water supplies. *Source: Dow.*

SUSTAINABILITY METRIC

Water optimization plays an important part in Dow's overall quest for improved sustainability of its processes and products. The company has developed a sustainable chemistry index that considers how well managed resources are; it uses that metric to set goals and measure its performance (see "Sustainability Metric Spurs Efforts," p. 55, http://goo.gl/EVqItu). The company already has significantly exceeded its 2015 target.

For water, Dow uses a three-step approach. The first step, reduce, focuses on fairly routine activities such as optimizing plant pipework and wastewater treatment systems, and using high efficiency cooling towers. Second is reuse, which includes the Terneuzen and Tarragona projects. Desai sees further improvements coming in this step as techniques pioneered by the food and beverage and hydraulic fracturing sectors for reusing their plant outflows become more widely accepted in the chemical industry.

The third step is renew, which brings desalination of seawater and brackish aquifers into the equation. "However, our view is that you have to pursue the first two "Rs" very, very aggressively before you move on to the third one," he notes.

Desai also believes that future success will lie in "courageous collaboration" with organizations that might not be obvious partners for chemical companies.

One example is the Value of Water Coalition, Washington, D.C., www.thevalueofwater.org. Established in March, this group aims to increase understanding of water challenges in the U.S. and the need for major investments in infrastructure to address them. It was formed originally by water utility companies in very large U.S. cities and engineering companies that work with them.

"The industrial water user was missing from this setup… and you have to remember that, in terms of water use, the industrial sector is second only to the agricultural sector. Remember, too, that the industrial users, particularly chemicals, rely on robust and reliable municipal wastewater-treatment systems," Desai stresses.

Initiatives such as the Value of Water Coalition will bring broader attention to water challenges. However, successfully addressing these challenges will require improvements in technology, he believes, adding that filtration and RO are very much part of the mix. He sees several critical issues. One is scale. Another is development of technologies that can treat increasingly difficult waste streams while suffering less fouling, cutting energy use and offering longer lives. Then there is technology integration. "We'll need more integration, experimentation and willingness to use new technologies — along with an increased incorporation of green infrastructure such as [at] Dow's Seadrift operations in Texas," he concludes.

STRATEGIC EFFORT

Water optimization efforts at Solvay, Brussels, Belgium, are part and parcel of its Solvay Way sustainability strategy.

"There are two main aims of the strategy: first, to reduce by 10% by 2020 (from a 2012 baseline) the water drawn from groundwater or drinking water networks and, more importantly, to ensure that hydraulically stressed sites have sustainable water management in place by 2020," notes Laurent Sapet, Solvay global environmental director, Lyon, France.

A detailed water balance carried out in 2014 found that 13 sites were at risk from water scarcity. Of these, four already are making strides in demonstrating sustainable water management.

One is the Banksmeadow plant in Sydney, Australia. Here, the company has replaced potable city water with non-potable water from the nearby Orica treatment plant that handles contaminated groundwater from the Botany aquifer. The Orica plant now provides half of Bankmeadow's water needs. The use of treated groundwater has necessitated more sophisticated control of treatment chemicals within the cooling water circuits and changes to the operation of the demineralized water unit.

Similarly at the company's site in Monterrey, Mexico, more than 90% — 115,000 m^3/y — of its needs come from a water recycling project at the local municipal wastewater treatment plant.

At Panoli, India, the focus has been on reusing the company's own wastewater, especially as cooling water makeup and boiler feedwater. The project has involved upgrading several items of plant equipment, including the biological treatment unit, RO units, a multiple effect evaporator and a water hardness abatement unit. Thanks to these investments, the plant reuses 80% of its wastewater multiple times, while 35% of water now comes from contaminated groundwater rather than good quality surface water.

Its Vernon, Texas, plant originally depended on water supplied by the city. The manufacturing process there relies on water-intensive product washing steps. Redefining washing conditions enabled minimizing water use while still meeting product specifications. This, in combination with a successful recycling project, has cut water consumption by 20%.

The next target is to implement sustainable water management at the remaining nine plants in water stressed areas.

Sapet emphasizes that not all water optimization projects require huge commitments of time and money: "At our Baotou plant in India, we just picked the low-hanging fruit, which meant using better detection technologies to identify leaks in underground water pipes. At Vernon, we simply implemented a multi-stage washing process for a raw material which originally underwent several single-stage washings.

They were all common-sense solutions that were quick to implement and didn't require great investment."

Solvay is looking beyond what it can do on its own. The company is involved in the EU's Economically and Ecologically Efficient Water Management in the European Chemical Industry (E4Water) project.

E4Water aims to achieve a reduction of 20–40% in water consumption, 30–70% in wastewater production and 15–40% in energy use at its industrial case study sites.

One such site is that of Solvay's subsidiary Solvic in Antwerp, Belgium. There are three objectives here: evaluation and implementation of an innovation plan to decrease drinking water intake to 20% from 60%; a reduction of emission load in final effluent by replacing waste generating steps or applying advanced treatment options to concentrate streams; and the transition of the demonstration unit known as the "industrial experimental garden" into a larger-scale plant where chemical companies will be encouraged to work together to develop water reuse strategies.

Figure 2. Third-phase PTA plant at Zhuhai Chemical uses technology that reduces water discharges by 75%. *Source: BP.*

"As soon as new cost-effective technologies emerge from this project, they will be combined with the other chemical engineering technologies in our design guide which is used to optimize water use during plant designs and revamps. The name of the game here is to recycle at low cost," says Sapet.

INTERNAL COLLABORATION

At DuPont, interactions between teams of energy champions and environmental experts appointed at each site are helping to identify ways in which to improve the company's environmental footprint.

Once a month, the teams meet to collaboratively solve problems, share ideas and pinpoint ways to further reduce emissions.

At the company's Dordrecht site in the Netherlands, this strategy has helped to cut water consumption by 28% and energy use by 14% in the last nine years — reducing operating costs by over $1 million/y.

"The local energy champions have an annual target set in dollars and an evergreen list of opportunities related to utility savings or utility cost reduction. The areas focused on have to maximize the internal rate of return because they don't have their own budget and have to compete with all other business projects," explains Erik van Kempen, energy champion at Dordrecht.

One of the main factors in the 28% reduction in water consumption is improved cooling tower management. "Our cooling towers were the biggest user of drinking water because we are not allowed to use water from the nearby river. Following discussions with the vendors who supply our cooling tower technology, we were able to change our water treatment routine on one tower and this reduced the amount of tap water we purged. Due to this success, we implemented the same treatment on the site's other cooling tower."

Groundwater has become another vital resource. Normally, the plant would not be allowed to extract groundwater for cooling purposes. However, due to long-standing soil pollution in the area, DuPont received a dispensation from the local authorities to extract contaminated groundwater. "This we now treat, use and then return to the local river — again reducing our dependence on tap water," adds van Kempen.

ADVANCED TECHNOLOGY

BP's water optimization efforts are focused on developing new technologies, both with other vendors and in-house. For example, in December, BP Ventures invested in Saltworks Technologies, Vancouver, B.C., a specialist water treatment company that offers a number of technologies to help address and manage global water scarcity issues, either by using saline water sources instead of freshwater ones or by recycling wastewater, including produced waters from oil and gas operations.

Specifically, Saltworks develops new desalination processes that lower the cost and energy of making freshwater from saline water sources.

The investment follows successful bench and pilot scale tests between BP and Saltworks, although a BP spokesperson declined to comment on these.

In another thrust, in July of this year, the company announced the startup of the phase-3 purified terephthalic acid (PTA) plant at Zhuhai Chemical in China (Figure 2). With a design capacity of 1.25 million mt/y, it is the world's largest single-train PTA unit, says BP. It also is the first to use the most recent version of BP's PTA technology, which the company says boasts 75% lower water discharge than conventional technologies. (The technology also produces 65% fewer greenhouse gas emissions and 95% less solid waste, while also offering higher product yields, thus cutting demand for raw materials, claims the firm.)

BP explains the new technology reduces both the volume of freshwater feed and the volume of water that must go for wastewater treatment. Water-based streams containing small amounts of impurities that were sent for treatment in earlier generations of the technology now are more efficiently reused and recycled, resulting in reduced wastewater flow.

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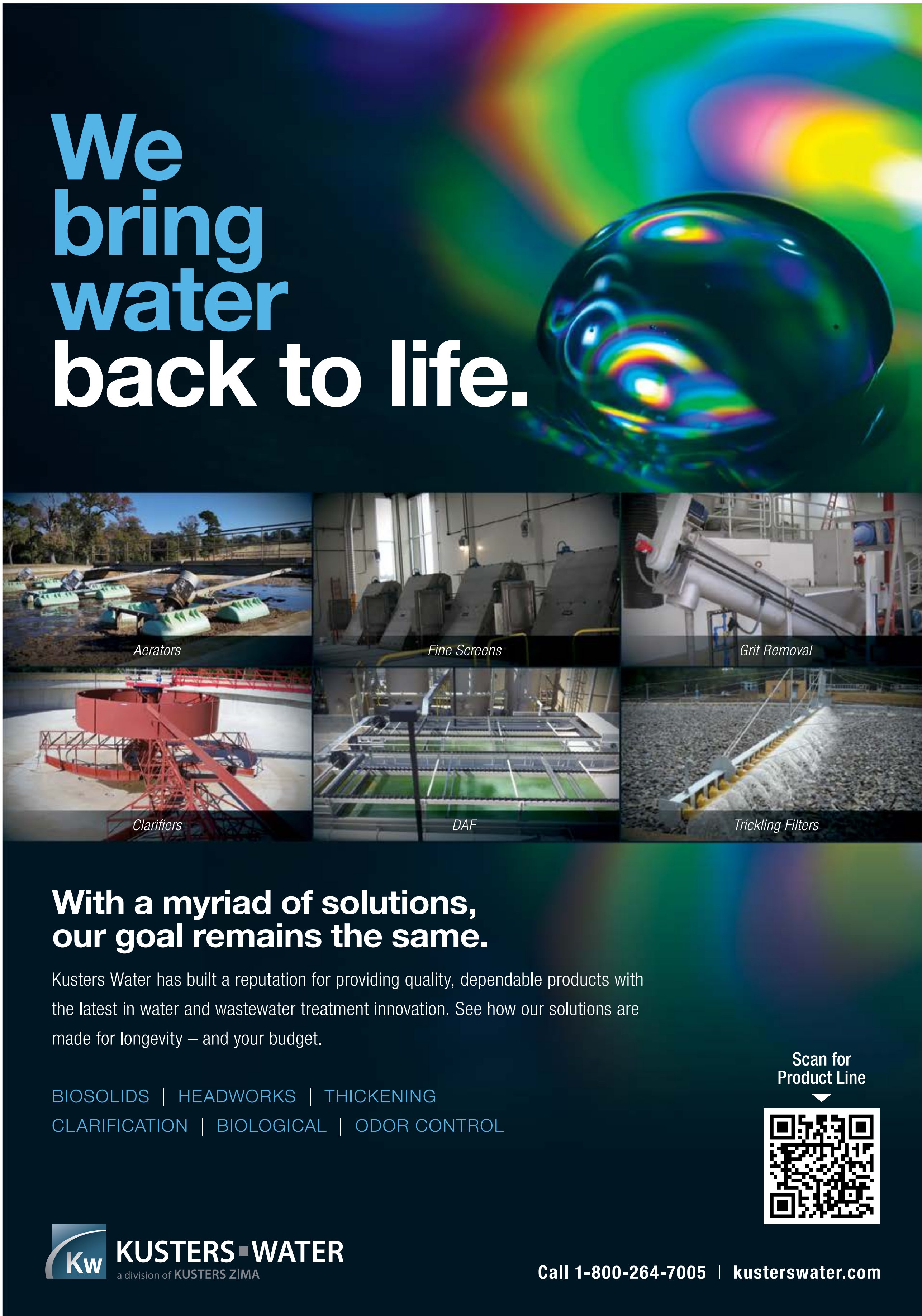
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Wastewater Treatment Method Saves Energy

Researchers develop a purification process that's carbon-negative and energy-positive

By Seán Ottewell, Editor at Large

ENGINEERS AT the University of Colorado Boulder have developed a wastewater treatment process that both mitigates carbon dioxide emissions and actively captures greenhouse gases.

Known as microbial electrolytic carbon capture (MECC), the process purifies wastewater in an environmentally friendly fashion by using an electrochemical reaction that absorbs more carbon dioxide than it releases while at the same time creating renewable energy.

Wastewater is used as an electrolyte for microbially assisted electrolytic production of hydrogen gas and OH^- ions at the cathode, and protons at the anode. The acidity dissolves silicate and liberates metal ions that balance the OH^- ions, producing metal hydroxide, which transforms carbon dioxide in situ into bicarbonate.

Results from different industrial wastewaters show 80–93% of the carbon dioxide derived from the organic oxidation — making the process carbon-negative. High rates and yields of hydrogen gas were produced with 91–95% recovery efficiency, resulting in a net energy gain of 57–62 kJ/mole of carbon dioxide captured. The pH remained stable without buffer addition and no toxic chlorine-containing compounds were detected.

"This energy-positive, carbon-negative method could potentially contain huge benefits for a number of emission-heavy industries," says Zhiyong Jason Ren, an associate professor of civil, environmental, and architectural engineering at the university and senior author of the new study, which appears in the June issue of the journal *Environmental Science and Technology*.

Wastewater treatment typically produces carbon dioxide emissions in two ways: from the fossil fuels burned to power the machinery, and the decomposition of organic material within the wastewater itself. Existing wastewater treatment technologies also consume high amounts of energy. Public utilities in the United States treat an estimated 12 trillion gallons of municipal wastewater each year and consume approximately 3% of the nation's grid energy, say the authors.

Current carbon capture technologies are energy-intensive and often entail costly transportation and storage procedures. MECC uses the natural conductivity of saline wastewater to facilitate an electrochemical reaction to absorb carbon dioxide from both the water and the air. The process transforms carbon dioxide into

stable mineral carbonates and bicarbonates that can serve as raw materials for the construction industry, as a chemical buffer in the wastewater treatment cycle itself or to counter acidity downstream from the process, such as in the ocean. The reaction also yields excess hydrogen gas, which can be stored and harnessed as energy.

The findings offer the possibility that wastewater could be treated effectively on-site without the risks or costs typically associated with disposal. Further research is needed to determine the optimal MECC system design and assess the potential for scalability.

"The results should be viewed as a proof-of-concept with promising implications for a wide range of industries," says Ren.

One he particularly points out is power; the U.S. Environmental Protection Agency's Clean Power Plan will take full effect in 2020, thus strategies to reduce carbon dioxide emissions are coming into sharp focus.

The technology also may have positive long-term implications for the world's oceans, he believes. Approximately 25% of carbon dioxide emissions are subsequently absorbed by the sea, which lowers pH, alters ocean chemistry, threatening marine organisms, especially coral reefs and shellfish. However, dissolved carbonates and bicarbonates produced via MECC could help chemically counter these effects if added to the ocean.

Many wastewater treatment plants are located on coastlines, raising the possibility that future MECC implementation in these facilities could couple both carbon dioxide and ocean acidity mitigation.

Ren's work also involves broader investigations into the use of microbial and electrochemical systems to directly convert biodegradable materials, such as wastewater and biomass into hydrogen gas, electricity and other value-added commodity chemicals. Here, his team uses molecular microbiology tools and electrochemical analyses to understand the fundamental determinant factors of those systems to enhance design, operation and monitoring — in concert with traditional approaches.

The team's microbial electrochemical technologies have two main focuses: bioenergy and commodity chemical production from wastewater and biomass; and the development and characterization of microbial fuel cells, electrolysis cells and desalination cells as part of an overall bioelectrochemical system development strategy.

Their other main focus is developing sustainable water desalination systems. Here, they are exploring technologies such as novel membranes and capacitive deionization to deal with water from oil and gas production, and in seawater and groundwater desalination.

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Sustainability Metric Spurs Efforts

Index provides insights about product portfolio and new developments

By Anne Wallin, The Dow Chemical Company

TODAY'S GLOBAL challenges — climate change, water scarcity, food provision, declining ecosystem services, human development, and the overall transition to a sustainable society and planet — require solutions of unprecedented scale. Public policy and behavior change will play a significant role in addressing these challenges. So, too, will business and technology. Indeed, in the decades ahead, these challenges offer tremendous opportunity for organizations that can contribute to tackling them.

Dow recognizes that chemistry can enable development of solutions to many of today's most pressing problems. To help strengthen the link between its efforts and these global challenges, the company created its sustainable chemistry program, which applies lifecycle thinking to help evaluate the sustainability benefits delivered by its products and science-based solutions. A key component of Dow's 2015 sustainability goals, this concept has helped drive a culture change toward understanding more holistically how the company's products and technology can address these global challenges.

As part of its 2015 sustainable chemistry goal, Dow developed the sustainable chemistry index (SCI), a metric used to assess the relative sustainability performance of its entire product portfolio. The SCI defines the 2015 goal, which is to achieve 10% of the company's sales from products "highly advantaged" by sustainable chemistry.

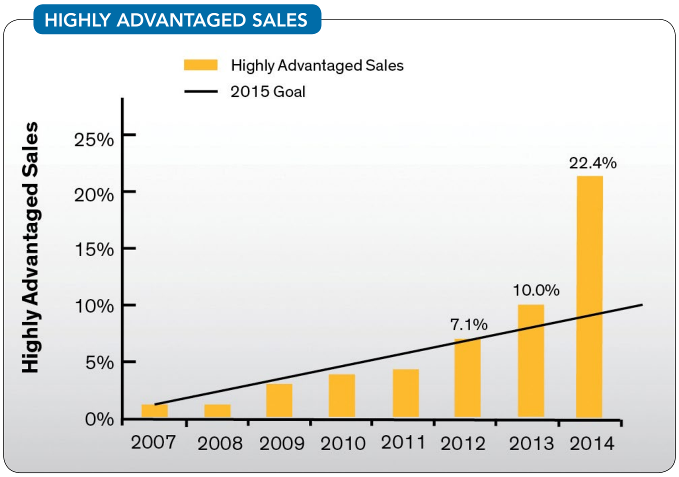

Figure 1. The company reached its 2015 goal of 10% two years early and advanced significantly further in 2014.

Building on the increasing sustainability momentum in its business units since 2007, Dow deliv-

ered 22.4% ($13 billion) of sales from products that are highly advantaged by sustainable chemistry in 2014. This result surpasses the aggressive 10% target by more than twofold, and represents the realization of sustainable chemistry efforts that have been accelerated over the last seven years under the 2015 sustainable chemistry goal (Figure 1). Additionally, our aggregate SCI score hit an all-time high of 25.0 points then, up from the 2007 baseline value of 20.4 (Figure 2). These accomplishments clearly underline the shift in the company's portfolio toward products that deliver value to society based on their ability to address sustainability challenges like energy efficiency, food production and water scarcity.

The rise in SCI performance during the 2015 goal timeframe reflects increased sustainability awareness within the Dow culture. This awareness has enabled Dow employees to better understand how to integrate sustainability into their roles, from informing business strategies to developing and communicating solutions that capture opportunities to improve sustainability. These actions demonstrate the value of the sustainable chemistry approach, which utilizes lifecycle thinking to identify products that help address sustainability challenges today, and helps position the company for success over the long term.

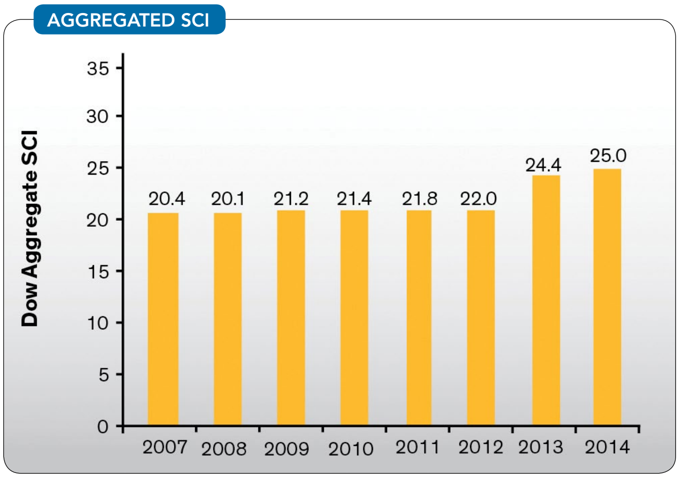

Figure 2. This score for the company as a whole reached an all-time high in 2014.

THE SUSTAINABLE CHEMISTRY INDEX

Dow developed the SCI as a tool to quantify the relative sustainability performance of the company's product portfolio. The metric is based on eight categories related to product sustainability:

- *Renewable or recycled content.* How much of the product is derived from renewable or recycled resources?
- *Resource management.* How abundant and well managed are the resources that have been used to make the product?
- *Manufacturing efficiency.* Are Dow's operations becoming more efficient relative to past performance?
- *Environmental lifecycle benefit.* Are there envi-

ronmental benefits associated with the product when evaluated from a lifecycle perspective?

- *Social need benefit.* Does the product address societal needs?
- *Manufacturing and transportation risk.* What is the level of manufacturing and transportation risk associated with the product?
- *Value chain risk.* What is the level of product risk related to the product value chain?
- *Public policy and end-of-life risk.* What is the level of risk related to public policy initiatives and posed by product end-of-life scenarios?

Dow products are rated based on questions that cover these eight categories to come up with an SCI score. The SCI defines "highly advantaged" sales based on a threshold score; sales scoring above this threshold are considered to be highly advantaged sales and are counted toward the 2015 goal. Highly advantaged products are likely to contain renewable materials, deliver environmental benefits like energy efficiency and water resource availability, address social needs like food production and drinking water, and have relatively low product sustainability risk.

Each category accounts for five possible SCI points, with a score of "five" signifying "full credit" for that category — so the best possible SCI score is 40 points. Dow business SCI scores are calculated based on the SCI scores of all products sold by each business, with scores weighted by revenue. These business scores are then similarly aggregated to produce an overall SCI score for the company.

As already noted, by 2014 Dow had surpassed its 2015 SCI target, growing highly advantaged sales from 1.7% in the baseline year of 2007 to 22.4% in 2014, and increasing its aggregated SCI from 20.4 to 25.0 over this time frame.

The company assesses and publishes an annual update of the SCI that shows its performance against the quantitative goal for highly advantaged sales and aggregated SCI under the 2015 sustainable chemistry goal.

Two examples of products that have achieved highly advantaged scores on Dow's SCI are Omega-9 oils and Filmtec Eco Reverse Osmosis (RO) Elements for water treatment.

A HIGH SCORE

The Filmtec Eco RO Elements, which are used in wastewater, power, electronics and beverage applications, are more energy-efficient than comparable membranes and have been declared a "Breakthrough to World Challenges" as part of Dow's 2015 sustainability goals. The SCI process provided a balanced look at the sustainability profile of Filmtec Eco Elements; it detailed both positives and negatives during the scoring for the eight categories. Highlights of the analysis include:

- The elements do not contain renewable or recycled content, and they use fossil resources which are limited. The product is composed of

a polymeric material that is not readily degradable according to standard test methods.

- The Dow Water & Process Solutions business unit that produces and sells the elements has improved its manufacturing process efficiency.
- All sales of this product are in applications that support water availability lifecycle benefits, which earns full credit for this key criterion in the SCI.
- A lifecycle assessment has been conducted on RO product applications, which earns the technology a bonus point in the SCI.
- Filmtec Eco Elements support water reuse, a critical need in the coming decades, which also earns the technology full credit for a key criterion in the SCI.

The total SCI score for Filmtec Eco RO Elements was slightly higher than the "highly advantaged" scoring threshold in the SCI.

IMPACT OF THE SCI

The SCI metric has helped build awareness of key sustainability concepts within Dow and assists our businesses in identifying both opportunities and risks related to sustainability across the portfolio. Among the greatest benefits of the SCI has been the sustainability-related dialogue and learning spurred by the scoring sessions and follow-up discussion of SCI scores throughout Dow business units. These dialogues have enlightened marketers on how to understand and communicate the sustainability-related attributes of their products; researchers on related opportunities that could be addressed through product innovation; and production engineers on possibilities to improve manufacturing efficiency. By creating opportunities for these discussions and interactions across business units and functions, the SCI has helped drive culture change within Dow — not only building awareness of sustainability more broadly but also helping instill throughout the company a lifecycle mindset toward evaluating product sustainability.

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ANNE WALLIN is director of sustainable chemistry for The Dow Chemical Co., Midland, Mich. E-mail her at APWallin@dow.com

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Sort Out a Sewer Snafu

Storm water may contribute to ongoing problems

By Dirk Willard

WE'RE HAVING problems with our plant wastewater system (Figure 1). First, we can't seem to get the nominal flow out of our new fiberglass neutralization system — we constantly back up in the neutralizer. Second, the drains in the plant are backing up. Our plant manager is convinced we're seeing overflow from a 4-in. storm-water line that was in use before the process and storm-water treatment systems were separated back in the 1970s. In addition, the city water plant complains that our wastewater is spilling over into the storm water and corroding the line from two sewer sump pumps. What do you think the problem is and what can we do to address these issues?

CHECK YOUR DESIGN BASIS

I found the velocity, V, using the Darcy-Weisbach equation:

$$V = (8g \times R_H \times S/f)^{1/2}$$

where g is the gravitational constant, R_H is the hydraulic radius, S is the pressure drop/run (i.e., head loss per length, h/L), and f is the Darcy friction factor derived from the Colebrook-White equation:

$$1/f^{1/2} = -2\log\{\varepsilon/12R_H + 2.51/(Re \times f^{1/2})\}$$

where ε is the roughness and Re is the Reynolds number.

I solved for $fV^2 = 8g \times R_H \times h/L$ and substituted into

PROCESS AND STORM SEWERS

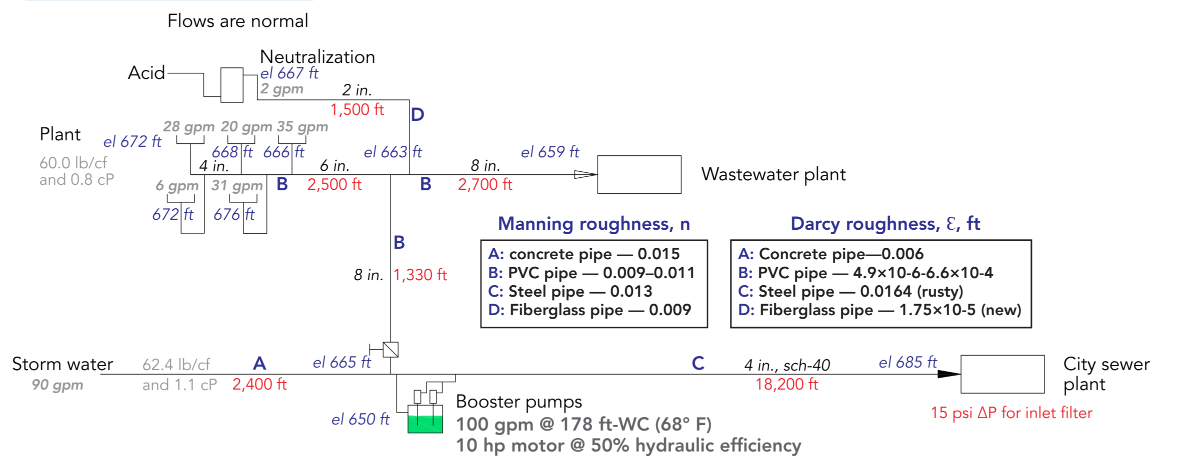

Figure 1. Backups plague wastewater treatment system.

Colebrook-White:

$$Re \times f^{1/2} = R_H V \times \rho / \nu \times f^{1/2}$$
$$= R_H \times \rho / \nu \times f^{1/2} V^2,$$

taking density, ρ, as lb/ft^3 and viscosity, ν, as lb (mass)/ft-sec. (Multiply cP by 6.72×10^{-4} for conversion.) I estimated a flow of 9 gpm assuming a 98%-filled pipe.

(Instead of Darcy-Weisbach, some would use Manning's equation:

$$Q = 624.98 R_H^{0.67} S^{1/2} / n$$

where Q is flow rate and n is roughness. However, Manning suffers from several problems: 1) n values are based on limited velocities for water; 2) it does not account for changes with Reynolds number; and 3) unlike Darcy-Weisbach, it only applies to water.)

For fiberglass or plastic pipe, the 9 gpm flow rate indicates a restriction. So, take the pipe apart and look for glue-glob joints at fittings. As a rule-of-thumb, never build with a pipe diameter less than 2 in. if the joints are to be glued. And it's a good idea to be overly generous to avoid problems — this should have been a 4-in. line.

Now, let's look at the PVC pipe. A flow of 122 gpm should be possible for the 6-in. and 8-in. lines at 60% of capacity, i.e., slightly more than a half-filled pipe using a Darcy roughness of 4.9×10^{-6} ft for new PVC pipe. For old PVC pipe with a roughness of 6.6×10^{-4} ft, 63% of the total pipe area would be required. If there's blockage in the pipe, then this area simply isn't available. There is another possibility. Roughness is based on an experiment, not your actual conditions. In addition, there is the flow upstream of the sewer catch basins. Broken concrete isn't conducive to smooth flow to the basins like well-maintained concrete.

Next, consider the city's complaint about their wastewater line. Given the elevation difference between the plant junction at 663 ft and the storm water junction at 665 ft, on the surface this seems unlikely. However, the top catch basin is at 672 ft, well above the elevation of the storm water junction. If the plant sewer line is plugged and the block valve leaked, it's possible that the plant water/toxic waste drained to the booster pumps. This line should be inspected and the connection line should be abandoned.

DIRK WILLARD, consultant, Wooster, Ohio

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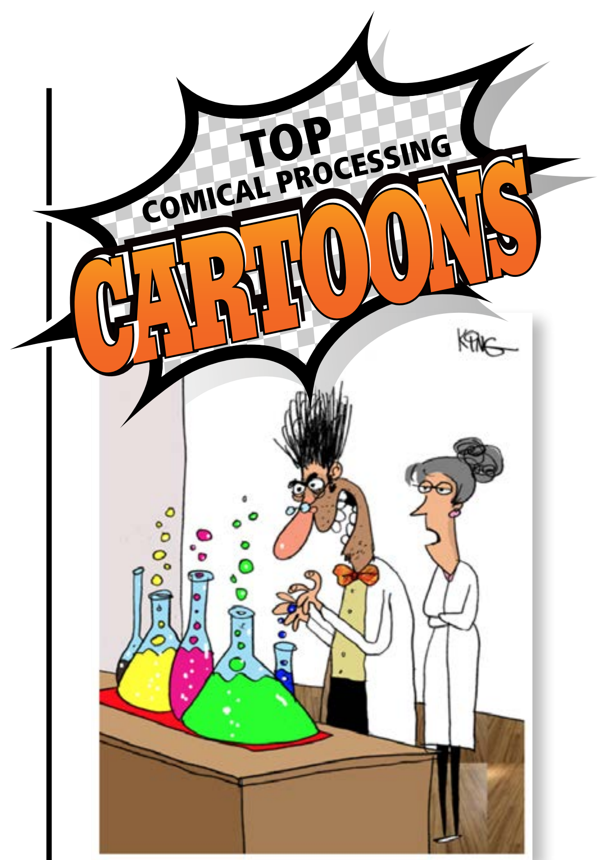

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