## HEMICAL September 2009 MWW.che.com



MULTIVARIABLE PREDICTIVE CONTROL

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## BPA

### **Editor's Page**

## **Honoring innovation**

he first round of judging in *Chemical Engineering's* 2009 Kirkpatrick Chemical Engineering Achievement Award competition (CE, January, p. 19) has produced the following five finalists (in alphabetical order):

- The Dow Chemical Co. (Midland, Mich.) and BASF SE (Ludwigshafen, Germany), for an industrial process for producing propylene oxide (PO) via hydrogen peroxide
- DuPont (Wilmington, Del.), for commercializing Cerenol a new family of high-performance polyether glycols made from corn-derived 1,3-propanediol (Bio-PDO)
- Lucite International (Southampton, U.K.), for its Alpha technology a new process for making methyl methacrylate (MMA)
- Solvay S.A. (Brussels, Belgium), for its Epicerol process a new process for producing epichlorohydrin from glycerine
- Uhde GmbH (Dortmund) and Evonik Industries AG (Essen, both Germany), for the HPPO process for making PO via  $H_2O_2$

From these five finalists — selected by heads of chemical engineering departments of U.S. and European universities — the winner will be chosen by a board of judges composed of chemical-engineering-department heads that were selected by their peers. In the December issue, the winner will be announced, along with process details for all five technologies being honored.

The aim of the biennial competition (established in 1933) is to honor the most noteworthy chemical engineering technology to have been commercialized during the previous two years, the key criteria being the novelty of the technology and the difficulty of the chemical engineering problems encountered and solved. As editor of this magazine's Chementator department, it gives me great pleasure to congratulate the chemical engineers and chemists involved in developing these noteworthy process technologies because they — the people involved — are the ones being honored. It is through their efforts and innovations that keep the chemical process industries (CPI) at the forefront of improving our standard of living, by enhancing the performance of products that are made and by reducing the environmental impact of the methods used to make them.

Each of the five process technologies being honored involve alternative routes with "greener" feedstocks, when compared with the conventional routes used to making the products. They all tout lower energy consumption, reduced side products and, thus, lower production costs. And while their employers will be happiest about the "bottom-line" advantages, we residents of planet Earth can take some comfort that efforts to cut costs also reduce the impact to our climate, the air we breath, the water we drink and the land in which we grow our food.

While the five finalists now join a distinguished list of former Kirkpatrick honorees, they, and the nominees not making the final round, already belong to an ever-growing list of companies and the engineers and chemists they employ to continuously improve the process technologies used to make products.

CE takes pride in honoring these achievements every two years with the Kirkpatrick Chemical Engineering Achievement Award, every two alter-

nate years with the Personal Achievement Award, and every month in the Chementator department. Readers of *CE* regularly look to those pages to keep abreast of the latest process technology and equipment innovations that have been discovered, scaled up or commercialized for the first time. If you are working on such a process and believe you and your employer deserve to be recognized, too, please let us know; we'd love to hear from you.



Gerald Ondrey

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CHEMICAL ENGINEERING WWW.CHE.COM SEPTEMBER 2009 6

### Letters

### Honoring the man behind the scenes

The readers of Chemical Engineering rarely get an inside look at how this publication is put together. Since it would easily have gone undetected, we wish to recognize a longstanding tradition that is coming to a close. The October issue will mark the first issue



in 50 years that does not involve Bill Graham, the person who handles our print production.

Our readers do not know him, but most of our advertisers have communicated with him in one way or another since Aug. 24, 1959 (photo). For our readers, he has put together an award winning publication every month and never asked to be recognized. For our salespeople, he has worked endless times to squeeze in a last minute ad or to try to get a better position for one of their clients. For the editors, he is the one who puts together the puzzle and makes everything fit each month.

Over the last 50 years, a lot of things have changed in the publishing industry. When Bill started, we had prepress rooms, typesetting and negatives for all of the advertisements. These days everything is done digitally. Bill has mastered the production work regardless of how it was done.

Bill has been many things to me since I joined Chemical Engineering. He has been my historian, mentor and coworker, but mostly he has been my friend, and I am going to miss him. Thank you, Bill, for your 50 years of service!

Mike O'Rourke, Publisher Chemical Engineering

### True loyalty deserves recognition

Over one's career, colleagues frequently come and go sometimes without much pomp or circumstance marking their departures. In fact, an employee with five or more years working with a single company has come to be thought of as relatively loyal by today's standards. A higher exhibit of loyalty, however, is why we take pause to honor our colleague Bill Graham, who, with this issue, celebrates 50 years with Chemical Engineering.

Bill has devoted his entire career to this publication and holds it in the highest esteem. He never seeks recognition and vet has been a key contributor to its success. The magazine would never be what it is today without his flexibility, advice, hard work and, above all else, respect for the reader.

As our previous Editor-in-Chief once reassured me upon the departure of another colleague, there has never been, and never will be, a single individual whose exit would cause this magazine to cease publication. But Bill's departure does mark the end of an era here. It will be another 32 years, at the very least, before we can celebrate an employee's 50 year anniversary. Thank you for your loyalty, Bill. We will miss you.

Rebekkah Marshall, Editor in Chief Chemical Engineering



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States when when

Guidelines for Chemical Transportation Safety, Security, and Risk Management, 2nd Edition. By the Center for Chemical Process Safety/AIChE. John Wiley & Sons, Inc. 111 River St., Hoboken, NJ 07030. Web: wiley.com. 2008. 166 pages. \$125.00

Reviewed by: Stanley S. Grossel, Process Safety & Design Consultant, Clifton, N.J.

azardous chemical transport poses significant public health and environmental risks. In 1995, the CCPS published "Guidelines for Chemical Transportation Risk Analysis." The book reviews risk analysis techniques used to evaluate chemical transportation operations. The new edition serves as a complement to, rather than a replacement for, the 1995 edition, and the earlier guidelines are included in CD form along with four other appendices. The new publication addresses transportation security and risk management broadly and provides tools and methods for a wider range of transportation professionals and stakeholders. In particular, it introduces qualitative and practical techniques for identifying and managing higher-level risk issues that balance safety and security. Together, the two books can help effectively analyze and manage chemical transportation risk.



Chapter one introduces transportation risk management, as well as key stakeholders in the supply chain and risk management process. Chapter two discusses baseline programs for safety and

security management for all modes of hazardous material transport that need to be in place prior to a risk analysis.

Risk assessment fundamentals are discussed in Chapter three, as is a protocol for conducting transportation risk assessments. Chapter four focuses on qualitative and semi-qualitative techniques that can be used to analyze the safe transport of hazardous materials. Chapter five provides an overview of quantitative risk analysis (QRA) techniques for evaluating hazardous materials transportation issues, including data sources and requirements, analysis techniques, and the generation and interpretation of quantitative risk results.

Chapter six presents current security guidelines and regulations, and a methodology for adapting and applying security vulnerability assessment (SVA) techniques designed for fixed chemical facilities to account for the differences specific to transportation. Risk reduction strategies are discussed in Chapter seven, which provides guidance on developing risk reduction strategies and



highlights the factors that influence the different types of safety and security measures that can be selected and ultimately implemented. The book concludes with tips for keeping risk management practices current with changing trends and regulations. It is an excellent information source for those involved with chemical transport safety.



Petroleum Microbiology, Concepts, Environmental Implications, Industrial Applications, vols. 1 and 2. By Jean-Paul Vandecasteele. Editions Technip, 25 rue Ginoux, 75015 Paris, France. Web: editionstechnip.com. 2008. 816 pages. \$200.00



Scaling Analysis in Modeling Transport and Reaction Processes: A Systematic Approach to Model Building and the Art of Approximation. By William Krantz. John Wiley and Sons, 111 River Road, Hoboken, NJ 07030. Web: wiley.com. 2007. 529 pages. \$115.00.

Polymer Melt Processing: Foundations in Fluid Mechanics and Heat Transfer. By Morton Denn. Cambridge Univ. Press, 32 Avenue of the Americas, New York, NY 10013-2473. Web: cambridge.org. 2008. 250 pages. \$99.00.



Reactive Distillation Design and Control. By William Luyben and Cheng-Ching Yu. John Wiley and Sons, 111 River Road, Hoboken, NJ 07030. Web: wiley.com. 2008. 574 pages. \$130.00.



**Diffusion: Mass Transfer in Fluid Systems**, 3rd Ed. by E.L. Cussler. Cambridge University Press, 32 Avenue of the Americas, New York, NY 10013-2473. Web: cambridge.org. 2009. 631 pages. \$80.00.

Nanotechnology: Basic Calculations for Engineers and Scientists. By Louis Theodore. John Wiley and Sons, 111 River Road, Hoboken, NJ 07030. Web: wiley.com. 2006. 459 pages. \$105.00.



Nano and Microsensors for Chemical and Biological Terrorism Surveillance. Edited by Jeffrey Tok. RSC Publishing, Milton Road, Cambridge, CB4 0WF, UK. Web: rsc.org. 208 pages. \$148.00.

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Circle 12 on p. 62 or go to adlinks.che.com/23018-12 CHEMICAL ENGINEERING WWW.CHE.COM SEPTEMBER 2009 9 At least two thirds of the earth's surface is covered with water, yet less than one percent is usable fresh water—and that supply is diminishing and becoming more expensive.

## **SRI Consulting Special Report:** Water and Sustainability in the 21st Century

It is imperative that companies in large water consuming industries establish and implement smart water management strategies. To address this need, SRI Consulting (SRIC) examines the way water resources are allocated, planned, constructed, and managed.

This report provides an understanding of the current global water supply, water quality issues, and the long-term outlook, as well as details on reclamation technologies.

For companies that are concerned about water supply, use and management, this report addresses why these issues are critically important and presents technical developments and business economics to improve water management systems. Water and Sustainability in the 21st Century provides water consuming industries with the framework for understanding global water resources, including:

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  - Treatment systems
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## Chementator

Edited by Gerald Ondrey

### September 2009

### A cost-effective process for recycling wastewater

Awastewater treatment process that con-sumes less energy, produces less sludge and makes available up to 75% of the water for reuse — including that of potable water quality — has been commercialized by Linde Gases, a division of The Linde Group (Munich, Germany; www.linde.com). The socalled Axenis process is suitable for treating wastewater with soluble organic pollutants, such as that generated by biodiesel production and the food, dairy, paper-and-pulp, pigments and cellulose (starches) industries, says Darren Gurney, process engineer at Linde Gases. Axenis handles wastewater with COD (chemical oxygen demand) levels in the range of 2,000 to 100,000 mg/L, he says.

Axenis utilizes the patented, oxygen-based Vairox technology in a membrane bioreactor (MBR) in combination with cross-flow ultrafiltration (UF) and reverse osmosis (RO) in an integrated, automated unit. In the process (flowsheet), wastewater is first fed to an MBR, where bacteria oxidize the COD into  $CO_2$  and water. The waste stream is then pumped through a tubular UF (cutoff range of 0.001 to 0.03 microns) membrane module to remove suspended solids. Finally, RO is used to remove dissolved inorganic compounds. Final water quality with BOD (biological oxygen demand) and suspended solids levels of less than 5 mg/L are achieved.



The return flow from the UF membranes is used for injecting  $O_2$  and air, and to achieve mixing in the MBR, thereby eliminating the need for an additional aeration device and agitator, says Gurney. This configuration also has the effect of recovering some of the energy needed for separation, he says. The controlled use of  $O_2$  (for biological treatment) and air (to control pH) enables the MBR to operate at about 5–10°C higher than conventional MBRs without the associated production of surplus biological sludge. Operating at this higher temperature can lead to a 10% or more increase in flux rate. As a result, the reactor can be at least onehalf, and in some cases, as much as one-third the size of conventional MBRs for the same capacity, says Gurney.

The first commercial reference of Axenis — a retrofit at a U.K. company treating 2 m.t./d (metric tons per day) of COD — is now being built, and Gurney anticipates the first greenfield application to be announced in 6 mo., with startup in 2010.

### Making a C-F bond

Pharmaceuticals and agrochemicals often incorporate a fluorine atom within their molecular structure to improve properties, such as keeping the body from metabolizing a drug too rapidly. However, adding a fluorine to an aromatic ring at a late stage of the synthesis can be difficult and expensive due to the harsh conditions needed by traditional methods. Now, chemists at the Massachusetts Institute of Technology (MIT; Cambridge; www.mit.edu) have devised a new way to add a fluorine atom to an aromatic compound with a single catalytic step. In the reaction, a palladium catalyst is used to exchange a triflate group (CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>) with a fluoride ion, which is taken from a salt such as CeE

## A protective coating helps fine powders flow, without agglomeration

A team from Monash Institute of Pharmaceutical Science at Monash University (Melbourne, Australia; www. pharm.monash.edu.au), has developed an approach — a hybrid mixing and milling process — for producing fine (1-20 µm) pharmaceutical powders with good flow and de-agglomeration properties. Team leader David Morton says similar methods have been applied for bulk pigments and ceramics, but are not generally known for such fine and cohesive powders that tend to form clumps that stick stubbornly together.

The team used a very high shear system — a Nobilta "Mechanofusion" processor developed by Hosokawa Micron Corp. (Osaka, Japan; www.hosokawamicron.co.jp/en) — that has a specially designed fast blade, providing a fast moving compressive surface. The process the team has developed involves coating the particles with a nano-layer of an additive, which is polished into the particles' surface. The coating is believed to improve flow properties by reducing interparticle forces.

Fine-milled lactose samples were used as model cohesive pharmaceutical powders, and about 1–2 wt.% magnesium stearate served as the additive. For comparison, the samples were processed in a conventional mixer and the Mechanofusion processor. Scanning electron mi-

croscopy revealed significant differences in morphology: untreated and mixed batches were mostly agglomerated or had particles with smooth surfaces and sharp edges, whereas the Mechanofusion-processed samples were de-agglomerated, and had rounded edges due to the attrition and deformation during the highshear dry-coating process. Changes in surface textures indicated that the additive had effectively coated the particles.

The dry-coating process leads to a substantial improvement in flow properties for these fine lactose powders. Changes in powder-packing structure are thought to be responsible for an observed doubling of the pour density.

## Process optimization software allows rapid setup, cost savings

New industrial process-optimization software can be fully operational in seven days — months ahead of existing predictive monitoring systems, according to Slipstream Software (Alpharetta, Ga.; www.slipstreamrpm.com). The company's proprietary data-modeling tools are responsible for the reduced setup time. By mining process history information, and collecting data from sensors installed in the process stream, Slipstream software "dynamically reads, models and auto-corrects customer recipes," the company says.

The process optimization software can be used in wet processes (using infrared spectroscopy as the basis for the sensors) or dry (using characteristic sound vibrations) and is designed to interface with a plant's distributed control (DCS) or supervisory control and data acquisition (SCADA) system.

Designed for industrial processes with

recipe requirements that need constant correction, the software reduces out-ofspecification product and improves process efficiency. Companies can realize a 1-5% increase in efficiency, which, in a typical chemical plant, could mean a few million dollars of savings annually, explains company CEO Gary Hopkins. In addition, predictive process systems can take four to six months of engineering time to set up, and can cost close to \$1 million. Slipstream software can achieve the same functionality in a week for around one-fifth of the price, he adds.

According to Slipstream, a Belgian foodadditive manufacturer using its software saw a 4% efficiency jump, and a paper-pulp maker saw its profits jump by 20% after installing the pattern modeling software.

The new software represents an addition to the company's portfolio of root cause analytics products.

### More efforts to make biofuels from algae . . .

**U**ver the past few weeks there has been a number of announcements on projects aimed to further develop algae-to-fuels technology (see also, "Pond Strength," CE, September 2008, pp. 22–25). Plankton Power (Wellfleet; www.planktonpower.com) and the Regional Technology Development Corp. of Cape Cod (RTDC; Woods Hole, both Mass.; www.regionaltechcorp.org) have formed a consortium to establish the Cape Cod Algae Biorefinery, which will focus on pilot- and commercial-scale development of algae-based biodiesel. The proposed biorefinery will be located on 5 acres of land at the Massachusetts Military Reservation (Bourne). Starting in the fall of 2010, Plankton Power expects to produce 1-million gal/yr of biodiesel in pilot-scale operations, using the company's cold-saltwater algae species. Commercial-scale operations on 100 acres could produce 100-million gal/ yr, which would meet 5% of the demand for diesel and home heating fuel in the state of Massachusetts, says the firm.

Meanwhile, petroleum major ExxonMobil (Irvine, Tex.; www.exxonmobil.com) has formed an alliance with Synthetic Genomics Inc. (SGI; La Jolla, Calif.; www.syntheticgenomics.com) to develop next generation biofuels from algae, following earlier leads by Shell (*CE*, January 2008, p. 15), Akzo-Nobel (*CE*, July 2008, p. 16) and ConocoPhillips (www.che.com, July 2, 2008).

In July, The Dow Chemical Co. (Midland, Mich.; www.dow.com) said it would work with Algenol Biofuels, Inc. (Bonita Springs, Fla.; www.algenolbiofuels.com) to build and operate a pilot-scale, algae-based integrated biorefinery to make ethanol.

In Germany, scientists at the Karlsruhe Institute of Technology (Germany; www. kit.edu) are developing a closed, vertically arranged photobioreactor that is said to be five-times more efficient at converting solar energy into biomass than open ponds. A pulsed electric treatment process is also being developed at KIT for extracting oils and other chemicals from biomass.

### ... and from microorganisms

Last month, BP Corp. (London; www.bp.com) signed a joint-development agreement with Martek Biosciences Corp. (Columbia, Md.; www.martek.com) to work on the production of microbial oils for biofuels applications. The two companies aim to establish proof of con-

cept for large-scale, cost-effective production of microbial biodiesel. The concept is to utilize microorganisms to ferment sugars into lipids, which will then be processed into liquid fuels. BP is contributing \$10 million to the initial phase of the collaboration.

### More efficient smelting

The energy efficiency at two record-breaking aluminum smelters in the Middle East has been increased by 18%, thanks to ABB's (Zurich, Switzerland; www.abb.com) new rectiformers - the high-power components that control and convert alternating current from the grid to direct current needed to power the electrolytic process and produce molten Al in pots. The rectiformers were developed for the Sohar Al smelter in Sultanate of Oman, which consists of 360 pots and produces up to 360,000 ton/yr of Al — the world's largest potline (startup June 2008) - and the Qatalum smelter in Qatar, which will become the world's largest aluminum smelter when it starts up in late 2009, with a production capacity of 585,000 ton/yr and 704 pots.

For these massive projects, ABB was able to extend the voltage limit of the rectiformers from 1,200 V d.c. to 1,650 V d.c. (for Sohar) and 2,000 V d.c. for Qatalum. This enables the devices to convert and deliver more power than previously possible. As a result, each smelter requires only five rectiformers instead of the six needed at the lower voltage, resulting in a "huge" savings in investment, says ABB.

### Ag/polymer reflector

Scientists at SkyFuel Inc. (Arvada, Colo.; www.skyfuel. com) and the National Renewable Energy Laboratory (Golden, Colo.; www.nrel.gov) have developed a silvered polymer film as a less expensive alternative to glass mirror reflectors. Curved sheets of the reflective material are used in solar troughs, which reflect concentrated solar radiation on a tube filled with a heat transfer fluid. Developers claim the cost advantage of the multi-layered polymer material is 30% when compared to glass mirrors, which are more expensive, heavier and more difficult to install for collecting solar radiation. A pilot system including the polymer-silver reflectors is operational at SkyFuel's facility in Arvada, Colo.

### New MAK & BAT values

New heating technique improves zeolite membrane performance

Adding a rapid heat-treatment step to the process of making zeolite membranes improves separation performance by eliminating grain boundary defects, according to researchers from the University of Minnesota (UMN; Minneapolis, Minn.; www.umn. edu), who published their study in the July 31 issue of *Science*.

The study could inform efforts aimed at producing zeolite films for gas, liquid and vapor membrane separations processes, as well as for hybrid membrane-distillation processes that separate industrial mixtures. If zeolite membranes could be fabricated to deliver expected performance in flux and selectivity, they could reduce the energy costs associated with distillation by 10-fold, notes professor Michael Tsapatsis, a UMN chemical engineer who led the research.

Large-scale production of zeolite films has been plagued by the formation of cracks and grain boundary defects. Membrane defects degrade selectivity by allowing molecules to bypass the zeolite pores that are designed to discriminate among mixture components. Grain boundary defects form during calcination, a heating process required to remove structure-directing agents (SDAs) from zeolite pores. SDAs are added during synthesis to define zeolite pore size and shape.

The research group developed a rapid thermal processing (RTP) technique that may strengthen bonding between adjacent zeolite crystal grains prior to removal of the SDAs. In RTP, an infrared-lamp-based furnace is used to heat synthesized zeolite membranes to 700°C within one minute prior to removal of the SDAs. The elevated temperature is maintained for 30 s to 2 min before the membrane is cooled by water circulation.

Tsapatsis hypothesizes that the increased crystal-to-crystal bonding — which may result from condensation reactions of Si-OH groups on neighboring crystals — reduces the development of cracks and grain boundary defects in the membrane. When SDAs were removed in a subsequent heating step, the researchers observed an increased selectivity when the RTP-treated zeolite films were used to separate *o*-xylene from *p*-xylene.

### Pt-free catalysts promise to lower fuel-cell costs . . .

Showa Denko K.K. (Tokyo; www.sdk.co.jp/ html/english) has developed a platinumsubstitute catalyst system for polymer electrolyte fuel cells (PEFCs) under the New Energy and Industrial Technology Development Organization's (NEDO; Kawasaki, Japan) project led by professor Kenichiro Ota of Yokohama National University. The new catalysts — based on niobium oxide and titanium oxide, each containing nitrogen and carbon atoms — are used in both the cathode and anode of a PEFC and are said to achieve the world's highest level of

efficiency, in terms of open-circuit voltage and durability, among non-Pt catalysts announced so far. Enhanced durability has also been observed, with operation extending to more than 10,000 h, says the firm.

Production costs for the new catalysts are about ¥500/kW (\$5/kW), or less, which is about 1/20th that of today's Pt-based catalysts. The company is working to improve the catalyst performance using fine-particle manufacturing technologies and high-conductivity carbon, and anticipates commercial production by 2015.

### ... as does reducing the Pt load

A technique for making PEFC electrodes with one fourth the amount of platinum catalyst compared to conventional PEFCs has been developed by Hosokawa Micron Corp. (Osaka, Japan; www.hosokawamicron.co.jp/en) in collaboration with professors Kiyoshi Kanamura, Tokyo Metropolitan University, and Makio Naitou, Osaka University. The method, known as mechanochemical bonding (MCB), produces stable, complex materials with a high performance level when used in the membrane-electrode assembly (MEA) of PEFCs. Naitou fabricated the composite catalyst, composed of commercially available platinum-carbon particles and tungsten-carbide particles. Kanamura fabricated the MEA by incorporating a Nafion membrane, and evaluated the MEA's power-generation characteristics.

The scientists obtained similar power-

The Senate Commission for the Investigation of Health Hazards of Chemical Compounds in the Work Area, established by the German Research Foundation (DFG; Bonn) has issued the MAK (maximum concentration at the workplace) and BAT (biological tolerance) Values List for 2009, which contains 62 changes and new entries. These include revised assessments of oxides of nitrogen, and zinc and its inorganic compounds.

Although the trace element zinc, which is ingested through food, is a component of important enzymes, it can have toxic effects on the lungs if inhaled. Therefore, the maximum concentration of zinc oxide fumes in the breathing air to which workers can be exposed without suffering adverse health effects is considerably lower than was previously stated, says the DFG. There are also seven revisions or alterations in the carcinogenic substances category. including the categorization of the chromates (except lead and barium chromate) as carcinogenic to humans. The complete list can be downloaded at www. dfg.de.

### **Dust explosion advice**

The U.S. Occupational Safety and Health Admin. (OSHA; Washington, D.C.; www.osha. gov) has recently published a new guidance document Hazard Communication Guidance for Combustible Dusts — that helps chemical manufacturers and importers to recognize the potential for dust explosions, identify appropriate protective measures and the requirements for disseminating this information on material safety data sheets and labels. The document can be downloaded from OSHA's Website for free.

generation characteristics as conventional systems even when reducing the Pt content by 75%. The enhanced catalyst activity is thought to be the result of increasing the electrochemically active surface created by MCB technology. The researchers believe the Pt load can be reduced by 90% through optimizing the fine structure of the particles. Hosokawa Micron is continuing to improve its AMS-Mini device for MCB applications.

### This process may produce electricity from low-temperature geothermal resources

The world has vast geothermal resources in the temperature range of 150–250°F, but these temperatures are too low for economical exploitation, using today's technology. A process that could change the benchmark is being developed at Pacific Northwest National Laboratory (PNNL, Richland, Wash.; www.pnl.gov).

PNNL's process would pump hot water from a geothermal reservoir and extract heat into a working fluid through a heat exchanger, a conventional process. The new twist is that PNNL uses a biphasic working fluid. It consists of a metalorganic heat carrier (MOHC) suspended in, for example, butane, pentane or propane, which drives a turbine via a Rankine cycle. The biphasic fluid's properties promise to boost the power-generation capacity of the turbine to near that of a conventional steam turbine, says Laboratory fellow Peter McGrail. "We have synthesized a number of MOHCs," he says, "and the best ones we have discovered so far have a latent heat of adsorption that is 20 times the standard heat of vaporization of the working fluid."

McGrail declines to give details on the composition of the MOHCs, but says the material is dispersed in the alkane as particles of less than 100 nm and adsorbs as much as 30 wt.% of the fluid, so that the working density of the alkane is not reduced. He adds that the MOHCs are inexpensive and the main question is whether the nanoparticles will withstand longterm cycling. PNNL plans to answer that question with a bench-scale, electricity-generating prototype unit.

### An activated carbon for picking up heavy metals

The Agricultural Research Service (ARS, Beltsville, Md.; www.ars.usda. gov) has received a patent on a process for producing activated carbon from poultry litter, which consists of bedding materials such as sawdust and peanut shells, along with droppings and feathers. U.S.-grown broiler chickens and turkeys produce an estimated 15-million tons/yr of litter, according to the ARS.

The process was developed and has been laboratory-tested at the ARS Southern Regional Research Center (New Orleans, La.). Litter is ground into a fine powder, pelletized, then pyrolyzed at 1,300–1,500°F in a nitrogen atmosphere. Unlike conventional activated carbon, produced from coal, the



## Fast digestion makes better use of municipal sludge

The use of residual sludge from municipal sewage plants as fertilizer in agriculture is controversial (due to heavy metals and other pollutants), and slurry can no longer be disposed of in landfills in many countries. A less expensive alternative to incineration — high-rate digestion of sludge into biogas — can lead to substantial savings (even for small sewage plants) despite the need to in-

vest in the technology that is now stateof-the art in larger plants, according to a cost-benefit analysis performed by the Fraunhofer Institute for Interfacial Engineering and Biotechnology (IGB; Stuttgart, Germany; www.igb.fraunhofer.de).

In the fast-digestion process developed at IGB, sludge only needs to remain in the tower for 5–7 d instead of 30–50 d as typical for conventional digestion sys-

ARS material has a relatively high concentration of phosphorous, which adds a negative charge. This enables the carbon to adsorb heavy metal ions, such as those of cadmium, copper, lead and zinc, says Isabel Lima, a research chemist at the center.

Lima estimates that the process could produce activated carbon for about \$1.44/kg, or 65¢/lb. This compares with roughly \$1/kg for coal-derived carbon. However, she points out that conventional activated carbon is commonly used to adsorb organics. The adsorption of metal ions would require post-treated carbon or ionic resins, both of which are much more expensive. Lima says the technology is open for licensing by companies interested in building small plants in poultry-producing areas. tems. About 60% of the organic matter is converted into biogas. Using the biogas to make electricity to run the plant, and the reduced volume of sludge needed to be disposed of, can save the operator of a small (28,000 inhabitants) sewage plant about  $\in$  170,000/yr, according to IGB.

### Waste-heat recovery

GE Energy (Atlanta, Ga.; www.ge.com/ energy) and ECOS Ltd. (Slovenia) plan to demonstrate a new waste-heat recovery system that is expected to boost the electrical efficiency of a 7.2-MW biogas power plant by five percentage points. GE's pilot ORC (organic Rankin cycle) waste-heat recovery system will allow ECOS to capture more waste heat created by its Bioplinarne Lendava biogas plant, in eastern Slovenia. The extra thermal power will be used to produce steam, which in turn will generate more electricity.



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## CPI ENERGIZED BY BATTERY FUNDING

## DOE Awards \$1.5 billion to scale up battery production for electric-powered cars

fforts toward large-scale production of lithium-ion (Li-ion)-based car batteries got a big boost in early August, when the Obama Administration announced \$2.4 billion in U.S. government investment aimed, in part, at dramatically ramping up the supply chain for advanced batteries for the auto industry. A majority of this funding is funneling directly into the chemical process industries (CPI), which are responsible for developing and commercializing the necessary technology. But CPI companies involved in this area will be challenged to produce batteries that meet the performance needs of the auto industry at affordable cost.

Part of the recent economic stimulus package (American Recovery and Reinvestment Act), the U.S. Dept. of Energy's (DOE; Washington, D.C.; www. energy.gov) Electric Drive and Vehicle Battery and Component Manufacturing Initiative awarded the \$2.4 billion in grants to 48 different battery-technology and electric-vehicle projects in 20 states. Of the \$2.4 billion total, \$1.5 billion in grants went to manufacturers of batteries or their components, while the remaining \$900 million went to makers of electric drive components and vehicles themselves. Each DOEgrant dollar will be matched by investments from the awardees.

The auto industry is poised to roll out new hybrid electric and plug-in hybrid electric vehicles (HEVs and PHEVs) in the next several years, and are depending on a ready supply of automotivegrade Li-ion batteries. But the lack of manufacturing capacity has been a bottleneck, especially for U.S. automakers. The competitively awarded DOE grants accelerate progress toward scaling-up production of viable battery technologies for road vehicles.

In an Aug. 5 speech to announce the funding, U.S. Energy Secretary Steven Chu stated that the grants were handed out "not simply to boost a few companies, but to start an entire advanced battery industry in America."

The \$2.4 billion in grants represents the single biggest government investment in electric vehicles ever. "It's a big deal," says Jennifer Watts, communications manager at the Electric Drive Transportation Assn. (Washington, D.C.; www.electricdrive.org). Establishing a domestic manufacturing base for advanced batteries is critical to the future of the auto industry, and the grant funding shows that government and industry "are on the same page," she commented.

Meanwhile, it gives a shot in the arm to an already expanding market for battery technologies. Mid-August estimates from the market research firm Innovative Research and Products Inc. (iRAP; Stamford, Conn.; www.innoresearch.net) place the global market for large-format Li-ion batteries for transportation at \$77 million in 2009. HEVs and PHEVs currently represent a negligible portion of that total. The global market for Li-ion batteries in transportation is projected to reach \$332 million by 2014, with electric automobiles accounting for \$87 million. Heavy-duty hybrid electric vehicles (buses, train engines, trucks) will garner the largest portion of the market, at \$150 million by 2014, iRAP projects.

### Varying cathode approaches

Among the crucial factors affecting battery performance, safety and cost, is the cathode active material. Cathodes for Li-ion batteries generally consist of layered metal oxide or metal phos-



Transition metal slab

Li slab

**FIGURE 1.** The structure of layered metal oxides is similar among several types of cathode materials used in Li-ion batteries that are designed specifically for hybrid electric and plug-in electric vehicles

phate material, the crystal structure of which contains intercalated lithium ions (Figure 1). The dominant cathode material in batteries for portable electronic devices has been lithium cobalt oxide (LiCoO<sub>2</sub>), a material that is too costly and that carries too many safety concerns to be used in HEV/PHEV batteries. The DOE grant awards (Table 1) support large-scale production of batteries containing several cathode types, each exhibiting a unique structure and different metal contents.

One approach to synthesizing cathodes that can handle automobile environments involves a metal oxide structure that includes manganese and nickel along with cobalt. Known as an NMC cathode, the material forms the basis of a proprietary battery technology called superior lithium polymer battery (SLPB). SLPBs may be attractive to automakers because the technology has already been commercialized for specialized military and industrial applications. Dow Kokam, a joint venture of the Dow Chemical Co. (Midland, Mich.; www.dow.com) and Kokam America (Lee's Summit, Mo.; www. kokamamerica.com), was awarded \$161 million in DOE funds to produce SLPBs for the HEV/PHEV markets.

The NMC cathodes employed in the SLPB batteries exhibit low impedance, good safety characteristics and rapid charge and discharge, says Ravi Shanker, corporate director of Ven8 HUMAN 7E+09

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Company name (project locations)	Award amount (in millions of U.S. dollars)	Technology	Editor's notes
Johnson Controls Inc. (Holland, Mich.; Lebanon, Ore.)	299.2	Production of nickel-cobalt-metal battery cells and packs, as well as production of battery separators (by partner Entek) for hybrid and electric vehicles	Converted Michigan facil- ity to be operational by end of 2010
A123 Systems Inc. (Romulus, Mich.; Brownstown, Mich.)	249.1	Manufacturing of nano-iron phosphate cathode pow- der and electrode coatings; fabrication of battery cells and modules; and assembly of complete battery pack systems for hybrid and electric vehicles	Initial public stock offering coming soon
Dow Kokam (Mid- land, Mich.)	161.0	Production of manganese-oxide cathode / graphite Li- ion batteries for hybrid and electric vehicles	Battery production slated for 2011
Compact Power Inc. - LG Chem Ltd. (St. Clair, Pontiac and Holland, Mich. )	151.4	Production of Li-polymer battery cells for the General Motors Volt using a manganese-based cathode and a proprietary separator	Manganese spinel-struc- tured cathode material
EnerDel Inc. (India- napolis, Ind.)	118.5	Production of Li-ion cells and packs for hybrid and electric vehicles. Primary lithium chemistries include manganese spinel cathode and lithium titanate anode for high-power applications, as well as manga- nese spinel cathode and amorphous carbon for high- energy applications	Initial capacity increase at existing plants, followed by later purchase of new facilities space

**TABLE 1.** Selected DOE grant recipients in the areas of battery, cell and materials manufacturing under the Electric Drive and Vehicle Battery and Component Manufacturing Initiative

tures and Business Development at Dow. In addition, NMC cathodes have 40% higher energy density than that of another cathode material alternative, lithium iron phosphate. The venture plans to begin construction of an 800,000-ft<sup>2</sup> SLPB plant in Midland, Mich. this autumn. SLPBs will likely appear in road automobiles in 12–18 months, Shanker projects. When operational, Dow Kokam expects the facility to produce enough batteries to supply 60,000 HEVs/ PHEVs annually.

(Source: U.S. Department of Energy)

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Company name (project locations)	Award amount (in millions of U.S. dollars)	Technology	Editor's notes
General Motors Corp. (Brownstown, Mich.)	105.9	Production of high-volume battery packs for the GM Volt. Cells will be from LG Chem and other cell provid- ers to be named later	Chevy Volt anticipated to be launched at the end of 2010
Saft America Inc. (Jacksonville, Fla.)	95.5	Production of Li-ion cells, modules and battery packs for industrial and agricultural vehicles and defense application markets. Primary chemistries include nickel-cobalt-metal and iron phosphate	New plant to make Li-ion batteries for military, avia- tion, energy storage
Celgard LLC - Poly- pore (Charlotte, N.C.; Aiken, S.C.)	49.2	Production of polymer separator material for Li-ion batteries	Funding will help expand existing plant and build new one
Toda America Inc. (Goose Creek, S.C.)	35	Production of nickel-cobalt-metal cathode material for lithium-ion batteries	Experienced metal oxide producer
Chemetall Foote Corp. (Nev.; N.C.)	28.4	Production of battery-grade lithium carbonate and lithium hydroxide	Raw material production
Honeywell Interna- tional Inc. (N.Y.; III.)	27.3	Production of electrolyte salt (lithium hexafluorophos- phate, or LiPF6) for Li-ion batteries	First U.S. producer of LiPF6
BASF Catalysts LLC (Elyria, Ohio)	24.6	Production of nickel-cobalt-metal cathode material for Li-ion batteries	New plant operational in 2012

choice of another DOE grant recipient. BASF Catalysts LLC (Iselin, N.J.; catalysts.basf.com) was awarded almost \$25 million to help build a plant in Elyria, Ohio for production of cathode powders. Prashant Chintawar, BASF senior manager for advanced cathode materials, explains that NMC-type cathodes contain only about one third the cobalt in  $LiCoO_2$  cathodes, allowing a corresponding price reduction. NMC-type cathodes "offer the best combination of cost, safety and performance," adds Chintawar. By 2012,

BASF hopes to begin production of the cathode material.

Johnson Controls Inc. (JCI; Milwaukee, Wis.; www.johnsoncontrols.com) recipient of the single largest DoE award (\$299 million), will produce batteries containing another layered



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metal-oxide cathode — nickel-cobaltaluminum (NCA). Adding a small amount of aluminum improves cathode performance at low cost, said Michael Andrew, director of government affairs and external communications at JCI. Batteries with NCA cathodes satisfy customer requirements in a host of areas, including cost, abuse tolerance, and peak power generation, Andrew notes. Production will begin in summer 2010.

A manganese oxide cathode with a spinel structure also appears to have gotten a vote from a major customer. Battery cells made by LG Chem (Seoul, S. Korea; www.lgchem.com) with Mnspinel cathodes will be part of battery packs assembled by Compact Power Inc. (Troy, Mich.; www.compactpower. com) for General Motors' (Detroit, Mich.; www.gm.com) PHEV, the Chevy Volt. Compact Power and its parent, LG Chem, were selected as suppliers for the Volt, which is anticipated to be available in late 2010. Compact Power was awarded a \$151-million DOE grant to scale up production of batteries with the Mn-spinel cathode, which has better thermal stability and can discharge at higher current than cobalt oxide cathodes, but has a lower energy density.

Manganese spinel cathodes are the foundation of HEV/PHEV batteries at another DOE awardee, EnerDel Inc. (Indianapolis, Ind.; www.enerdel.com). The company's vehicle-suitable batteries couple a lithium-manganese-oxide (LMO) spinel cathode with a lithium titanate anode to boost power. This chemistry "provides the best power-tosize ratio that we've seen, high safety levels, and excellent cold-cranking capability," said EnerDel CEO Ulrik Grape. EnerDel's \$118-million DOE grant will aid an expansion that includes increasing production capacity to 20,000 HEV/ PHEV battery packs at existing facilities, followed later by the purchase of new space that will allow capacity to grow to 60,000 packs by 2012 and 120,000 by 2015, EnerDel says.

A different cathode technology underlies batteries developed by A123 Systems, Inc. (Watertown, Mass.; www. a123systems.com), which received one of the largest awards (over \$249 million) from the DOE program. A123 Systems' nanostructured lithium-ironphosphate cathode, based on technology licensed from MIT (Cambridge, Mass.; www.mit.edu), employs particles an order of magnitude smaller (100 nm versus 10 µm) than conventional lithium cobalt oxide cathode material. Coupled with a proprietary doping technique to improve intrinsic conductivity, the smaller particle size allows high discharge power and fast recharging. Lithium iron phosphate batteries have more favorable safety characteristics than cobalt oxide, and A123 will use its DOE award to sup-(Continues on p. 23)





Security at many U.S. chemical facilities is currently regulated by the U.S. Department of Homeland Security (DHS; Washington, D.C.; www.dhs.gov) under the Chemical Facility Anti-Terrorism Standard (CFATS). This rule, however, is about to expire next month, October 2009. All expectations are that CFATS will be extended for a year, while proposed modifications to the standard continue to be debated in the U.S. Congress.

As they work to comply with CFATS, the chemical process industries (CPI) are keeping a watchful eye on the Congressional proceedings that are leading to proposed changes in the regulation."CFATS — it is by far the most dramatic issue affecting chemical plant security today," notes Robert Hile, director of integrated security solutions at Siemens Building Technologies, Inc. (Buffalo Grove, Ill.; www.usa. siemens.com/security).

### **CFATS** in action

CFATS has come a long way in a short time. The approval of the DHS Appropriations Act in October 2006 gave the DHS authority to regulate the security of high-risk chemical facilities. CFATS, the implementing regulation, was published in April 2007 and its Appen-

dix A, which lists approximately 300 chemicals of interest (COI) and their individual screening threshold quantities (STQ), was published in November of the same year. In May 2009, a document entitled Risk-Based Performance Standards Guidance was published. This guide elaborates on the eighteen risk-based performance standards (RBPSs) that are established in CFATS, and identifies the areas for which a facility's security will be examined, such as perimeter security, access control, personnel surety (a check on personnel credentials) and cyber security.

Compliance with CFATS begins with an assessment tool developed by DHS called the Top-Screen, to assist DHS in determining which chemical facilities meet the criteria for being high-risk. Sites possessing chemicals as listed in Appendix A at or above the STQs must submit the Top-Screen questionnaire to DHS for review. As Steve Roberts, an attorney who specializes in CFATS issues (Roberts Law Group PLLC; Houston; www.chemicalsecurity.com) explains, those facilities deemed high-level risk are then required to submit a security vulnerability assessment (SVA), after which a facility is categorized into a final risk tier. These facilities must then develop and submit a site security

plan (SSP) to DHS within 120 days. Roberts says that the first 140 or so "final tier letters" were sent out in May 2009, followed by about another 400 in June. More tier letters are forthcoming. Those companies in receipt of the letters are now in the stage of submitting their SSPs. DHS will review the SSPs and determine compliance. However, "because the regulations are performance-based and risk-driven, what 'compliance' means can change from facility to facility," says Roberts. He further explains that denial leads to further consultation and "The process of compliance [with CFATS] is continuous as facilities change." Roberts refers to a chart as a quick summary of the overall CFATS compliance process (Figure 1).

### The big issues

There doesn't seem to be any disagreement among the CPI that security regulations are a good idea. In fact the Society of Chemical Manufacturers and Affiliates (SOCMA; Washington D.C.; www.socma.com) commends the U.S. Senate for approving legislation that would extend existing chemical security standards for one year. The American Chemistry Council (ACC; Arlington, Va.; www.americanchemistry.com) notes that security has long

been a priority for its members, who have invested about \$8 billion on facility security enhancements under ACC's Responsible Care Security Code. In a recently issued statement, Marty Durbin, ACC's vice president of Federal Affairs says, "We believe the ongoing implementation of the Chemical Facility Anti-Terrorism Standards demonstrates a smart and aggressive approach to both securing and protecting the economic viability of this essential part of the nation's infrastructure."

There also doesn't seem to be any dissension "on the Hill" about extending CFATS. As she addressed the approximately 350 participants at the 2009 Chemical Sector Security Summit held in Baltimore, Md. on June 29 to July 1, Holly Idelson, majority counsel for the Senate Homeland Security and Government Affairs Committee put it this way, "The debate is what should the program be, not should there be a program." Ms. Idelson made it clear that as the Senate committee works on defining what the program should be, it welcomes input from the CPI to let the members know what is working and what is not working in CFATS, saying, "Our [the Senate Committee's] door is open."

Since the clock has just about run out for a standalone security bill this year, CFATS is well on its way to a one-year extension. It is also expected that in this upcoming year discussions about what a permanent rule should look like will intensify. While the U.S. Senate has not yet formed its own version of a bill, The House of Representatives has proposed a revision to the current CFATS standard. The details are where the dissension begins.

Bill Allmond, vice president of Government Relations and ChemStewards for SOCMA explains that the two main points in the House's bill that SOCMA opposes are: 1) mandated inherently safer technologies (IST); and 2) a civil suits clause.

IST encompasses a wide breadth of chemical processing procedures, equipment, protection and the use of safer substances. Allmond states that SOCMA "adamantly opposes mandatory IST" and more to the point "What SOCMA opposes the most is getting into [mandatory] chemical substitution." He explains that SOCMA agrees **FIGURE 2.** Ground retractable automobile barriers (GRAB) stop the unauthorized entry of vehicles up to 15,000 lb, traveling at speeds up to 50 miles per hour

it is appropriate for DHS to encourage the use of IST, but it should be on a voluntary basis, possibly with incentives (not necessarily financial) to facilities that implement it. SOCMA's opposition to mandatory IST is founded on several fronts. First, IST within a security framework is already addressed by two other well-entrenched regulations: 1) the U.S. Environmental Protection Agency's (EPA) Risk Management Program Rule (RMP); and 2) the U.S. Occupational Safety and Health Admin.'s (OSHA) Process Safety Management Regulation. A great concern is that a chemical deemed to be a safer alternative might be mandated by government officials without a full understanding of the many ramifications of that chemical substitution.

Allmond uses manufacturers of active pharmaceutical ingredients (APIs) as an example of where unexpected complications could arise. API manufacturers go through a lengthy process of U.S. Food and Drug Administration (FDA) approvals. If, for example, a so-called "safer alternative" compound were mandated, this new compound might require an untenable amount of retesting before the switch could occur, and it might not be approved by the FDA.

The ACC also opposes mandatory IST. Scott Jensen, director of communications for ACC says that making IST mandatory in a security regulation brings "discomfort and concern for facility operators since determination is based on one factor, whereas a facility makes that determination based on many factors." Jensen states simply that ACC's position is that "it is not necessary to include [mandatory] IST" in the security bill because the current CFATS program allows for and encourages IST implementation.

Both SOCMA and the ACC also oppose the civil suits clause in the House's proposed legislature, which would allow any citizen to sue a company if their perception is that the CFATS regulation is not being fol-



lowed. Jensen says that the ACC feels adamantly that it is not necessary for courts to get involved. SOCMA's Allmond notes that a citizen suit provision is common in environmental law, but it doesn't even seem feasible in a security framework since the details of a facility's security plan would not be accessible to the public because they are deemed CVI (chemical-terrorism vulnerability information), which is confidential and known only to DHS and designated facility employees.

While the IST and civil suits issues are the main areas of disagreement between the organizations representing the CPI and the proposed House bill, there are other areas of discussion. These questions include who should be covered in CFATS, such as when it comes to water-treatment facilities and industrial versus agricultural uses of ammonium nitrate. ACC's Jensen puts it into perspective, though, when he says, "We [the CPI, U.S. Congress and DHS] agree on more than we disagree" including the overall objective of having permanent Federal chemical security regulations.

### **Integrators and suppliers**

As tiered facilities move forward with their site plans, a number of companies are positioning themselves to help with the process of CFATS compliance and implementation. Hile says that Siemens can help "from start to finish", offering "assistance from the very early stages all the way through to the implementation." One form of assistance is a survey package that helps to break down CFATS into "layman's" terms giving a facility a sort of template to help form the SVA, and then further down the line to help with the plan (SSP). Siemens is poised to offer an array of surveillance products and perimeter-intrusion-detection systems. The majority of RBPSs in CFATS deal with the physical security of a site, so these types of products are expected to be an important part of a site's security plan.

Andrew Wray, senior global marketing manager with Honeywell Process Solutions (Phoenix, Ariz.; www.honeywell.com) says that to achieve increasing levels of security, more and more technology needs to be integrated. Honeywell is well-positioned to offer integration with a single system for control, he adds. Looking ahead, Wray says that "as more and more systems are integrated into the network, more products need to make decisions 'at the edge'." To explain what he means by at the edge, Wray gives the example of a card reader at a facility perimeter. While the card reader likely has local decision-making capabilities, new technology is emerging that will check the integrity of the reader's data prior to gaining access to the network.

"Integration of multiple technologies is key," agrees Ryan Loughin, director of the Petro-Chem and Energy Div. of ADT Advanced Integration (Norristown, Pa.; www.adtbusiness. com/petrochem-ce). He goes on to say that "The overall security philosophy at a plant is changing. Security is now a program much like safety has been for years...CFATS is driving this program-related process." Loughin explains that a tiered facility faces two basic threats: toxic release, and theft and diversion. ADT's approach to working with a facility with one or both of these threats is to consider three key factors: deter, detect and delay. "Many of the technologies being used on these facilities have been around for some time, but never utilized in the private sector the way they are now," says Loughin as he gives examples of fiber-based fence detection, thermal imaging, video analytics and radar. "I believe the day of the six-foot chain-link fence is over for the highest-risk facilities," he says, citing that K-rated and highsecurity-fencing and barrier technology are now being used (Figure 2). Loughin notes that ADT has Safety (Support Anti-terrorism by Fostering Effective Technologies) Act Certification for electronic security services. This DHS-designated certification is a way to manage the risk of liability, says Roberts, who advises companies to consider Safety Act protection as a factor when selecting a security vendor during the procurement process.

### The cyber side

While the bulk of CFATS focuses on the physical plant, it also addresses cyber security, which is undoubtedly an integral part of overall security. Part of the issue with regulating cyber security is how to quantify what level of cyber security one needs, or has. Experts are using their experience with safety standards to focus on this issue.

In the safety arena, metrics can be assigned according to probability on a scale of safety integrity levels (SILs; see *CE*, Sept. 2007, pp. 69–74). Assigning metrics to security, however, poses a bigger challenge. As Eric Cosman, co-chair of the ISA99 Committee and who works

at the Dow Chemical Co. puts it, "In security you have a purposeful, intelligent adversary. How do you measure that?" Still, Cosman and his colleagues on the ISA99 Committee, with contributions from other groups, such as ACC's Chem ITC, are making headway in defining cyber-security standards that will be applicable to a broad industry base. A concept gaining momentum is the development of security assurance levels (SALs), comparable to SILs. Cosman says that the "SAL concept has a lot of promise. It is going to get us somewhere, I just don't know how far."

John Cusimano, director of security solutions for exida (Sellersville, Pa.; www.exida.com) explains that it has been a long process, but the IT security and control-system communities have successfully cooperated to develop cyber standards and methodologies, and that "Recently the safety system community has joined this effort, bringing [its] proven risk-mitigation engineering methods to the table." Among other services, exida offers a Control System Security Assessment to review the cyber-security environment of a facility and compare it with industry best practices with recommendations to address possible gaps. As momentum increases in the efforts to standardize cyber security, everyone seems to agree in the prediction that it will become a more integral part of future security regulations. Dorothy Lozowski

### CPI ENERGIZED

(Continued from p. 20)

port construction of a Michigan facility to produce battery component materials, battery cells and battery packs for HEVs and PHEVs.

### European battery activity

While the U.S. DOE grant program was grabbing attention in August, efforts to develop batteries for HEVs/PHEVs continued elsewhere. In July, the European Commission (Brussels, Belgium; ec.europa.eu) identified "high-density batteries" as a priority in its funding to develop HEVs and PHEVs.

With €20 million from its own economic stimulus package, the German government is setting up a research consortium headed by the Karlsruhe Institute of Technology (Karlsruhe, Germany; www.kit.edu) to develop novel battery materials that will increase energy density in cells intended for electric vehicles.

Private sector players in Europe are positioning themselves for the advanced battery market as well. Evonik Industries AG (Essen, Germany; www.evonik. com) and Daimler AG (Stuttgart, Germany; www.daimler.com) established a development and production partnership and launched plans to construct a Li-ion battery plant in Kamenz, Germany. Production will begin in 2011. SB LiMotive, a joint venture of Robert Bosch GmbH (Gerlingen, Germany; www.bosch.com) and Samsung SDI (Suwon, S. Korea; www.samsungsdi. com) was selected by BMW (Munich; www.bmw.com) to supply Li-ion batteries for its "Megacity" electric vehicle.

Even as commercial production of Li-ion batteries draws near, industrial R&D moves forward on several fronts, including exploring new electrode material combinations and structures, as well as processing improvements to lower cost and improve consistency and quality. At the same time, academic laboratories are further investigating the application of nanoscale engineering to electrode materials, reaction dynamics on electrode surfaces, novel electrode materials and electrolytes.

Scott Jenkins

## Measuring Dust and Fines In Polymer Pellets



FIGURE 1. Many types of dust and fines form during the handling of bulk plastic pellets. A single pellet is shown here for size comparison

The ability to carry out such measurements can help operators improve quality control, assess equipment performance and optimize the process

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Plastics are most commonly produced and sold in pellet form due to the superior handling characteristics of pellets in downstream applications. From the moment the polymer is pelletized from its molten state, the pellets or granules undergo a series of handling steps as they move from the producer to the consumer. For instance, postpelletization steps include:

- Hydraulic conveying
- Drying (typically via spin drying)
- In-process pneumatic conveying
- Silo storage
- Packaging (via bulk shipment, or in bags or boxes)
- Unloading (via pneumatic conveying) and silo storage
- Conveying to processing equipment
- Blending and feeding

As a consequence of this repeated handling, the pellets often become contaminated with various unwanted species, namely:

• Dust or fines that are generated during pelletization, conveying and

100 8 90 80 Differential fraction, vol. % umulative fraction, vol. 30 20 1 10 0 0 1,000 10 100 10,000 Particle size, micrometers



collection in cyclones (Figure 1). The particle size distribution of dust and fines (Figure 2) can vary depending on type of polymer, process conditions and specific hardware of the handling system

- Chips, undersize pellets, miscuts and broken fragments that are generated during pelletization, conveying and collection in cyclones
- Chopped or smashed pellets, so-called worms or smeared polymer crumbs that are generated by rotary airlocks (feeders)
- Broken tails that result from poor pelletization and subsequent handling
- Streamers, floss, angel hair, ribbons or snake-skins that are generated during pneumatic conveying (Figure 3)

Many of the terms noted above are synonymous and thus are used interchangeably, based on the shape and size. Streamers can be up to a couple of meters in length.

The presence of these contami-

nants in pellets can lead to numerous problems in the downstream processes, including the following:

- 1. Gel formation in film applications
- 2. Frequent clogging of filters in pneumatic conveying systems
- 3. Cross-contamination problems in multi-product plants
- 4. Defects in the finished product
- 5. Variability of slip additives or processing aids
- 6. Color issues (such as black specks or color inconsistencies) resulting from degraded fines dislodging from process equipment
- 7.Process safety issues (such as increased risk of dust explosion in the fines-collection system)
- 8. Industrial hygiene concerns associated with respirable dust
- 9. Plugging problems at various stages of the end user's process, resulting from streamers, floss, angel hair and ribbons
- 10. Inconsistent pellet feedrates into the throat of an extruder, resulting in gage variations of profiles and films





FIGURE 4. This illustration shows how the separation of fines, tails and short streamers can be improved when the wet separation process incorporates a screen with elongated apertures

To alleviate these problems and deliver the cleanest possible product to the customer, many of today's plastics producers use dust- and streamerremoval devices in their processes. Further discussion of these devices is beyond the scope of this article.

Efforts to quantify the unwanted species in the plastic pellets have long been a source of confusion, contention and miscommunication among plastic producers, users of the pellets (converters) and vendors of solids-handling equipment. Such problems can be avoided if there is mutual agreement by all stakeholders on an appropriate standard for the measurement of dust, fines and streamers. A reliable, robust and welldocumented standard serves a variety of purposes including the following:

- Ensures greater quality control in a manufacturing process
- Provides a basis for product specification
- Serves as a troubleshooting tool to relate pellet quality with process conditions
- Helps to identify opportunities for process optimization
- Enables performance evaluation of pellet-cleaning devices

A varied and creative collection of dust- and fines-measurement techniques have evolved over the years based on experiences derived from a wide spectrum of applications. Historically, these techniques have been based on dry sieving or counter-flow air-classification concepts.

However, for plastics applications, the quality of data gathered using these methods is often compromised, due to the presence of electrostatic charges, the existence of waxy and sticky additives, and the presence of fines at particularly small particle sizes (< 50 µm) and low levels (< 50 ppm).

Dust / fines

This article summarizes the existing standards for quantifying unwanted contaminants such as dust, fines and streamers in plastic pellets, discusses the limitations of these approaches, and highlights some of the recent advances.

### Measurement techniques

In general, unwanted species contaminating a batch of plastic pellets can be broadly classified into three groups, based on their size relative to the pellets or granules (the prime product) themselves:

- Group 1 (size < pellets). Fines, dust, chips, fragments, undersize pellets, miscuts, smears, worms and illformed pellets
- Group 2 (size ~ pellets). Tails, smears, worms and small streamers
- Group 3 (size > pellets). Streamers, floss, angel hair, ribbons and snake skins

Group 1 species can typically be separated from the pellets by dry sieving or air classification if there is no tendency for the particles to adhere to the pellets, for instance, due to electrostatics, van der Waals forces, surface tension and other adhesive tendencies. Anti-static additives are used to minimize the electrostatic buildup. However, dry sieving is often unable to separate sticky fines (such as those that are rich in waxy additives).

Using an air-classification approach, the finer fraction is elutriated by the

counterflowing air. This method is quick but usually results in relatively poor separation efficiency and high variability. Separation via air classification can also be affected by the relative humidity of the elutriation air.

By contrast, wet classification is the most effective method for separation of Group 1 species from pellets and granules. Dispersing the pellets in a liquid or washing them with a liquid breaks down the attractive forces between the fines and the pellets, thereby allowing them to then be easily removed by mechanical separation. However, this approach adds a drying step to the measurement process.

Demineralized water, ethanol or a mixture of water and ethanol are commonly used for washing. Safe handling characteristics and inertness to the polymer (and its additives) are key considerations when selecting the liquid washing media.

Group 2 species are the most difficult and challenging to separate from the pellets, since most separation techniques rely on differences in particle size. The air-classification approach can be used if the aerodynamic diameters of various fractions are significantly different and electrostatic forces are minimal.

One may also exploit the differences in shape for separation. For instance, a new, innovative approach has been developed by the authors of this article, to effectively separate Group 2 species from plastic pellets. The core idea is to use a rectangular aperture (such as a wedge-wire screen) coupled with a wet washing approach, to separate the pellets from the unwanted species.

The width of the aperture is slightly smaller than the diameter of the pellets, which prevents them from passing through. However, the longer dimension of the aperture allows the tails, polymer smears, agglomerates and small streamers that are longer than the pellet size to pass through, along with the wash liquid (Figure 4).

Group 3 species are most effectively separated by dry screening. The screener can be a vibrating type, or a Trommel (rotating cylinder) type. For a meaningful estimation, the sample size must be large enough to capture a sufficient number of streamers.

Water

flow with

bubbling air

Tails and short streamers

### **Solids Processing**

### **Existing standards**

Today, there are three primary standards for measuring fines in plastic pellets or granules, and each is discussed below:

- FEM-2482: Test method to determine the content of fines and streamers in plastic pellets (1999)
- ASTM D 1921-06: Standard test method for particle size (sieve analysis) of plastic materials (2006)
- ASTM D 7486-08: Standard test method for measurement of fines and dust particles on plastic pellets by wet analysis (2008)

### **FEM-2482**

The European Federation of Materials Handling (FEM) put forth a well-documented and comprehensive procedure (FEM-2482) in 1999 to address the ambiguity associated with measuring fines and streamers in plastic pellets. In this standard, the fines are defined as the particle fraction below 500 um. The lower limit of this fraction depends on the needs of downstream processes. Three classes of fines were proposed, namely:

- *Type A:* 63 to 500 µm
- *Type B:* 45 to 500 µm
- *Type C:* 20 to 500 µm

The process schematic for measurement of fines using FEM-2482 is shown in Figure 5.

When it comes to plastic pellets, the typical level of fines in the final product can range from 10 to 2,000 ppm. Pellets with fines content in excess of 500 ppm are usually deemed "dusty." It should be noted that the fines fraction below 20 µm is not measured by this method, since this ultrafine fraction passes through the retention medium (Column C2). However, the ability to measure this fraction can be important for certain applications (such as the manufacture of optical lenses and digital storage media).

The particle fraction above 500 um with a form deviating from the usual pellet shape is defined as the streamer content. Streamers are also known by numerous other names - angel hair, floss, snake-skins, ribbons, film or foil. As noted earlier, dry screening is an effective way to separate these species from pellets.

The FEM-2482 method is based on

FIGURE 5. The elements of the wet process that is defined in FEM-2482 are shown here



wet process with two possible operating modes.

Mode 1. Fluidization mode is used when the density of washing liquid is lower than the true density of the pellets. A retention sieve (Figure 5) is not used in Column C1 during fluidization mode. The upward velocity of the liquid is set according to the Stokes velocity for the largest particle to be separated. The carryover fraction is further classified in Column C2.

Mode 2. Flotation mode is used when the density of the washing liquid is higher than the density of the pellets. Since water is the safe choice as the washing liquid for most polyolefins pellets whose density is lower than water, this mode is most commonly used.

Using the FEM-2482 method, the agitation and circulation of pellets are achieved by injecting air bubbles in Column C1. The intensity of circulation can be adjusted by the air-flow throttle valve (Figure 5). The authors of this article have evaluated numerous alternatives for mixing and agitation (such as the use of directional water jets and agitators) and have concluded that the use of air bubbles is the most effective means of agitation and recirculation of pellets in the wash column. The top retention sieve shown in Figure 5 is a 500-µm wire mesh that prevents the pellets from being carried over to Column C2.

The FEM-2482 standard also provides details on various aspects of the measurement process, such as:

- Sizing and configuration of the apparatus
- Selection of classification screens
- Ancillary equipment
- Selection of guidelines for wash liquid
- Test procedure
- Interpretation of results
- Error analysis

Sampling guidelines per FEM-2482). A sample size of 1 L or larger is recommended for fines analysis. As a general rule of thumb, the maximum size of a sample is dictated by the size of the washing column (C1). To achieve good dispersion and washing, the volume of a sample should not exceed half the volume of Column C1.

For streamer content analysis conducted using the dry-screening approach, the sample volume should be at least 50 L. Since streamers are not dispersed homogenously within the bulk, larger samples are always pre-



**FIGURE 6.** A typical pellet with a tail formed during pelletization is shown in the inset, while the larger image shows the typical size distribution of broken tails

ferred. Note that this standard lacks details regarding methods and devices to use for separation of streamers from the pellets.

Special care must be given when handling samples during filling, discharging and transportation. The methodology of sampling depends on product and plant surroundings.

*Limitations of FEM-2482.* Despite the comprehensive nature of this standard, it has several shortcomings, including the following:

1. Fines smaller than 20 µm in size are not measured or collected by the finest retention medium (Column C2). The limit on the lower cut is due to physical limitations posed by the screening operation.

2. In this standard, fines are defined as the fraction with particle size smaller than 500  $\mu$ m. However, particles with size greater than 500  $\mu$ m can exist in the fines (Figure 2). Dry screening may not be the appropriate method for separating these fines from the pellets, especially when the fines are sticky, waxy and specifically fibrous in nature. Similarly, quantification of broken tails with size varying from a fraction of the pellet size to several pellet diameters is especially challenging (Figure 6). Typical pellet size is between 3 and 5 mm.

The first limitation has been addressed by a recent ASTM standard (D 7486-08, discussed below), which recommends using a filtration disc made of glass microfibers to collect fines as small as 0.7 µm.

The second limitation can be addressed by replacing the 500-µm wiremesh retention screen (shown in Figure 5) with a wedge-wire screen (see Figure 7). The rectangular aperture of the wedge-wire screen is designed to retain the pellets while allowing



the fines, tails and small streamers to efficiently pass through. The tails and small streamers align themselves with the liquid flow and pass through the rectangular aperture (Figure 4).

Alternatively, a punched plate with elongated openings can also be used. However, the use of square wire-mesh with larger opening inevitably results in occlusion of the openings as the tails and streamers hang up on the mesh.

The wedge-wire retention screen also allows chips, undersize pellets, miscuts and broken pellet fragments to pass through and get carried over to Column C2 (Figure 5). Therefore, it is recommended that the fines classification screen-stack (Figure 5) preferably have a top sieve with 1-mm opening. The remainder of the sieves can be chosen per the FEM-2482 guideline.

### ASTM D 1921-06

This method covers the measurement of particle-size distribution of plastic materials in various forms — pellets, granules and powders. It is based on the dry-sieving approach, hence the lower limit of measurement is about  $38 \mu m$  (No. 400 sieve).

The standard proposes two methods — A and B — both of which are discussed below.

**Method A.** This method uses multiple screens stacked on top of each other. A complete distribution of particle sizes can be obtained, which can then be used to determine the mean particle diameter. The suggested sample size is 50 g.

**Method B.** This is an abbreviated version of Method A that uses limited screens. It is typically used to get specific cuts (such as percent passing through, or the percent retained) on certain screens. The suggested sample size is 100 g.

The problem of electrostatic charge

FIGURE 7. As noted in the in FEM-2482 wet process, a wedge-wire screen with elongated aperatures (right) is a more-effective alternative to the standard 500-µm retention screen (left).

buildup during dry sieving is addressed by adding an anti-static additive (up to 1 wt.%). However, the problem of sticky fines and agglomerates is not addressed in this standard and thus remains unresolved.

One fundamental problem with separation processes using sieves is the inherent inefficiency of sievebased separation methods to separate fibrous fines that are longer than the mesh opening size, even if the fiber diameter is much smaller.

### ASTM D 7486-08

This is a recent addition to the standards for fines and dust measurement in plastic pellets. It proposes a wet washing technique. The sample (typically 100 g) is placed on a filter funnel assembly, consisting of a 200-mm diameter, wire-cloth sieve with 500-µm opening. The filtration disc (90 mm in dia.) is made of glass microfiber, and the media has a pore size of 0.7 µm to 2.7 µm. The typical lower limit is 1.6 µm due to filtration rate limitations.

The pellets are washed with a strong jet of water (500 mL/min) until they are visibly clean and no particles are observed in the wash liquid. The filter disc is then removed from the assembly, dried in an oven and then weighed to measure the fines content.

This method addresses the deficiency of FEM-2482 in its inability to quantify fines smaller than 20  $\mu$ m, since fines as small as 0.7  $\mu$ m can be captured on the filter disc. However, smaller sample size (100 g) and possible operator dependence for effective washing of pellets are the shortcomings of this method.

When streamers (such as a fraction greater than 500  $\mu m)$  are present, the standard proposes using the ASTM D 1921-06 method.

TABLE. SUMMARY OF FINES-MEASUREMENT TECHNIQUES AND STANDARDS						
Fines/Dust Mea- surement Method	Pros	Cons	Applicability			
Dry sieving (ASTM D1921-06)	Easy to implement	Loss of fines during handling	Suitable for coarse fines (> 500 µm)			
	Inexpensive	Poor separation if electrostatic or adhesive forces are present				
		Fibrous fines longer than sieve opening do not separate effectively				
		Small sample size				
Air classification (Fluidized beds, zig-zag classifiers)	Short test duration Good for qualitative testing	Accuracy affected by air humidity	Excellent qualitative test Generally not recommended for			
		and static generation				
		when the adhesion forces are present	More suitable for non-polymer			
		Poor recovery of separated fines	applications			
Wet separation process (FEM-2482)	Robust method Operator independent	Upper and lower cuts on particle size are restrictive	Applicable for most polymers			
	Well defined procedure	Sample size is limited for commercial units				
	available	Fibrous fines longer than sieve opening do not separate effectively				
Wet separation process (Modified FEM-2482 sith wedge-wire retention screen)	Robust method	Limitation due to lower cut size	Wider applicability			
	Operator independent	(20 µm) still remains	than original method			
	Well defined procedure					
	Eliminates the limitation on upper cut (500 µm) for fines					
	Wedge wire enables efficient separation of broken tails					
Wet sieving (ASTM D7486-08)	Address lower cut size limita- tion of FEM-2482 down to 0.7 µm	Small sample size Washing is manual and may not remove strongly adhered fines	For applications where fines less than 20 µm are important			
	Commercial equipment available	Fibrous fines longer than sieve opening do not separate effectively				

The methods discussed above are summarized in Table 1. The applicability range for each method based on particle size is shown in Figure 8.

### **Tips for success**

To ensure maximum reliability during measurement of fines or dust in plastic pellets, readers are encouraged to do the following:

- Understand the nature and content of typical non-pellet fraction (such as fines, dust, streamers) in the bulk material
- Identify the key requirements for downstream processes and be clear about the purpose of the measurement (for instance, are the measurements being sought to reduce process variability, meet product specification, assist in troubleshooting or optimize equipment performance?)
- Identify the most suitable test method(s) for the purpose, and establish specific testing parameters based on the material at hand
- Understand the accuracy, precision and reproducibility of the chosen test method
- Obtain representative samples and follow good sampling guidelines



FIGURE 8. This figure shows the range of applicability for the various measurement standards discussed here, based on particle size

Readers should note that obtaining a "representative sample" for fines and dust analysis is a difficult task that presents its own challenges. Specifically, the samples inevitably become biased, due to the attraction of fines towards any sampling device or sampling container. For example, the use of a plastic scoop can result in significant loss of fines from the sample, due to electrostatic attraction between the fines and the scoop itself. large sample from the process and reduce it to the appropriate analytical size using a sample splitting process (such as a riffler). However, one must pay close attention to the loss of fines during this step, otherwise the results will be biased. Purging the sampling line before taking the sample, taking spot samples to create a composite, analyzing the entire sample, rinsing the sample container to recover fines and the use of anti-static sprays will help to reduce sampling errors.

It is a common practice to obtain a

### **Solids Processing**

### **Closing thoughts**

One of the key metrics of product quality for polymer pellets is the amount of fines, dust and streamers that are generated during handling. The presence of such unwanted species has a direct bearing on downstream applications, and therefore to the acceptability and value of the final product.

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During the past decade, significant progress has been made toward the standardization of measurement methods available to quantify these unwanted contaminants. These standards provide a common basis for evaluating product quality, for assessing the performance for pellet-cleaning systems, and for troubleshooting processes. The success of these standards hinges upon the user's understanding of the underlying concepts and careful attention to the details. In this article, the authors have also introduced an innovative approach to measure tails and short streamers in the pellets.

Edited by Suzanne Shelley



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more than 20 years of experience in particle characterization, aerosol science, air filtration and sol-ids processing technology. He has authored some 20 papers, has been an instructor of the course on Particle Characterization at the International Powder & Bulk Solids Conference/Exhibition for the past 15 years, and has authored an article on particle characterization for the "Kirk-Othmer Encyclopedia of Chemical Technology."



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Associate of Science degree in physics and chemistry. For the past 10 years, he has worked on numerous projects related to fluid mechanics and mixing technology. He has extensive laboratory experience in both lab equipment and wet chemistry.



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### Midwesco<sup>®</sup> Launches One Piece Molded Bottom Pleated Bag

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### BWB Technologies Model XP Flame Photometer

The BWB- XP is a high quality, high performance instrument employing modern technology to measure alkali and alkaline earth metals Sodium (Na), Potassium (K), Lithium (Li), Calcium (Ca) and Barium (Ba). Liquid samples, when introduced to a flame fuelled by pro-



pane or lpg, will emit light of a specific wavelength, the intensity of which will be proportional to the concentration of the ions present. The principle has been understood for over one hundred years, but the BWB-XP brings 21st century technology to the technique, making analysis more reliable, accurate and simple than ever before.

BWBTechnologies www.bwbtech.com/ce Circle 291 on p. 62 or go to adlinks.che.com/23018-291

### NEW 3 Inch Stainless Steel 2-Way Solenoid Valves



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struction with continuous duty coils for all AC and DC voltages, available normally open or normally closed with 150 and 300lb flanged connections. For literature or same day quotation contact: **MAGNATROL VALVE CORPORATION** PHONE: 973-427-4341 E-MAIL: info@magnatrol.com WEB SITE: www.magnatrol.com Circle 293 on p. 62 or go to adlinks.che.com/23018-293

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for the accurate measurement of whitening agents. APHA, Saybolt, Gardner, ASTM D 1500, Yellowness, Whiteness and Haze can be measured. The sphere minimizes effects introduced by sample haze. www.hunterlab.com 703-471-6870 info@hunterlab.com

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### People

### WHO'S WHO



Coote

Roscoe

Arthur D. Little (London) appoints Joseph L. Coote as global energy and chemicals practice leader.

Aaron Cunningham is named marketing specialist at Oseco (Broken Arrow, Okla.).

Choren Industries (Freiberg, Germany) appoints Marcell Ulrichs CEO.

Peter Roscoe becomes general manager of the power generation group of the consultancy ESR Technology (Warrington, U.K.).



VanDyke

AIChE (New York) names Miriam Cortes-Caminero executive director of its Society for Biological Engineering.

*Rick VanDyke*, a senior group manager of factory automation control system technology systems for the Frito-Lay division of PepsiCo, joins the board of directors of the Organization for Machine Automation and Control (OMAC; Research Triangle Park, N.C.).

**OPW Fluid Transfer Group** (Mason, Ohio) appoints Jeff Reichert vice-





Reichert

Welp

president of the global chemical and industrial business unit.

Mark Henning becomes general manager for Dow Microbial Control (Buffalo Grove, Ill.).

Bill Harvey becomes director of logistics engineering for ChemLogix LLC (Blue Bell, Pa.).

Martin Welp is head of the polyesters and adhesive resins product line at Evonik (Essen, Germany). Suzanne Shelley

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### CHEMICAL CHEMICAL FACTS AT YOUR FINGERTIPS

Department Editor: Scott Jenkins

### **EXPANSION TANK**

- A well designed expansion tank:
- 1. Maintains a static pump-suction head
- 2. Compensates for temperature-related
- volume and pressure changes
- 3. Provides a means of venting moisture and low boilers
- 4. Prevents fluid oxidation

Usually, the expansion tank is installed at the highest point in the system and is connected to the suction side of the pumps. It should serve as the main venting point of the system, as well as provide for system fluid expansion, which can be 25% or more depending on fluid choice and on the operating temperature range. For heating circuits, the expansion tank should be sized so that it is one-quarter full at ambient temperature and three-quarters full when the system is at operating temperature. For cooling, it should be vice versa.

The double drop-leg expansion tank provides greater flexibility of operation than a single leg tank. From a single-leg expansion tank, venting of noncondensibles is often difficult in heating systems as is purging of air and water on startup. A double-leg expansion tank provides uninterrupted flow on startup and significantly improves the venting capability of the system. All vent lines should be routed to a safe location.

Experience indicates that systems with expansion tanks open to the atmosphere have fluid contamination problems related to oxidation and excessive moisture. Therefore, open expansion tanks should not be employed in systems using organic heat transfer fluids.

An effective way to minimize fluid oxidation is to blanket the expansion tank vapor space with an inert gas (for example, nitrogen,  $CO_2$ , or natural gas). When using a nitrogen blanket, moisture should be driven off from the fluid before the gas pressure is set. If this is not practical, air contact can be minimized by a cold seal trap arrangement. Low boilers and moisture can collect in the cold seal trap, so the fluid in the trap should be discarded periodically.

### CONTROLS

Install heater controls to regulate the firing mechanism in direct proportion to the required output. These controls should increase or decrease the heat input to maintain the heat transfer fluid at the operating temperature required by the energy demand. Small units may be operated satisfactorily by relatively simple "on-off" or "high-low" controllers. However, units of all sizes will operate more uniformly if equipped with modulating temperature controls. Install user controls to regulate the flow of the heat transfer fluid in proportion to the energy consumption of the equipment. In a multiple-user system, separate controls should be installed on each consuming unit to assure the proper energy delivery.

### **FIRE RESISTANCE**

- Materials considered NOT fire-resistant:
- Low melting point metals: aluminum,
- copper
- Elastomers
- Polytetrafluoroethylene (PTFE) gaskets and packing
- Non-asbestos, fiber-reinforced rubber bound gaskets
- Materials considered fire resistant:
- High-melting-point metals: carbon and stainless steel, nickel alloys
- Flexible graphite packing and gaskets
- Asbestos packing and gaskets

### HEATER

Two basic fired-heater designs for indirect heat transfer systems are available: liquid tube and fire tube types.

- In liquid tube heaters, fluid is pumped through the tubes as it is heated. The fire is outside the tubes.
- In fire tube heaters, fluid flows through the heater "shell" around the outside of the fire tubes.

Liquid tube heaters are preferred at all temperatures. At temperatures below 500°F (260°C), fire tube heaters with a special baffle design to eliminate hot spots can be used.

Two basic configurations for electrical heaters are available: container design and tubular design.

- In the container design, one or more electrical heating elements are inserted into a container through which fluid flows.
- In the tubular design, the heating elements are inserted longitudinally into tubes through which the fluid flows.

The tubular design is preferred for the heating of organic fluids. If the container design is to be used, due to the unpredictable flow conditions around the elements, heat flux should be limited to 1–2 W/cm<sup>2</sup>. For all heater types, the maximum heat flux at the surface of the heat source and the fluid velocity over it should be in proper balance to avoid excessive film temperature. Careful

### Heat Transfer: System Design II

attention must be paid to achieving turbulent flow (without stagnation zones) around the heat transfer surfaces to eliminate hot spots and localized fluid boiling.

### VALVES

Cast- or forged-steel valves with 13-chrome trim are satisfactory for service in organic heat-transfer-fluid systems. Globe valves with an outside screw (as a protection against high temperatures) should be used throughout the system when tight sealing of fluids is desired, and should be installed upstream and downstream of each pump and at each user. Gate valves are acceptable for use, but not to provide reliable positive shut-off.

The use of valve stem seals can be effective in minimizing system leakage. For valve stem seals:

- Flexible graphite packing with inner and outer anti-extrusion rings of braided graphite fiber gives the best results for elevated temperature systems.
- PTFE packing often works in systems operating up to 400°F (200°C).
- Metal bellows-sealed valves are frequently used with excellent results, but these valves are relatively expensive, especially in larger sizes.
- Fiber packing materials have given poor performance in service with organic fluids, and are not recommended.

### **References and further reading**

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### Acknowledgment

Material for this "Facts at Your Fingertips" was supplied by Solutia Inc.

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# ISA Show Preview

MARTEL

he Instrument Society of America (ISA) 2009 exhibitor show Expo 2009 will be held October 6-8 at the Reliant Center in Houston. Over 300 exhibitors are expected to display automation-and-control technology products and services. The show is organized into six different tracks, including categories for safety, process automation and control. as well as a new section on energy and the environ-

ment. In addition to exhibitors' booths, the anticipated 11,000–12,000 attendees will be able to listen to daily keynote addresses and a newly added program highlighting industrial security. Participants also will have an opportunity to sit in on the ISA Industry Standards Forum or attend several exhibitor educational programs. In addition, a larger-than-usual number of co-locating meetings are scheduled to coincide with the Expo. Additional information about the show can be found at www.isa.org.

Expo 2009 attendees are encouraged to visit *Chemical Engineering* at Booth 1604. Examples of technology slated for exhibit at the Expo include the following new products.

#### These power supplies are optimized for driving inductive loads

These 200- and 400-W bipolar-operational power supplies (photo) are designed for stable operation in current or current-limit mode to electric inductance loads of up to 1 Henry. The models are suitable for applications such as motor testing, magnetic component testing, industrial applications with inductive loads, driving CRT coils, cryogenic applications and powering correcting magnets for particle accelerators. Booth 2610 — Kepco Inc., Flushing, N.Y.

www.kepcopower.com

Kepco

### A new gage with data logging feature is introduced

A data-logging feature is now available for the BetaGauge PI digital pressure-test gages (photo), and can be used with a new software application. BetaLOG can collect pressure data on multiple BetaGauge PIs and can accommodate varying time intervals and lengths of data logging runs. Four different types of data capture allow users to log either all data or only points of interest. Booth 2316 — *Martel Electronics Corp., Derry, N.H.* **www.martelcorp.com** 

#### This oxidation and reduction potential sensor is built to last

A newly released oxidation-reduction sensor is built with a patented technology, known as axial ion path, to allow stability, long life and reliability. The sensor (photo) is available in several models for inline, hot-tap or quick-change fittings and can be used for process measurements at temperatures up to 140°C and pressures exceeding 3,000 psi. Booth 2735 — Barben Analyzer Technology LLC, Carson City, Nev. www.BAT4ph.com

AMETEK Services Instruments

### Measure water and CO<sub>2</sub> to low ppm range with this gas analyzer

A new gas analyzer using diode-laser absorption spectroscopy cost-effectively measures water vapor and carbon dioxide in natural gas and hydrocarbon streams. The model 5100-NCM (photo) is tunable and has a limit of detection in the low ppm range. The laser-based analyzer features compact, fully enclosed optics and sample conditioning. Booth 1907 — Ametek Process Instruments, Pittsburgh, Pa. www.ametekpi.com

### **Show Preview**

### Industrial electronics firm offers a host of new products

This company is trotting out a host of new products at the ISA show. Company offerings include pre-assembled specific interface cables, new industrial Ethernet routers (photo), industrial power supplies, a new line of a.c. DIN-rail receptacles, and a new

#### universal isolator. Booth 1949 — Weidmuller Group, Richmond, Va. www.weidmuller.com

### Customers can configure these valves using online tool

The 8262/8263 Series solenoid valves are available with a Web-based tool that customers can use to rapidly build





a valve to meet specific requirements before ordering. The two-way valves have higher pressure ratings and can be used to control the flow of air, water and light oils in industrial-, agricultural- and food-products-machinery applications. The valves are available in brass and stainless steel, and come in three pipe sizes, from 1/8 in. to 3/8 in. Booth 1743 — ASCO Valve Inc., Florham Park, N.J.,

www.ascovalve.com

### This fluid-level transmitter has a simple design and installs easily

The digital E3 Modulevel detects liquid level changes using a simple buoyancy principle. Features of the transmitter include a simple linkage between the level-sensing element and the output electronics, as well as a vertical construction to allow low product weight and easier installation. The transmitter is available in multiple configurations and pressure ratings for use in a variety of process applications. Booth 2133 — Magnetrol International, Downers Grove, Ill. www.magnetrol.com

#### These shielded Ethernet switches can reduce wiring costs

The ToughNet M12 Series of Ethernet switches are designed for installation directly on electronic devices at field sites without an enclosure, which reduces wiring costs. The switches can be used for applications where electronics devices must withstand harsh conditions, such as vibrations, voltage variations and electromagnetic interSealevel Systems

Universal Monitors





ference. The switches operate within a temperature range of -40°C to 75°C. Booth 2501 — Moxa Americas Inc., Brea, Calif.

### www.moxa.com

### **Plastic flowmeters that avoid** paddlewheel replacement cost

These polyvinyl chloride (PVC) and chlorinated PVC (CPVC) flowrate transmitters are offered at the same price as paddlewheel meters, but con-

tain no moving parts and so avoid the costs of replacing paddlewheels. P420 Series plastic flowmeters (photo) are designed for cost-effectiveness in processing water, brine and corrosive fluids in water treatment, chemical and desalination applications. PVC and CPVC types are available in six pipe diameters for flowrates from 6 to 200 gal/min. Booth 2504 — Universal Monitors Inc., Hazel Park, Mich. www.flowmeters.com

#### This gas-sample probe is coupled with an ammonia converter

The newly introduced model 270/NH3 Gas Sample Probe and Ammonia Converter (photo, p. 32D-4) is designed to provide users with both a converted and an un-converted sample stream. This ability provides the means to measure ammonia slip normally found at the exit of a selective catalytic reduction (SCR) process, using the "Dual NOx Differential Method." The sample

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### **Show Preview**

probe and ammonia converter are configured as one unit, providing filtration and conversion directly at the source of measurement. The model includes filter purging and a calibration gas inlet port for EPA (Environmental Protection Agency) compliance. Booth 2735 — Universal Analyzers Inc., Carson City, Nev. www.universalanalyzers.com

### Plant instrumentation software is for contractors and operators

Newly introduced plant instrumentation software aids in specifying, designing and maintaining plant instrumentation and control systems. AVEVA Instrumentation represents an addition to this company's software portfolio and is designed for both plant EPC (engineering, procurement and construction) contractors and plant owner-operators. The product



can be used as standalone software or be integrated with other company applications. Booth 2649 — Aveva Group PLC, Houston www.aveva.com

### This flowmeter delivers high accuracy in small lines

Designed for liquid or gas line sizes from one to six inches, the Wafer-Cone flowmeter can achieve accuracies of  $\pm 1.0\%$ . The flowmeter can be used to measure natural gas flow from wellheads, as well as in small process lines, burners or cooling systems. The unit is easy to install and requires minimal maintenance. It requires a smaller straight pipe run than many other flowmeters — 1–3 pipe diameters upstream of the flowmeter and 0–1 downstream. Booth 2434 — *McCrometer* 

Inc., Hernet, Calif. www.mccrometer.com

### This embedded computer offers input and output flexibility

The Relio R9 embedded computer (photo, p. 32D-3) is designed to maximize I/O flexibility. The reduced instruction set computer (RISC) is rated for a wide temperature range and has a compact housing that can be mounted in many locations. Booth 2437 — Sealevel Systems Inc., Liberty, S.C.

www.sealevel.com

Scott Jenkins

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### Jamesbury Emission-Pak<sup>®</sup> valves keep your emissions under control

Many process streams encourage fugitive losses. Metso Automation's Emission-Pak provides a quick, easy way of assuring compliance with emissions standards.

Mounted on Jamesbury<sup>®</sup> valves, Emission-Pak combines a PTFE/graphite body seal and gasket, which maintains a leak-free joint at the valve bonnet, with a double-packed, live-loaded V-ring steam seal mechanism that maintains a constant packing force without over-compression.

Emission-Pak is available in a wide range of corrosion resistant trim materials, and is suitable for use in extreme pressure and temperature situations.



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Management

### SEPTEMBER

#### Coriolis meters for low-flow applications

The Micro Motion Elite Coriolis meter range has been expanded for low-flow applications (photo). Available in two sizes (2- and 4-mm nominal dia.), the new meters deliver flowrates of 2 to 330 kg/h with accuracies of ±0.05% (liquid flow), ±0.35% (gas flow), and ±0.0000 g/mL (liquid density). Wetted parts are of 316L stainless steel and the sensor enclosure is available with polished-316L external surface and rounded corners. For corrosive and high-pressure applications, the meters are also available in nickel alloy construction and are rated to 413 bar. — Emerson Process Management. Baar, Switzerland www.emersonprocess.eu

### An optimum valve for reciprocating pumps

The CL pump valve (photo) for reciprocating pumps combines the two key factors for cutting operating costs into one valve: optimum performance and efficient service. The CL pump valve has an optimized design and a combination of proven materials. They can be incorporated into any reciprocating pump and are suitable for use with any aqueous solution. The valve features heavy duty, non-metallic sealing elements, springs that do not come in contact with the medium being handled, and optimized flow control. -Hoerbiger Kompressortechnik Holding GmbH, Vienna, Austria www.hoerbiger.com

### This thermocouple connector communicates wirelessly

The MWCT Wireless Smart Thermocouple Connector Series (photo) features stand-alone, battery-powered thermocouple (TC) connectors that transmit measurement data back to a mating receiver up to 90 m away. Each unit is factory set as a Type J, K, T, E, Omega Engineering

R, S, B, C or N calibration connector. When activated, the connector will transmit readings continuously at a preset time interval that was programmed by the user. Each unit mea-

sures and transmits TC input readings and connector ambient temperatures to a receiver, which are displayed on the PC screen in real time using free software. — Omega Engineering, Inc., Stamford, Conn. www.omega.com

#### A kneader for high-fill, rigid-PVC compounding

The 4-flight quantec Kneader (photo) performs rigid PVC compounding with up to 100 phr (parts-per-hundred rubber) fillers possible. Among the Kneader's new engineering features are an extension of the process zone to 15 L/D (screw length-to-diameter ratio), and the addition of a downstream vertical Inlet Screw for feeding fillers directly into the gelled PVC melt. Both the intake zones have a larger housing and screw diameter, enabling the biggest possible fillers uptake volume in the process zone. Trials on the quantec 50EV test facility have shown that with 100 phr chalk filling, throughputs as high as 390 kg/h are possible with consistently excellent compound quality. These results have been confirmed with quantec Kneader sizes up to 110EV. — Buss AG, Pratteln, Switzerland www.busscorp.com

EM-Technik

#### Save space with a new size of mini ball valves The Series 61 mini ball valves area

The Series 6L mini ball valves are now available with a nominal diameter of

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DN 02 and female G-thread 1/16 in. This makes them especially suitable for space-saving mounting. The ball is manufactured in one piece with the PTFE stem centered by sealing sleeves, and the stem sealed with an O-ring. The mini ball valves are used in laboratory and analytical applications and the pharmaceutical

industry. — EM-Technik GmbH, Maxdorf, Germany www.em-technik.com

### -- -

### Monitor processes remotely with this station

The new AutoLog RTU (photo) is suitable for remote monitoring and control of oil and gas pipelines, cathodic protection, tanks, pumping stations, buildings, water treatment plants and environmental supervision. It can be used for any small to medium I/O quantity applications. RTU has PLC features, PID controllers, clock



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and calendar controls, data logging. ModBus interface and so on. The unit allows many communication possibilities, including GSM, GPRS, WLAN, Internet, RS-485 and TETRA. Application programs and configuration parameters can be changed remotely, without costly onsite visits. — *FF-Automation Oy, Vantaa, Finland* **www.ff-automation.com** 

### An aseptic valve is designed for critical areas

This patented, compact aseptic control valve (photo) newly added to the Bad-

ger Meter valve range, is suitable for use in critical areas, such as bioreactors pharmaceuticals, biologics and food processing. The Series SCV-09 is a modulating diaphragm style valve that meets the manufacturing standards of

3A Sanitary Standards. The valve uses a patented sealing arrangement that avoids metal-to-metal contact, which could result in metal particles being released into sensitive products, while providing a similar level of control to a metal plug and seat. The valve is available in sizes 1/2, 3/4 and 1 in. with 316L stainless-steel body. It is suitable for low to medium flowrates and has a maximum operating pressure of 10 bar. — *Pump Engineering Ltd., Littlehampton, U.K.* 

www.pumpeng.co.uk Gerald Ondrey



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# Strategies for Maler Reuse

Membrane technologies increase the sustainability of industrial processes by enabling large-scale water reuse

#### Peter Aerts and Flora Tong Dow Water & Process Solutions

n more and more locations, the availability of fresh water resources is limited and water reuse is becoming increasingly important. For many industrial applications, the availability of water is essentially a "license to operate".

A large component of the water consumption in many chemical process industries (CPI) is high- and lowpressure boiler water. As such, reusing cooling water blowdown — water discharged from the cooling water system — for boiler water makeup can be a very attractive option in water-stressed areas. Another option gaining attention is recycling municipal wastewater for industrial uses. In this article, the technology options, advantages and disadvantages of using membranes to reuse water for these key industrial applications are discussed.

### THE DRIVERS FOR REUSE

Water reuse has several drivers. First of all, the need for water reuse is related to freshwater availability, which depends on the natural environment, climate and the industrial and urban pollution related to the use of water. The affordability of water treatment compared to the price of freshwater is a driver for reuse in areas where the two are similar. In regions where freshwater is relatively inexpensive, unfortunately, water conservation and reuse are not high priorities.

Secondly, population growth and urbanization, which go hand in hand with industrialization and an improvement of the living standard, create a local imbalance between water supply and demand. This is currently occurring in Asia and is influencing policy makers to stimulate water reuse. Water reuse has some practical challenges in these regions, though. First, the lack of infrastructure drives the popularity of modular technology offerings; and second, the need to achieve very stringent quality specifications of reused water drives technology development.

Membranes are an important technology used for water treatment, and various types of membranes are available to address different needs, as illustrated in Figure 1. Figure 2 offers an illustration of the multiple layers that allow wastewater to be successfully treated using membrane technology.

#### PROCESS WATER FROM COOLING TOWERS Blowdown characteristics

Cooling tower blowdown water is often discharged to the sanitary sewer system, however, for power plants, petroleum refineries, petrochemical and chemical plants, as well as natural-gas process plants, cooling tower blowdown water is recognized as the best available water source to reuse because of the large volume that is available and the mature technology options that are proven to achieve the right water quality. The main technical challenge to reuse this blowdown water is the unstable pH of the water with high salt content (referred to as total dissolved solids or TDS), high hardness (high concentration of  $Ca^{+2}$ ) and high alkalinity (HCO<sub>3</sub><sup>-</sup>). Sometimes blowdown contains high levels of Si, SO<sub>4</sub><sup>-2</sup>, chemical oxygen demand (COD) and quite often high levels of suspended solids. The water quality varies substantially with region, since the feed source for cooling towers is surface water.

In a cooling tower, the absorbed heat is released to the atmosphere by the evaporation of some of the cooling water in mechanical forced-draft or induced-draft towers. More than 90% of all the water used by industry and about two-thirds of the total wastewater generated by U.S. manufacturing plants is the result of cooling operations. The circulation rate of cooling water in a typical 700-MW coal-fired power plant with a cooling tower amounts to about 71,600 m<sup>3</sup>/h (315,000 gal/min) and the circulating water requires a makeup rate of perhaps 5% (or 3,600 m<sup>3</sup>/h). In many petroleum refineries, makeup water to the cooling tower can account for up to 50% of the total demand for fresh water. A typical large refinery processing 40,000 metric tons (m.t.) of crude oil per day (300,000 bbl/d) circulates about 80,000 m<sup>3</sup>/h of water through its cooling tower system of which half  $(40,000 \text{ m}^3/\text{h})$  needs to be replenished.

In open, recirculating cooling-water systems, the concentration of mineral salts increases as evaporation occurs.



FIGURE 1. Membranes are used in a spectrum of filtration applications



**FIGURE 2.** This spiral-wound RO membrane actually consists of two membranes with a brine channel spacer at the feed side and a permeate channel spacer at the permeate side, which allow the product water to move to the center of the element

When the concentration of mineral salts exceeds their solubility, fouling and scale formation on heat exchange surfaces will occur. The water is cycled through the cooling water system numerous times before the water becomes saturated and must be discharged out of the system. This discharged water, which is called blowdown water, is controlled by a conductivity sensor and bleed valve in the tower basin to monitor the upper concentration limit of the

mineral salts and dissolved contaminants. The discharged volume needs to be replenished with fresh makeup water. Clearly, management of cooling tower blowdown is necessary to prevent fouling and scaling and to efficiently use the makeup-water resource. Water consumption of cooling towers can be reduced significantly by minimizing blowdown in coordination with an integrated operation and maintenance program. Obviously, when the blowdown is minimized, the concentration ratio increases. The amount of blowdown minimization that is possible and its potential savings is guided by the quality of the feedwater.

Most of the scaling impurities in cooling water are alkaline, usually in the form of  $Ca^{+2}$ ,  $Ba^{+2}$ ,  $Sr^{+2}$  and  $Mg^{+2}$ associated with bicarbonate and silica. The higher the concentration of these impurities, the higher the pH value of the water will be. These impurities, especially calcium bicarbonate, are less soluble at higher pH values. Therefore, acid (usually sulfuric) is added to the circulating water to lower the pH and increase the solubility of the impurities so they can be removed by proper blowdown of the system.

Corrosive salts are part of the dissolved solids, sulfates and chlorides, which can be kept under corrosive limits by disposing of a percentage of the re-circulated water and by adding fresh water to the cooling tower. Corrosion can be minimized by the addition of a corrosion inhibitor that reacts with a metallic surface, or the environment this surface is exposed to, as a result giving the surface a certain level of protection.

tegrated operation and maintenance Despite the various qualities of coolprogram. Obviously, when the blow- ing-tower blowdown water, it is often

### **Cover Story**

### recycled as boiler makeup water. **Quality needed for boilers**

Boilers are mainly classified by low pressure (< 600 psig), medium pressure (600-2,400 psig) and high pressure (>2,400 psig) systems. Any water used for this application needs to be pretreated or polished. The type of condensate polishing operation depends on the operating parameters.

Low pressure: For low pressure boilers at steam pressures below 600 psig (41 bar), boiler feedwater is treated to prevent hard scale formation and corrosion in the boiler. Some type of chemical addition, such as phosphate addition, is used together with gross particulate filtration and decarbonation. Boiler water salts are kept from the steam cycle by control of the entrainment carryover and by boiler blowdown.

Medium pressure: For medium pressure boilers with steam pressures of 600 to 2,400 psig (41 to 165 bar), control of silica, control of corrosion, and removal of particulate matter are required. Control of silica is necessary to prevent silica from volatilizing with the steam and depositing on the turbine blades. Makeup feedwater demineralization with an anion bed can control the silica levels in the water if it cannot be controlled economically with boiler blowdown. Control of corrosion is mainly done by adding phosphates or using all volatile treatment (AVT). AVT uses ammonia or other volatile amines (morpholine, monoethanolamine) to adjust water pH and control corrosion in that way. Condensate "scavenging" is often used to remove corrosion products from condensate returning from the turbine. Condensate scavenging uses a cation-resin deep bed operated in the sodium or amine form to filter particulate matter and to remove all hardness ions.

While many systems in the 600 to 2,400 psig (41 to 165 bar) pressure range do not require condensate polishing, there are exceptions. For example, nuclear-fueled boiling water reactors (BWR) have historically been "zero solids" systems, even though the boilers used typically operate near 1,250 psi (86 bar). They have stringent feedwater-quality requirements and

fulltime condensate polishing requirements. Neither AVT nor phosphate chemistry is practical in BWR primary systems since condensate circulating through the nuclear reactor has the potential for induced radioactivity. High pressure: As the boiler pressure increases beyond 2,450 psig (169 bar), demineralization of makeup water of the major contaminant ions, such as sodium and silica. becomes mandatory to satisfy the water quality requirements. Chemical treatment of the boiler or steam generator system shifts from phosphate treatment to the use of AVT using ammonia or amines to elevate pH and control corrosion in the high temperature and wet-steam areas of the steamcondensate loop. The optimum pH range depends on the materials of construction; at least 9.3 for all-ferrous systems and 8.8-9.2 for systems containing

copper. For high pressure boilers, fullflow condensate polishing is a critical operation for the removal of soluble and insoluble corrosion products, and for the removal of contaminant ions as a result of a condenser in-leakage.

In North America, pressurizedwater-reactor (PWR) plants using recirculating-type steam generators (RSGs) have focused their secondary cycle, water-chemistry program on the minimization of insoluble-corrosion-product transport and sodiumto-chloride molar ratio control in the tubesheet crevice areas of the steam generator. A shift to the use of organic amines (monoethanolamine in most cases) for pH control and procedural changes in the resin-regeneration process have been instrumental in achieving the desired improvements in secondary-cycle water chemistry. In addition to AVT chemistry, hydrazine is added to scavenge trace amounts of dissolved oxygen and maintain reducing conditions.

#### **Boiler-water preparation**

There are several main routes used to prepare boiler water. The most known method is using strong-acid-cation exchange resins (in the H<sup>+</sup> or Na<sup>+</sup> form)



**FIGURE 3**. This is an example of a fiberglass reverse osmosis (RO) membrane element

followed by strong-base-anion exchange resins (in the OH<sup>-</sup> or Cl<sup>-</sup> form) to remove ions. This is followed downstream with a mixed bed.

The main considerations for demineralization operation using ion exchange resins are operating economics, quality and reliability of resin performance and minimizing environmental costs. The primary variables in determining the operating economics are costs associated with regeneration, waste neutralization and disposal, as well as, resin replacement and disposal. Field experience and laboratory tests show that ion-exchange resins of uniform particle size offer numerous advantages over resins with a conventional Gaussian particle-size distribution. These advantages include, but are not limited to, higher regeneration efficiency, greater operating capacity, reduced leakage and better rinse characteristics. The second method uses reverse osmosis membranes at a recovery of 70-75% to remove >99\% of all the ions present in the water. As a second step downstream for further polishing to achieve low conductivity in boiler makeup water, either mixedbed ion exchange or electrodeionization (EDI) is used.

Electrodeionization: Electrodeionization is a continuous and chemicalfree process of removing ionized and ionizable species from the feedwater using direct current (d.c.) power. EDI can produce up to  $18 \text{ m}\Omega$ -cm high-purity water with high silica and boron rejection (micro-ohm centimeters are a unit of resistivity for pure water). As a result, EDI can replace conventional mixed-bed ion exchange, and eliminate the need to store and handle hazardous chemicals used for resin regeneration and associated waste neutralization requirements. Direct current is applied across the cells. The d.c. electrical field splits a small percentage of water molecules (H<sub>2</sub>O) into hydrogen (H+) and hydroxyl (OH-) ions. The H<sup>+</sup> and OH<sup>-</sup> ions attach themselves to the cation and anion resin sites, continuously regenerating the resins. Since hydrogen ions have a positive charge and hydroxyl ions have a negative charge, each will migrate through its respective resin, then through its respective permeable membrane and into the concentrate chamber due to ionic attraction to the cathode or anode. Cation membranes are permeable only to cations and will not allow anions or water to pass, and anion membranes are permeable only to anions and will not allow cations or water to pass. The H+ and OH- ions collect in the concentrate (C) chamber to yield water. Contaminant ions, dissolved in the feedwater, attach to their respective ion exchange resin, displacing H<sup>+</sup> and OH<sup>-</sup> ions. Once within the resin bed, the ions join in the migration of other ions and permeate the membrane into the C chambers. The contaminant ions are trapped in the C chamber and are recirculated and bled out of the system.

In many industrial systems, reverse osmosis (RO) elements (Figure 3) serve as pretreatment for ion exchange resin beds. When installed before ion exchange beds, RO elements reduce demineralizer operating costs dramatically. For example, pretreating water for boiler makeup with RO elements removes silica, dissolved solids and total organic carbon (TOC). This extends the life of ion exchange resins and lowers chemical regeneration usage, waste handling and maintenance costs. RO elements are also frequently used in double-pass RO systems to produce high purity water in a simpler continuous process.

#### Blowdown as boiler makeup

Currently, most newly built fossilfuel power plants with recycle cooling systems and some existing fossil-fuel power plants already employ wastewater reuse. There are mainly three types of reuse systems: chemical softening, a high-efficiency reverse osmosis, and ultrafiltration combined with reverse osmosis.

*Chemical softening:* Lime softening can be used to remove carbonate hardness by adding hydrated lime:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2 CaCO_3 + 2 H_2O$$
(1)

$$\begin{array}{l} Mg(HCO_3)_2 + 2 \ Ca(OH)_2 \rightarrow Mg(OH)_2 \\ + 2 \ CaCO_3 + 2H_2O \end{array} \tag{2}$$

As a result calcium, barium, strontium, and organic substances are reduced significantly. Colloids and suspended solids can be removed by adding coagulants or flocculants just before lime dosing.

The noncarbonate calcium hardness can be further reduced by adding sodium carbonate or "soda ash":

$$CaCl_2 + Na_2CO_3 \rightarrow 2 NaCl + CaCO_3$$
(3)

The lime soda-ash process can also be used to reduce the silica concentration. When sodium aluminate and ferric chloride are added, the precipitate will include calcium carbonate and a complex with silicic acid, aluminum oxide, and iron. After the clarification step, an RO operation is carried out. This requires a pH adjustment and media filters upfront in order to protect the RO membranes. A conventional RO system can tolerate 150 mg/L silica in feedwater.

With the hot lime-silicic-acid removal process at 60–70°C, silica can be reduced to 1 mg/L by adding a mixture of lime and porous magnesium oxide. This process requires a reactor with a high concentration of precipitated particles serving as crystallization nuclei. This is usually achieved by upflow solids-contact clarifiers. The effluent from this process requires media filtration and pH adjustment prior to the RO elements. Iron coagulants with or without polymeric flocculants (anionic and nonionic) may be used to improve the solid-liquid separation.

The advantages of lime softening are the high removal efficiency for hardness and alkalinity, and less scaling potential for RO membranes resulting in a lower cleaning frequency, which makes this technique suitable for large-scale wastewater reuse. The disadvantages are the large footprint, the fact that it is labor intensive and the need of pH adjustment and media filters prior to RO trains. Further potential risks include the residual hardness if only lime is applied (which will affect scaling on the RO membranes) and the possibility to clog subsequent filters due to slow reaction.

*High efficiency RO:* Increased ROprocess efficiency is obtained by combining several industry-proven treatment steps into a single process that has the ability to treat difficult water at high recoveries and increased flux rates.

In the first step, the feedwater undergoes a weak-acid cation (WAC), partial softening before a strong acid cation (SAC) completes the softening, followed by chemical injection to raise the pH. When hydrogen ions are exchanged with hardness ions, balanced hardness-to-alkalinity а ratio is achieved during the process, improving WAC efficiency. Hydrogen ions also reduce the pH, causing the water stream to be acidic and converting much of the alkalinity to carbonic acid and CO<sub>2</sub>. Adding more acid at this stage converts remaining alkalinity to CO<sub>2</sub>. Degasification (such as removal of carbon dioxide and other gases) follows. In this stage, the pH can be increased to 10.5: this will raise the solubility of silicates and destroy any biological components. Next, the feedwater enters the RO membranes. These membranes must be of sufficient quality and robustness to withstand the high pH operation (Figure 4). Under these conditions, there is little or no scaling or fouling. This allows operation at very high water recovery of 85-95%, relative to conventional RO at about 75%.

The advantages of this more-efficient RO process include total hard-

### **Cover Story**

ness removal (more than 99.5%) and substantial silica removal combined with high water recovery without the risk of scaling. This operation avoids biofouling and organic fouling because bacteria, viruses, spores, and endotoxins are either lysed or saponified at these operating conditions. Removal of scaling constituents in the pretreatment steps eliminates the need for scale inhibitors in the high efficiency RO. The combination of WAC and SAC increases the regeneration efficiency for resin beds. The disadvantages of this technology are the higher cost of regeneration chemicals and license fees together with the higher complexity of the system.

Coagulation followed by UF and **RO:** A third technology is based on coagulation-flocculation and clarification followed by membrane techniques. This process setup is designed to treat raw waters containing high concentrations of suspended matter resulting in a high silt-density index (SDI). Classical coagulation-flocculation techniques are used where hydroxide flocs grow and settle in specifically designed reaction chambers. The hydroxide sludge is removed, and the supernatant water is further treated by media filtration. For the coagulation-flocculation process, either a solids-contact type clarifier or a compact coagulation-flocculation reactor may be used.

In a second operation, ultrafiltration (UF) membranes remove virtually all suspended matter and also dissolved organic compounds, depending on their molecular mass and on the molecular mass cut-off of the membrane. Hence, an SDI <1 can be achieved with a well-designed and properly maintained UF system. Hollow fibers are the most commonly used UF membrane configuration (cover image), which can be operated in two different ways: feed flow can be from outside-in or inside-out.

For outside-in configurations, there is more flexibility in the amount of feed to flow around the hollow fibers, whereas for inside-out configurations the pressure drop through the inner volume of the hollow fibers is a limitation. Inside-out configurations, however, provide a much-more uniform flow distribution through the bore of hollow fiber compared to the outside-in configurations. UF systems are typically operated in crossflow mode at high recovery and flux rates. Cleaning is done frequently using backwashing, and airscouring techniques are often used to reduce fouling. The last step involves a classical RO setup that operates at a water recovery of 70–75%.

The advantages of the combined UF and RO technologies are highly efficient suspendedsolids removal and the ability to automate and expand the membrane filtration units. The disadvantages include a limited number of water types

that are applicable because of the lack of a removal step for hardness-alkalinity in pretreatment. Classical ways to prevent RO scaling by antiscalantpH adjustment use a large amount of chemicals. The recovery of RO units is also relatively low because of the lack of hardness-alkalinity removal.

Selection of RO membranes is highly dependent on the permeatewater quality requirements. Higherrejection, RO membranes are required and dependent on the type of boiler, the need for TDS removal (in case of ion exchange) and the cycles of concentration. Fouling resistant membranes can be chosen if the makeup water has a high tendency for biofouling or microbial growth. The typical recovery of an RO system is equal to or less than 70–75% (except for the more efficient process mentioned earlier). And most plants will experience a significant increase in cleaning frequency when the system recovery is >80%. Undoubtedly, a high recovery will cause a higher concentration factor, which increases the operational risk. In the case of the more efficient RO process described, the recovery can be as high as 90% but robust RO membranes need to be chosen to withstand the long exposure to high pH. Overall, one can say that the maximum system recovery and sustainable flux will depend on the actual water conditions, the pretreatment and operating condi-



**FIGURE 4.** Quality control is applied during membrane fabrication. Here a membrane sheet is being rolled on the manufacturing floor

tions, which are interrelated with the cleaning frequency and membrane replacement rates.

Reverse osmosis products with a higher fouling resistance for organic fouling, biofouling and scaling are naturally preferred in this cooling tower blowdown application. Higher pH tolerance will allow longer operation life. Large systems require low energy membrane with higher salt rejection and potentially could benefit from a 16-in. element where the availability of space is a constraint.

It is expected that UF products with a smaller pore size for lower molecular-weight cut off (MWCO) will be able to remove TOC more effectively. A higher flux will reduce the overall operating and capital costs. Furthermore, easy cleaning and improved cleaning protocols of membranes will establish UF as a premier solution in the water reuse industry.

#### MUNICIPAL WATER AS A SOURCE

Due to increasing water stress and resulting competition for high quality fresh-water resources, the use of conventional water sources for industrial cooling water and boiler water makeup may be limited or restricted. However, reclaimed water is a constant water source with little competition to access this resource. As a result, the use of treated wastewater from municipal sewage-treatment plants can be a valuable diversification strategy for industrial water supply, including cooling and boiler water. Furthermore, the cost of fresh water and wastewater, in addition to scarcity of fresh water, is driving the end user to reuse and recycle their water resources. Additional benefits of the use of municipal wastewater are that the treated effluent from highly urbanized areas is more stable in quality than river water and therefore, less maintenance and process control are required. Lastly, permits and administrative burdens are often less for reuse than for conventional water resources. In addition, public acceptance of this reuse scheme is high.

Municipal water reclamation for industrial water use (mainly cooling water use) has a long track record. The first installation was introduced in the 1940s, while most of the installations began operating in the 1990s in North America and Europe due to increased water stress and large-scale use of RO technology. Today, this reuse scheme is present on all continents. Generally, three main membrane technology solutions for the treatment of tertiary effluent for industrial water use can be distinguished: 1) The use of ultrafiltration pretreatment of the effluent before RO for use in cooling water; 2) Further polishing of the RO effluent by ion exchange or electrodeionization for the makeup of boiler feedwater; and 3) The use of membrane bioreactors (MBR) as a direct pretreatment of reverse osmosis is expected to be used more frequently in the future as a low footprint solution for onsite wastewater reclamation.

Edited by Dorothy Lozowski

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### **Feature Report**

# Multivariable Predictive Control: The Scope is Wider Than You Think

Rafael Lopes, Robert K. Jonas and Alexandre Dalmax Honeywell International

ore and more, the chemical process industries (CPI) are seeking out the benefits of flexible production and maximizing energy and material recovery. Process units are becoming tightly integrated, and the failure of one unit can seriously degrade overall productivity. Meanwhile, with the influx of larger and larger scale operations, even small changes in productivity can seriously affect profitability.

While the petrochemical industries have been successful in using multivariable predictive control (MPC) to manage such complexities, the rest of the CPI leaves room for much wider and more frequent MPC deployment and the higher productivity and lower costs that accompany it. These sectors have been slow to adopt MPC, but that trend appears to be changing. The reliability and amount of automation in industries, such as pulp and paper, and mining and metals have improved. MPC has been successfully implemented in ore grinding, smelting, and in all parts of alumina refining. In the pulp industry, MPC also is now a reality and has been implemented successfully in lime kilns and bleach plants.

MPC requirements are to deeply study and understand the process, use operators' and engineers' experience, find the key variables and solve the control problem. But, the main requirements that are consistent across the CPI for a good multivariable control implementation are an MPC controller and model that are robust enough to handle changing plant conditions. An MPC must be able to handle large With increasingly tighter integration between process units and more aggressive optimization goals, this technique is gaining attention throughout the CPI as an alternative to PID control

and sudden disturbances, varying transport delays, the anomalies of sensors (such as ore slurry densities and pulp consistencies), non-linear temperature behaviors, and many of the unique issues associated with a given process.

In order to successfully implement multivariable control, it is necessary to have a good methodology such as the following:

- $1.\,\mathrm{Assess}$
- 2. Define
- 3. Execute
- 4. Deliver
- 5. Sustain

The bottom line is that the selection process must strive for MPC software that is robust and can therefore sustain more time on-control and therefore generate more benefits.

#### Problems with the status quo

While proportional-integral-derivative (PID) controllers are applicable to many control problems, they can perform poorly in some applications.

PID controllers, when used alone, can give poor performance when the PID loop gains must be reduced so that the control system does not overshoot, oscillate or "hunt" about the control setpoint value. Another problem faced with PID controllers is that they are linear. In summary, PID limitations are:

• PID controls have difficulty handling

process delays, nonlinear processes, and noisy process signals. This leads to suboptimal control and increased tuning effort

- PID is not as robust as alternatives, often delivering higher process variability
- PID tuning is not easy to handle. Effective tuning requires experience, extensive training, and an investment in tuning software
- PID transfers process-signal noise directly to its controller output. This accelerates valve wear and increases energy usage

These weaknesses add up over time, with the net impact being that PID use may actually increase process variability, decrease production and product quality, and ultimately increase operating and maintenance costs. Figure 1 shows an example of poor PID behavior.

This case represents a heat duty control (QC) loop, cascaded with a steam flow loop, which is connected directly to a control valve. Any QC variation leads to a bottom level variation. This bottom level swing leads to a column-bottom temperature variation. The bottom temperature variation covaries with the exchanger outlet temperature. Meanwhile, the exchanger outlet temperature leads to a QC variation. Also, this control loop is sending two different signals for the same valve (QC level correction and



FIGURE 1. PID controllers can actually increase process variability, especially with multiple input, single output situations



**FIGURE 2.** The right half of this graph shows reduced variability after the implementation of MPC in an ASU and an oxygen purity within the 99.5% target



**FIGURE 3.** After the implementation of MPC (red lines) the vacuum distillation process experienced much less variability and a lower fraction of lights in heavies

flow variation correction), which generates a high frequency upset. This is an example of how the PID would deal poorly with a MISO (multiple input, single output) situation.

Because of the widespread use of PID — and the technology's inherent weaknesses — regulatory (or direct) process controls remain one of the last frontiers for pushing performance further.

One of the effective and leading advanced control technologies is MPC. The philosophy of MPC is to predict the plant behavior, based on heuristic models, in order to take more timely preventive and corrective actions to ensure better regulation and plant stability. These models consider the interactions between the key plant variables and, therefore, MPC is considered a multiple input, multiple output (MIMO) technology. In addition, the predictive capability of model-based MPC further reduces plant variability and allows plants to operate closer to the real plant limits, enabling more productivity and cost reductions than any other advanced control technology.

### EXPERT SYSTEMS AND MPC

An expert system is essentially software that provides a compilation of equations, rules of thumb, and do's and don'ts — all based on the knowledge and skills that an experienced engineer would apply to solving a problem.

On the other hand, MPC is based on empirical modeling, predicting the process behavior in the future. Thus, MPC has much higher capabilities than an expert system.

While MPC is certainly different than PID and expert systems (see box for more), a common perception is that MPC is more difficult to apply. Actually, the reverse is true. The complexity of application is internal to the software, thus the people implementing MPC need only to define models and then configure desired operation targets. Model definition has been made much easier through use of automated modeling software, process stepper applications, and online and on-control modeling software. In expert rules, fuzzy logic and complex PID strategies, the implementer needs to be a process and control expert, and needs to carefully design a system. The expert needs to consider how to deliver the majority of benefits given the limitations of these control technologies. For example, expert system and complex PID strategies have difficulties in the following areas:

- Time-based dynamics require some skill and effort to implement, and thus are often eliminated or simplified to reduce cost and effort
- Interactions between controls and process require some skill and effort to implement, and thus are often eliminated or simplified to reduce cost and effort
- Design, building, testing, commissioning, and maintaining a complex custom application, and the resulting complexity (cost) versus benefits
- Poor operator acceptance and utilization due to elimination and simplification of dynamics and interactions. Simply stated, the advanced controls do not respond to many situations. It is not uncommon to have

### **Feature Report**

### less than 50% control utilization **MPC examples in the CPI**

Air separation units compared with MPC for common petrochemical vacuum distillation towers. In this example, a petroleum refinery's vacuum distillation column will be compared with a steel mill's air separation unit (ASU).

Vacuum distillation of petroleum hydrocarbons is a well-known, refining process commonly used to minimize thermal cracking of heavier fractions of crude oil and obtain lighter desired products. Distilling these heavier materials under lower pressure decreases the boiling temperature of the various hydrocarbon fractions in the feed and therefore minimizes thermal cracking of these fractions. It is important in such systems to reduce pressure as much as possible to improve vaporization. Vaporization is enhanced by various methods, such as the addition of steam at the furnace inlet and at the bottom of the vacuum distillation column. Vacuum is created and maintained using cooling water condensers and steam driven ejectors. In a conventional system of this type, the first stage condenses the steam and compresses non-compressible gases, while the second and third stages remove the non-condensable gases from the condensers. The vacuum produced is limited to the vapor pressure of the water used in the condensers. If colder water is supplied to condensers, a lower absolute pressure can be obtained in the vacuum tower.

Cryogenic ASUs have been used to produce oxygen, nitrogen, argon and other gases, as desired. An ASU generates gases by refrigerating air and distilling it, so energy is the primary production cost of an ASU. ASUs may be integrated into a network, with a centrally managed pipeline network for transporting the output gases to customers, or can be stand-alone units without a network connection. Traditional regulatory controllers, such as PID controllers, can be used to control various flowrates in an ASU. For example, PID controllers have been used to control the flowrate of the rich liquid into the low pressure column in ASUs. PID controllers work well under steady state conditions, with only minor pro-



**FIGURE 4.** This example shows the reduced variability that MPC achieved in an alumina digestion plant. Similar benefits can be expected in cellulose digestion

cess variations, however, they are typically detuned in order to avoid large oscillations in the plant conditions, which can lead to variations in flowrate and purity of the ASU plant products.

In both vacuum distillation and air separation, the main challenges are as follows: increase throughput; reduce operator intervention; less downtime or fewer loss-producing events; the ability to change production rates very quickly, without upsetting the plant and the key purities.

Common manipulated variables for both cases would be as follows:

- Steam consumption
- Feedrate
- Top pressure control

Common controlled variables for both cases would be as follows:

- Steam valve openings
- Main product qualities (for instance, oxygen purity in air for ASU, lights in heavies in petrochemical vacuum distillation column)
- Pressure differential through the column
- Column bottom level

Figure 2 illustrates the oxygen purity before and after MPC, while Figure 3 shows the lights in heavy specification before and after MPC. Both figures show a clear reduction in variability and a clear shift toward the desired setpoint. For example, the oxygen-purity target was 99.5%, and the specification for total lights in heavies is lower than 0.8%

MPC for digestion units in alumina refinery and pulp-and-paper *industry.* The second example will describe the MPC similarities between a cellulose pulp, continuous digestion unit and an alumina digestion unit.

For cellulose production, wood and caustic soda are heated and then fed into the continuous digester. The wood can be impregnated with white liquor in countercurrent flow, while black liquor is added to the wood material at the inlet to the impregnation vessel. The object of this procedure is primarily to increase the concentration of active chemicals in the digesting liquor by withdrawing a certain amount of impregnation liquid in which the content of active chemicals has been substantially consumed. The liquid-towood ratio in the digester is thereby lowered, thus giving a high concentration of active chemicals, which results in rapid digestion. Then, the cellulose is withdrawn from the pulp, going to the purification processes.

For the alumina digestion unit, the digesters provide a means of: mixing the heated spent liquor and bauxite slurry to arrive at a target digestion temperature; maintaining that temperature for a lapse of time sufficient to dissolve the alumina from the bauxite; and reducing the silica dissolved by the desilication reaction to a tolerable level.

The digestion of bauxite to extract alumina is carried out in a train consisting of vertical digesters arranged in series. The digester train has one set of small digesters, followed by a set of large vertical digesters. The small



FIGURE 5. Most data gathered in a plant test such as this one are not suitable on their own for building an MPC model. In most CPI sectors robust software is needed

digesters, which are equipped with agitators, provide for dissolution of alumina and the large digesters, without agitators, provide additional holding time to ensure liquor desilication.

Some of the common manipulated variables in either the cellulose or alumina case are as follows:

- Steam flow to liquor heating (before it gets into the digesters)
- Liquor and pulp (wood or bauxite) flows
- Pressure controls

Some of the common controlled variables are as follows:

- Ratio of product to total caustic
- Steam valves
- Digestion residence times
- Feed temperatures

Figure 4 shows a real gain example in an alumina digestion plant, which is similar (from a process control perspective) to a cellulose digestion unit. Despite obvious similarities, many column distillation and cellulose digesters utilize MPC, while many ASUs and alumina digesters still only use expert systems.

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**Robustness is key.** Even though MPC can be implemented in areas different than traditional petrochemical applications, the software has to be much more robust. This is because, generally, the data gathered for the controller modeling are not very good. For example, in an alumina refinery, the feed is a slurry and not a liquid (as in petrochemical plants). Meanwhile, the number of operational procedures is larger than in a petrochemical plant.

Figure 5 shows an example of data gathered to make a modeling work. Less than half of the steps shown here can be used to model the plant. In this particular data set, there are gaps in the data, plant bumps and non-responsive loops. If the control engineer uses this data to build the controller models, there will be some model mismatches (gains smaller than reality, different dynamic responses than reality, wrong times to steady state and so on).

If a controller with these model mismatches is implemented, sources of controller inefficiency will exist.

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But, if the software is sufficiently robust, the effects of a model mismatch will be minimized. Some technologies consider this robustness in their algorithms and the controller behavior is smoother.

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### **Engineering Practice**

# **CSTR Design** for **Reversible** Reactions

Here, a design approach for continuous stirred-tank reactors is outlined for three cases of second-order reactions



### **Ralph Levine**

ultiple CSTRs (continuous stirred-tank reactors) are advantageous in situations where the reaction is slow; two immiscible liquids are present and require higher agitation rates; or viscous liquids are present that require high agitation rates. Unlike in plugflow reactors, agitation is easily available in CSTRs. In this article, batch and plugflow reactors are analyzed and compared to multiple CSTRs.

The number of reactors required in a CSTR system is based on the conversion for each stage. When the final stage obtains the fraction of unconverted reactant that is equal to the desired final value from the plug-flow case, the CSTR system is complete.

The volumetric efficiency of multiple CSTRs is expressed as a function of conversion per stage and gives the total conversion required. In this article, we will apply this to reversible second-order reactions.

#### 2nd-order, reversible reactions

The first case presented here is a kinetic process requiring a double component (2A) to be fed to a reactor, and producing two products (G and*H*). The design may be calculated for both CSTR and plug-flow reactors, determining the conversion in the first | not present in the feed. Therefore,  $C_{G0}$  |

stage, the number of stages of equal volume, as well as the volumetric efficiency of the CSTR stages and the plugflow reactor.

The reactor design is developed by selecting a conversion in the first stage. Then, the second-stage conversion is equal to that of the first stage, since it requires an equal volume. This procedure is continued until the fraction of reactant exiting each reactor stage reaches the desired value in the last stage, or slightly less than the plugflow case, as illustrated in Figure 1.

The kinetic rate conversion of a reversible bi-molecular reaction at constant temperature and flowrate is represented by Equation (1). The reaction is illustrated below (nomenclature is defined on p. 49.

$$2A \leftrightarrow G + H$$

$$-r = k_F C_A^2 - k_R C_G C_H$$
(1)

$$k_{R} = k_{F} / K \tag{2}$$

Assume that G and H compounds are

CSTRs for second order reactions is shown here. with conversion per stage shown for the CSTR case

> and  $C_{H0}$  are equal to zero, and the following expressions are true:

$$C_{Gf} = C_{A0} X_f \tag{2b}$$

$$C_{Hf} = C_{A0} X_f \tag{2c}$$

$$(C_{A0}X_f)^2 = (C_{A0} - C_{Af})^2 = C_{Gf} \cdot C_{Hf}$$
(2d)

The ratio may be different, as, for example, the concentration of G in the product may be five times that of H. However, we assume that the products are equal  $(C_{Gf} = C_{Hf})$ .

Expressing reaction rate. The rate equation can be modified to include conversion and equilibrium constant terms. Substituting Equations (1), and (2d) into Equation (1) give an expression for rate.

$$-r = k_F C_{A0}^2 \left(1 - X_f\right)^2 - \left(k_F / K\right) \left(C_{A0} X_f\right)^2$$
(3a)
$$-r = k_F C_{A0}^2 \left(1 - 2X_f + \left[\frac{X_f^2 (K - 1)}{K}\right]\right)$$
(3b)

$$-r = k_F C_{A0}^2 \left[ \left( \frac{K-1}{K} \right) X_f^2 - 2X_f + 1 \right]$$
(3c)

At equilibrium, the net reaction rate equals zero.

$$0 = \left(\frac{K-1}{K}\right) X_{e}^{2} - 2X_{e} + 1$$
 (4a)

Using the quadratic equation, Equation (4a) is simplified to Equation (4c).

$$X_{e} rac{2 \pm \sqrt{\left(-2
ight)^{2} - 4\left(K - 1
ight)/K}}{2\left(K - 1
ight)/K}$$
 (4b)

$$X_{e} = \frac{1 \pm \sqrt{1 - (1/K)}}{(K - 1)/K}$$
(4c)

The quadratic equation can also be used to simplify Equation (3c), resulting in Equation (5a).

$$X_{f} = \frac{2 \pm \sqrt{4 - 4\left[1 - (1/K)\right]}}{2(K - 1)/K}$$

$$X_{f} = \frac{1 \pm \sqrt{1 - (1/K)}}{(K - 1)/K}$$
(5a)

The reaction rate expression can then be expressed as Equations (5b) and (5c).

$$-r = k_F C_{A0}^2 \left( X_e - X_f \right)$$

$$-r = k_F C_{A0}^2 X_e \left[ 1 - \left( X_f / X_e \right) \right]$$
(5b)
(5c)

Stirred reactor in a batch or plug*flow reactor*. The batch reactor case and the ideal continuous plugflow case are given in Equation (6).

The reaction time is t for the batch case, and V/v for the plugflow case.

$$\frac{V}{vC_{A0}} = \int_0^{X_f} \frac{dX}{-r}$$
(6)

Substituting Equation (5c) into (6) and rearranging, gives Equation (6a).

$$\frac{V}{vC_{A0}} \left( k_F C_{A0}^2 \right) X_e = \int_0^{X_f} \frac{dX}{1 - \left( X_f / X_e \right)}$$

$$\frac{V}{v}k_{F}C_{A0}X_{e} = -\ln\left[1 - \left(X_{f}/X_{e}\right)\right]$$
(6b)

Volume of each CSTR stage. An expression for the first stage of a CSTR is given in Equation (7). The first stage conversion,  $X_1$ , occurs in each of the successive stages  $(X_2, X_3, \text{ and so on})$ , and each has the same volume and reaction temperature.

$$\frac{V_{1}}{vC_{A0}} = \frac{X_{1}}{-r}$$
(7)

Substituting Equation (5c) into (7) and rearranging gives Equation (7a).

$$\frac{V_{1}C_{A0}k_{F}}{v} = \frac{X_{1}/X_{e}}{1 - (X_{1}/X_{e})}$$
(7a)

Equation (7a) has only one independent variable  $(V_1)$ . If each stirred reactor stage is to be of equal volume and volumetric flowrate, then the result is a constant conversion per stage. That is, each stage, when at a fixed set of conditions, has the same conversion from each stage, expressed as:  $X_1 = X_2 = X_3 \dots = X_n$ 

Number of stages. Conversion for stage 1 is expressed by equation (8).

$$X_{1} = \left(C_{A0} - C_{A1}\right) / C_{A0}$$
 (8)

The equilibrium conversion is based on time to reach a net reaction rate of zero, which may be calculated by Equation (4b) or (9).

$$X_{e} = \left(C_{A0} - C_{Ae}\right) / C_{A0}$$
(9)

Subtract Equation (9) from (8) and divide by (9) to obtain Equations (10a) and (10b).

$$X_{e} - X_{1} = \left(C_{A1} - C_{Ae}\right) / C_{A0}$$
(10)

$$\frac{X_{e} - X_{1}}{X_{e}} = \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}}$$
(10a)

$$1 - (X_1 / X_e) = \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}}$$
(10b)

The exit concentration,  $C_{A1}$ , can be calculated from Equation (10b). Also, the exit concentration from the second (**6a**) | stage,  $C_{A2}$ , can be calculated from Equa- | for CSTRs, these terms are equiva-

tion (11a), based on each stage having the same volume and conditions.

$$\begin{pmatrix} 1 - \frac{X_1}{X_e} \end{pmatrix}^2 = \frac{C_{A2} - C_{Ae}}{C_{A1} - C_{Ae}} \cdot \frac{C_{A1} - C_{Ae}}{C_{A0} - C_{Ae}}$$
$$= \frac{C_{A2} - C_{Ae}}{C_{A0} - C_{Ae}}$$
(11a)

Continue this process for the *n*th stage to obtain the following equations.

$$\left(1 - \frac{X_1}{X_e}\right)^n = \frac{C_{An} - C_{Ae}}{C_{A0} - C_{Ae}}$$
(12)

$$n \log \left(1 - \frac{X_1}{X_e}\right) = \log \left(\frac{C_{An} - C_{Ae}}{C_{A0} - C_{Ae}}\right)$$
(12a)

$$\left(1 - \frac{X_1}{X_e}\right)^n = 1 - \frac{X_f}{X_e} = \frac{C_{An} - C_{Ae}}{C_{A0} - C_{Ae}}$$
 (12b)

Total volume of all stages. Substitute Equation (7a) into (13a).

$$V_{T} = nV_{1}$$
(13a)  
$$\frac{V_{T}}{v}k_{F}C_{A0} = n\frac{V_{1}}{v}k_{F}C_{A0} = n\left[\frac{X_{1}/X_{e}}{1-(X_{1}/X_{e})}\right]$$
(13b)

$$= \frac{\log \left(\frac{C_{An} - C_{Ae}}{C_{A0} - C_{Ae}}\right)}{\log \left[1 - \left(X_{1}/X_{e}\right)\right]} \cdot \frac{X_{1}/X_{e}}{1 - \left(X_{1}/X_{e}\right)}$$
(13c)

By definition,  $C_{An} = C_{A0}(1 - X_f)$ , where  $X_f$  is the total conversion in the *n*th stage or the final desired conversion of the plug-flow reactor. By the method used to obtain Equation (10), the following equation is similarly derived. Substitution of Equation (12b) into (13c) gives Equation (13d).

$$= \frac{\frac{V_T}{v}k_F C_{A0}}{\log\left[1 - \left(X_f/X_e\right)\right]} \cdot \frac{X_1/X_e}{1 - \left(X_1/X_e\right)}$$
(13d)

#### Volumetric efficiency

Since  $V_T/v$  in Equation (13c) is residence time, as is V/v in Equation (6b),

### **Engineering Practice**

lent. The volumetric flowrate is the same in all cases (a batch operation for one complete reaction cycle). Thus, the ratio of comparison should be V for plugflow or batch operation (reaction volume and time only) compared to  $V_T$  for multiple CSTRs. This ratio ( $V/V_T$ ), volumetric efficiency is expressed as Equation (14), and is derived from Equations (6b) and (13d).

$$\frac{\frac{V}{v}k_{F}C_{A0}X_{e}}{\frac{V_{T}}{v}k_{F}C_{A0}} = \frac{-2.303\log\left[1-(X_{f}/X_{e})\right]}{\frac{X_{1}/X_{e}}{1-(X_{1}/X_{e})} \cdot \frac{\log\left[1-(X_{f}/X_{e})\right]}{\log\left[1-(X_{1}/X_{e})\right]}}$$

$$V = -2.303\log\left[1-(X_{1}/X_{e})\right]$$
(14)

 $\frac{V}{V_{T}} = \frac{-2.303 \log[1 - (X_{1}/X_{e})]}{X_{e}(X_{1}/X_{e})} \quad (14a)$  $\cdot \log[1 - (X_{1}/X_{e})]$ 

Volumetric efficiency is independent of the initial or final concentration and velocity constant at constant temperature, as well as overall conversion. It is dependent on only the ratio of the first stage conversion compared to the equilibrium conversion. Calculations for Equation (14a) are shown in Table 1.

### Reversible production of a dimer from two reactants

Another case exists, where two components are reversibly reacted to form a single product, a dimer, rather than two products (as shown in the reaction below). This case is similar to the previous case, but but with only one product, as shown below in Equation (15).

$$C + D \leftrightarrow P$$
$$-r = k_F C_B C_D - k_R C_p$$

$$C_{B0}X_{f} = C_{B0} - C_{Bf} = C_{pf}$$
(16a)

$$C_{pf} = C_{B0} X_f \tag{16b}$$

$$-r = k_{F} C_{B0}^{2} \left[ \left( 1 - X_{f} \right) \left( M - X_{f} \right) - \frac{X_{f}}{K C_{B0}} \right]$$
(17)

At equilibrium, the rate is zero.

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(15)

#### TABLE 1. VOLUMETRIC EFFICIENCY FOR EQUATION (14A)

$$\frac{V}{V_{T}} = \frac{-2.303 \left\lfloor 1 - \left(X_{1}/X_{e}\right) \right\rfloor \times \log \left\lfloor 1 - \left(X_{1}/X_{e}\right) \right\rfloor}{X_{e} \left(X_{1}/X_{e}\right)}$$

$X_1/X_e$	X <sub>e</sub>	$1-(X_1/X_e)$	$\log[1-(X_1/X_e)]$	$(V/V_T)X_e$	V/V <sub>T</sub>
0.1	0.7	0.9	-0.046	0.948	1.355
0.2	0.7	0.8	-0.097	0.893	1.275
0.3	0.7	0.7	-0.155	0.832	1.189
0.4	0.7	0.6	-0.222	0.766	1.095
0.5	0.7	0.5	-0.301	0.693	0.990
0.6	0.7	0.4	-0.398	0.611	0.873
0.7	0.7	0.3	-0.523	0.516	0.737
0.8	0.7	0.2	-0.699	0.402	0.575
0.9	0.7	0.1	-1.000	0.256	0.366

TABLE 1. For any ratio of conversion per stage to equilibrium conversion, this table provides the corresponding volumetric efficiency, based on Equation (14a)

(**18a**)

$$0 = X_e^2 - \left(\frac{M+1}{KC_{B0}}\right) X_e + M$$

Using the quadratic equation, Equation (18a) becomes (18b).

$$X_{e} = \frac{\frac{M+1}{KC_{B0}} \pm \sqrt{\left(\frac{M+1}{KC_{B0}}\right)^{2} - 4M}}{2} \quad (18b)$$

Using Equations (17) and (18a), an expression for  $X_f$  is found.

$$-r = k_F C_{B0}^2 X_f^2 - \left(\frac{M+1}{KC_{B0}}\right) X_f + M$$
Equation (19a) can be simplified to
Equation (10b) using the guadratic

Equation (19b) using the quadratic equation.

$$X_{f} = \frac{\left(\frac{M+1}{KC_{B0}}\right) \pm \sqrt{\left(\frac{M+1}{KC_{B0}}\right)^{2} - 4M}}{2}$$
(19b)

$$-r = k_F C_{B0}^2 X_e \Big[ 1 - \left( X_f / X_e \right) \Big]$$
 (19c)

$$\frac{V_1(k_F C_{B0} X_e)}{v} = -\ln \left[1 - (X_1 / X_e)\right] 20a$$

The volume of each backmixed stage is equal.

$$\frac{V_1(k_F C_{B0} X_e)}{v} = \frac{X_1/X_e}{1 - (X_1/X_e)}$$
(20b)

$$1 - \left(X_{1} / X_{e}\right) = \frac{C_{B1} - C_{Be}}{C_{B0} - C_{Be}}$$
(21)

$$\frac{C_{Bn} - C_{Be}}{C_{B0} - C_{Be}} = 1 - \left(X_f / X_e\right)$$
$$= \left[1 - \left(X_1 / X_e\right)\right]^n$$
(22)

The volumetric efficiency is calculated as Equation (23).

$$\frac{V}{V_T} = (23)$$
$$\frac{-2.303}{X_e} \left[ \frac{1 - (X_1/X_e)}{(X_1/X_e)} \right] \cdot \log \left[ 1 - (X_1/X_e) \right]$$

### Reversible production of a dimer from twin reactants

In another alternate but similar case, Equation (15) is modified for double components that are reversibly reacted to form a dimer, as shown in the reaction below. As in this last case, there is only one product.

 $2A \leftrightarrow P$ 

$$-r = k_F C_{A0}^{2} - k_R C_P \tag{24}$$

$$C_{Pf} = C_{A0} X_f \tag{25}$$

$$-r = k_F C_{A0}^{2} \left(1 - X_f\right)^2 - \left(k_F / K\right) \left(C_{A0} X_f\right)$$
(26a)
$$k_F C_{A0}^{2} \left[X_{A0}^{2} - \left(0 / K C_{A0}\right) X_{A0}^{2} - 1\right]$$

$$-r = k_F C_{A0}^2 \left[ X_f^2 - \left( \frac{2}{KC_{A0}} \right) X_f + 1 \right]$$
(26b)

At equilibrium, the rate is zero.

$$0 = X_e^2 - (2/KC_{A0})X_e + 1$$
 (27a)

Using the quadratic equation, Equation (27a) becomes (27b).

$$X_e = 1/KC_{A0} \pm \sqrt{\left(1/KC_{A0}\right)^2 - 1}$$
 (27b)

$$X_{f} = 1/KC_{A0} \pm \sqrt{\left(1/KC_{A0}\right)^{2} - 1}$$
(28a)

$$-r = k_F C_{A0}^{2} \left[ 1 - \left( X_f / X_e \right) \right]$$
(28b)

2) For a plugflow reactor, the following expression is true.

SUMMARY OF EQUATIONS  

$$B+D \leftrightarrow P+S \qquad [6]$$

$$X_{e} = \frac{(M+1) \pm \sqrt{(M+1)^{2} - 4M(1/K)/K}}{2(K-1)/K}$$

$$X_{f} = \frac{(M+1) \pm \sqrt{(M+1)^{2} - 4M(1/K)/K}}{2(K-1)/K}$$

$$2A \leftrightarrow G+H$$

$$X_{e} = \frac{1 \pm \sqrt{1 - (1/K)}}{(K-1)/K}$$

$$C+D \leftrightarrow P$$

$$X_{e} = \frac{\frac{M+1}{KC_{B0}} \pm \sqrt{\left(\frac{M+1}{KC_{B0}}\right)^{2} - 4M}}{2}$$

$$X_{f} = \frac{\left(\frac{M+1}{KC_{B0}}\right) \pm \sqrt{\left(\frac{M+1}{KC_{B0}}\right)^{2} - 4M}}{2}$$

$$2A \leftrightarrow P$$

$$X_{e} = \frac{1/KC_{A0} \pm \sqrt{(1/KC_{A0})^{2} - 1}}{2}$$

$$Y(C = k X) = 5$$

$$\frac{V(C_{A0}k_FX_e)}{v} = -\ln\left[1 - \left(X_f/X_e\right)\right]$$
(29)

The expression for multiple CSTRs is given as Equation (30).

$$\frac{V_{1}C_{A0}k_{F}}{v} = \frac{X_{1}/X_{e}}{1-(X_{1}/X_{e})}$$

$$\begin{bmatrix} 1-(X_{1}/X_{e}) \end{bmatrix}^{n} = 1-(X_{f}/X_{e})$$

$$= \frac{C_{An}-C_{Ae}}{C_{A0}-C_{Ae}}$$
(31)

The volumetric efficiency is found to be Equation (32).

$$\frac{V}{V_{T}} = -\left(\frac{2.303}{X_{e}}\right) \left[\frac{1 - \left(X_{1}/X_{e}\right)}{\left(X_{1}/X_{e}\right)}\right] \qquad (32)$$
$$\cdot \log\left[1 - \left(X_{1}/X_{e}\right)\right]$$

The last two cases presented here are reversible and have only one product. The differences between these cases are the values calculated based on the quadratic equation for both  $X_{\rho}$ and  $X_{f}$ . All second order reactions that are reversible and produce one or two products require the quadratic equation for the calculation of  $X_e$  and  $X_f$  for each case. A summary of these equations is presented in the box above.  $\blacksquare$ Edited by Kate Torzewski

### NOMENCLATURE

- С Concentration,
- moles/unit volume Reaction rate
- constant
- Equilibrium constant
- Initial mole ratio of D/B м
- Number of stages n
- Reaction rate r
- Reaction time
- Reactor volume
- Volumetric flowrate
- X

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#### **Subscripts**

- 0 Initial conditions
- 1,2,3 First, second and third stages
  - A For component A
  - For component C С
  - **D** For component D
  - e Equilibrium conditions
  - **f** Overall or final conditions
  - F Conditions for forward reaction
  - **G** For component G
  - For component H Η
  - Any stage in the series of reactor stages i
  - **n** The *n*th stage
  - For component P Ρ
  - R Conditions for reverse reaction
  - T The total of all n stages

#### Author



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versity of New Jork, and the graduate work at Louisiana State University and the Uni-versity of Delaware. Levine later served as an engineer for the U.S. Army Chemical Corps. He has worked for DuPont, Cities Service Co., and most recently, Columbian Chemical Co. Levine has field express U.S. astrong big astrong has filed several U.S. patents during his career, and is a published author, with his work fea-tured in *Chemical Engineering* and *Hydrocar*bon Processing.

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Conversion



#### Donald Townley, The Lubrizol Corp.

here are many considerations when choosing piping materials for an industrial system. Historically, when options were more limited, the decision-making process was relatively straightforward. It was a matter of choosing what grade of metal to install. Today, there is a larger array of high-performance, nonmetallic options to also consider. Chlorinated polyvinyl chloride (CPVC) is an example of a newer generation of materials. Although it has a proven 50-yr track record in industrial environments (having been invented by The Lubrizol Corp., formerly BFGoodrich Performance Materials, back in 1959), it has made major inroads in the past decade into numerous industrial applications.

There are many reasons why CPVC piping is specified more often today. (for more on specifying CPVC, see CE. October 2006, pp. 34-38) Better education and general awareness of the highperformance thermoplastic have certainly factored into the market shift. In addition, ongoing price increases for metal products are also pressuring bottom-line conscious owners and specifiers to search for more cost-effective options. Fast and easy installations are certainly a contributing factor, as this not only contributes to the installer's ability to complete the project on time, but can also result in significant cost savings. Meanwhile, there is a certain reliability benefit, since CPVC has excellent resistance to a broad range of corrosive environments.

When considering which material offers the best solution for a specific application, a number of criteria commonly top the priority list. Is the material compatible with the chemistry of the liquids being transported? Is it designed to meet the specific temperature and pressure requirements of the system? What is the projected life of the system? Will it perform reliably over the life of the system without requiring costly, periodic downtime? How easy is the system to install and maintain? And, of course, the big question on everyone's mind is how much will the system cost to install and operate over the long term?

In an industrial setting that is closely monitored and regulated by the U.S. Occupational Safety and Health Admin. (OSHA) and Environmental Protection Agency (EPA) standards and where hundreds, or even thousands, of lives are at stake, there is one other significant consideration — the safety performance of the piping material. This article highlights common safety concerns associated with some of the most popular piping materials on the market today and compares their overall performance from a safety perspective. No torches, fewer burn hazards and outstanding fire characteristics make CPVC a safe, effective alternative for industrial piping

#### Metallic pipe safety concerns

Statistically speaking, metal dominates the industrial piping market. Still today, a large number of chemical processing plants utilize some grade of steel for their industrial piping system. This is somewhat surprising when considering the wide array of safety risks associated with metal. When referring to safety, this author is considering risks associated with installation, maintenance and ongoing operation.

Starting with installation, metal piping presents two primary safety hazards. The most serious is the fire risk associated with the open flame of the welding torch required to install a metallic piping system. This is an important consideration whether the project involves new construction or plant upgrades (additions). However, the risk is greatest when a line is being replaced or added to an existing operation because of the possible proximity of hazardous chemicals and other flammable materials. Due to the inherent fire risks associated with welding, a metal pipe installation requires a hot work permit, which requires a time-intensive approval process.

A second safety concern during the installation process relates to the weight of metal piping. As a heavier material (relative to most non-metallic piping), metal creates the additional risk of worker strains and sprains during installation. The weight creates the additional need for heavy machinery on the job site, which can create its own safety concerns.

Once a metal piping line is up and running, a significant safety concern stems from its burn potential. Metal is a tremendous heat conductor, which means it transmits heat easily from the interior to the exterior of the pipe. Contact burn injuries are addressed



by OSHA guidelines and are covered by ASTM, which has developed its Standard Guide for Heated System Surface Conditions that Produce Contact Burn Injuries. Depending on the temperature of the fluid being conveyed, the potential for burns must be mitigated with the addition of insulation around the pipe. At this point, the conductivity of metal not only represents a safety concern, but also a cost concern, since the addition of insulation increases the overall cost of any piping project in the form of increased labor and material costs.

By far the greatest ongoing safety concern associated with a metallic piping system, however, is the risk of leaks and premature failures as a result of corrosion. The financial ramifications of leaking pipes are obvious and include downtime, possible property damage, and the actual repair or replacement costs for the failed pipeline. An overriding consideration, and one that cannot be measured in dollars, is the risk to plant workers from a leaking pipe. The exact chemical makeup of the fluid being transported, as well as its temperature, will determine the severity of the risk.

### **CPVC: A safer alternative**

Choosing a non-metallic alternative, such as CPVC, eliminates, or at least minimizes, all of the safety risks mentioned above that are typical of any metallic pipe installation.

Installation. Starting with the installation process, CPVC is often preferred because it is lightweight roughly one eighth the weight of comparably sized steel pipe. Not only does its lightweight design minimize the risk of worker injuries, but it typically eliminates the need for heavy equipment, which can present additional safety risks.

**FIGURE 1. CPVC** stands up to many of the same aggressive chemicals that corrode steel

**Aromatic solvents** Esters and ketones

CPVC also completely eliminates the fire risk of welding pipe. Instead, CPVC systems can be installed by solvent cementing, flanging or threading. Any piping modifications or pipe repairs can also be made equally quickly, easily and safely without the need for a welder or lifting device to hoist equipment into place. This also means avoiding the hassle and delays of requesting a hot work permit.

*Cementing*. Solvent cementing, which is by far the most common installation method used for CPVC industrial piping systems, creates a highly reliable joint by chemically fusing the pipe to the fitting. When installed correctly, a solvent-cemented CPVC joint actually becomes the strongest part of the entire system, offering more durability than either the pipe or fitting alone. This contrasts sharply with metallic systems and other plastic piping materials for which the joint is often the most vulnerable and likely to be the source of initial leaks.

Solvents. Despite the proven superiority of CPVC solvent-cemented joints, it is important to choose the right solvent cement for a given application. The chemical process industries (CPI) routinely use many strong, inorganic acids, bases and salts, some of which may be chemically incompatible with the fillers used in standard solvent cements. That's why, beginning in the late 1990s, newer-generation solvent cements were tested and developed to resist chemical attack. These specially formulated CPVC solvent cements are designed to handle even the strongest oxidizing chemicals, such as sodium hypochlorite, sulfuric acid and other highly aggressive caustics. Over the more than ten years since their introduction to the market, these high strength, chemical-resistant solvent cements have been subjected to strenuous tests, not only in the laboratory under simulated real-world conditions, but also in actual pulp and paper mills and other CPI plants. Since not all solvent cements are derived from the same chemistries, it is critical to always check product labels and, if in doubt, talk directly with the manufacturer to ensure that the solvent cement is designed for a specific application.

Solvent safety. One safety concern that had been linked with the solvent cements used with CPVC pipe and fittings in years past was the presence of volatile organic compounds (VOCs). Fortunately, there has been a major trend in the industry, as a result of tougher ASTM standards and other protocols, for manufacturers to reduce the level of VOCs in the solvent cements they manufacture. Although it is still important to check the product label to determine the level of VOCs in a specific product, many leading manufacturers have chosen to meet the most stringent VOC emission limits in the U.S. — those set by Rule 1168/316A, which was established by California's South Coast Air Quality Management District (SCAQMD).

Proper safety precautions should still be followed. Similar to the guidelines in place when welding metallic pipe, there are common-sense safety guidelines that should be followed when solvent cementing CPVC pipe and fittings. Just as you wouldn't want to inhale the gases generated while welding steel pipe, neither should you inhale solvents. Always ensure adequate ventilation, especially when working in confined spaces where there is little or no air movement. Proper eye protection should also be worn to prevent solvents from splashing into the eves. Special solvent-resistant gloves should also be used to prevent epidermal absorption. Due to the vapors that could be ingested, installers should not eat, drink or smoke when using solvent cement. And, since solvents are flammable, always take care to avoid working near open flames or sparks.

Corrosion. Once installation is complete, CPVC offers many additional safety advantages over traditional metallic systems - starting with a highly reliable performance. In a large

### **Engineering Practice**

percentage of metallic piping failures, corrosion is identified as the root cause. Corrosion can occur for any number of reasons but, in the most basic sense, it is classified into two major categories. Internal corrosion, which is the most common, results from chemicals inside the transported fluid eating away at the metal surface. External corrosion, as the name implies, results from salts or acids that are in the air (or in the ground in the case of buried pipelines) and are incompatible with the metal surface. Whether the problem starts from the inside of the pipe and works its way out, or vice versa. the outcome is the same — a costly and potentially unsafe chemical leak. An overhead leak presents additional concerns for workers, while a leaking pipe outdoors or underground could potentially represent serious environmental concerns.

But CPVC stands up to many of the same aggressive chemicals that corrode steel (Figure 1), and it does so in very extreme temperature environments. In fact, CPVC is pressure rated for temperatures up to 200°F. That makes it ideally suited, with minimized safety concerns, in a number of process industries, including chemical, pulp and paper, metal treating, chloralkali, fertilizers, mining, wastewater treatment and semiconductors. That's not to say that CPVC is suitable for all applications. Like metal, it also has its limitations and areas where it cannot be used safely. For example, CPVC is not recommended for use with most polar organic materials, including various solvents.

**Contact burns.** Contact burn injuries were also previously discussed as a risk when working around metal piping systems. Hyperthermia (high temperature exposure) is a very real threat in many chemical processing environments and can lead to irreversible damage. The chemical reactions occurring within the skin cells upon exposure and the relationships between exposure temperature and duration on the transfer of heat into the skin have been subjects of extensive research.

Safety-conscious specifiers should be interested in noting that CPVC has a very low thermal conductivity value



— approximately 1/300th that of steel. As a result, the surface temperature of CPVC pipe is significantly lower than the internal fluid temperature. Metal, on the other hand, because of its high thermal conductivity, will have an exterior surface temperature nearly equal to the temperature of the fluid being conveyed (Figure 2).

The actual surface temperature of pipe in a working system is dependent on many factors, including ambient temperature, air circulation velocity and direction. ASTM sets very specific standards with regard to acceptable surface operating conditions for heated systems. Within the ASTM guide (Designation: C1055-03) is a specific notation that if the surface temperature exceeds 70°C (158°F) and the surface is metallic, it may present a hazard regardless of contact duration. It additionally notes that non-metallic skin contact may be safe for limited exposure at temperatures above 70°C.

#### CPVC versus other plastics

Much of this article has addressed the safety attributes of CPVC as they compare to metal. This is largely because metal is still frequently specified in many applications where CPVC has proven to be a more cost-effective, reliable and safer alternative. However, there are a number of applications where plastics other than CPVC are being considered.

All piping materials have their strengths and weaknesses. And in some cases, there may be more than one material that is well suited for a specific application. However, there are a number of situations for which CPVC offers additional safety benefits over other plastics.

**Outdoor installations.** Consider, for example, pipelines that are installed outdoors and subject to the effects of the sun and ambient temperature. In



the past, materials such as polypropylene (PP) and standard PVC have often been specified for low-temperature process fluids. The problem is that, as a result of the sun and ambient air temperature, pipe (even when painted white) retains heat. Recent testing has confirmed that this heat buildup can cause the pipe's surface temperature to rise above the maximum temperature rating of 170°F for PP and 140°F for PVC. The actual surface temperature is dependent on factors such as the ambient temperature the color of the pipe, angle of the sun, surface and air conditions. So even if the outside temperature is only 95°F for PP pipe or 80°F for PVC pipe, the surface temperature could easily be greater than the temperature rating of the material. The surface temperature of CPVC pipe, on the other hand, would not be expected to exceed the 200°F temperature rating even when the ambient temperature reaches 120°F (Figure 3).

Heat buildup is a problem for all plastics, because every plastic material has a maximum pressure rating after which point its performance and reliability are compromised (unlike metals with pressure ratings that are not significantly affected by temperature). So whether you've installed CPVC, PVC or PP, you need to consider more than just the process temperature if the pipe is going to be outdoors. It is the surface temperature that affects performance. This reinforces the need to consider all variables when choosing a particular piping material because, in this case, the ambient temperature could have a major effect on the final performance.

*Fire performance.* When comparing CPVC to other plastic piping materials, another key safety consideration is the product's fire performance. Not all plastics exhibit the same fire per-





formance characteristics in terms of flame propagation and smoke generation. But CPVC rates well in both categories — an important consideration in case of a catastrophic incident. CPVC has a flash ignition temperature of 900°F. This is the lowest temperature at which combustible gas can be ignited by a small, external flame. Many other ordinary combustibles, such as wood, ignite at 500°F or less.

Furthermore, CPVC will not sustain burning. It must be forced to burn due to its exceptionally high limiting oxygen index (LOI) of 60. LOI is the percentage of oxygen needed in an atmosphere to support combustion. Because the Earth's atmosphere is only 21% oxygen , CPVC will not burn unless a flame is constantly applied. Burning stops when the ignition source is removed. Other plastics have a much lower LOI — PP, for instance, has an LOI of 18 — and, as a result, will burn after the flame source has been removed.

### **Final remarks**

One of the most critical factors in the successful design, installation and operation of a safe industrial piping system is the use of a material that best suits the application. No single material is right for all applications. All materials, whether metal or plastic, have strengths and weaknesses and perform differently given varying temperatures, environments, flowrates and pressures.

For those people responsible for specifying materials that are both cost-effective and safe, it's important to note that CPVC has undergone more testing than many traditional materials to ensure a reliable performance, superior durability and long service life — all factors that can affect the overall safety of an industrial piping system. Testing has included minimum burst pressure requirements, dimensional tolerances, residual stress requirements, drop impact requirements and fusion property testing.

The reality is that CPVC can be safely used in systems throughout nearly any industrial plant because of its durability, long service life and high performance characteristics. CPVC industrial piping systems offer numerous benefits to industrial processing plants — most notably in their ability to stand up to aggressive chemicals and high temperatures. These features, combined with superior corrosion resistance, help make CPVC a safe, smart material choice in many industrial environments.

When teamed up with its excellent balance of mechanical strength, low thermal conductivity, and limited flame propagation and low smoke generation, CPVC provides an excellent value in terms of safety.

Edited by Gerald Ondrey

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### Achieve lower air leakage with these rotary valves

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blades, as well as redesigned air vents to help minimize leakage and optimize venting. The new rotary valves are available for medium (22 psi) to high (50 psi) pressure applications, and for conveying capacities of between 4,500 lb/h and 220,000 lb/h. — *Pelletron Corp., Lancater, Pa.* 

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#### These sampling valves are designed for ease of use

"Quick Advance" (QA) sampling valves offer "ease of use" in collecting truly representative samples. The QA valves employ a rack and gear combination that provides a full piston motion while the handle only travels one-third of a turn. Valve design also reduces dead space to eliminate the need to purge the valve prior to collection. The valve line is compliant with international standards and is available in a range of materials. — Strahman Valves Inc., Bethlehem, Pa. www.enr-corp.com

### This rotary valve is designed for complete shutoff and long life

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#### This valve packing achieves ultra-low emission

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Vortex Valves



#### Use this device to lock out plug valves

A new device to lockout plug valves is now available. The easy-to-use device secures manually actuated plug valves and can be used to comply with relevant Occupational Safety and Health Administration (OSHA) regulations. Available in four sizes to fit plug valves from 1 to 8 in. in diameter, the device is compatible with plug valves from many manufacturers. The valve lockout device has a base that remains in place once applied and does not interfere with valve activation by wrench or removable handle. — Brady Worldwide Inc., Milwaukee, Wis. www.bradyid.com

#### This valve is designed for slurries and corrosives.

The Series 75 pinch valve is designed to alleviate difficulties associated with ball and plug valves in applications involving tough slurries, and abrasive or corrosive chemicals. Its full port design eliminates dead spots, crevices, seats and bearings. The pinch valve has the same face-to-face dimensions as plug or ball valves up to 12 in. The valve can also function as a throttling manual-control valve. - Red Valve Company Inc., Carnegie, Pa. www.redvalve.com

### This valve is available in manual or actuated models

DAB Series diaphragm valves can be operated manually or actuated pneumatically or electrically. The valves are constructed of all plastic, and engineered to handle difficult media, such as corrosive fluids, abrasive mixtures and slurries. DAB Series valves feature a multi-turn design for control, are self-draining to reduce or eliminate dead volume, and are rated to 150 psi. — Haywood Flow Control Systems, Clemmons, N.C.

www.haywardflowcontrol.com

#### A valve control system with onboard diagnostics capability

The Axiom valve control system now offers an on-board diagnostics ability to predict potential problems in automated valves, thereby reducing process downtime and maintenance costs. The system can sound local and remote alerts for such occurances as a jammed valve or actuator, a drop in pneumatic supply or an open solenoid circuit. Alerts are cleared when normal operating conditions are restored. - StoneL Corp., Fergus Falls, Minn. www.stonel.com

### This line diverter can handle positive or negative pressures

The Quantum series line diverter (photo) can accommodate either positive or vaccuum pressures of up to 15 psig in pneumatic conveying systems. The four-way diverter can direct dry bulk material to four destinations or converge material from four sources to one destination. and is available in 2-in. to 6-in. pipe or tube diameters. A wide range of modifications are available for the diverter valve to allow its use in high- and low-temperature or humid environments, as well as with corrosive or hazardous materials. --Vortex Valves NA, Salina, Kan.

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Scott Jenkins

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The scientific emphasis of the professorship will be the fundamentals of electrochemistry, in particular in the development of new electrochemical storage for electrical mobility. The professorship is intended to strengthen existing activities in storage cell technology by improving the current technologies as well as developing completely new storage systems. We are looking for an internationally distinguished individual with research achievements in the area of electrochemical systems.

The teaching activity will cover the complete range of electrochemistry as well as energy sciences. The professorship will also include participation in the planned master course of studies for electrical mobility, as well as related courses of studies which will be set up. Appointment is planned at the level of Full Professor (W3).

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The TECHNISCHE UNIVERSITÄT MÜNCHEN is striving to increase the proportion of women in research and education. Female scientists are therefore especially encouraged to apply for this position.

Applications including CV, credentials, publication list, a short overview of research interests and relevant documents should be sent by **September 30, 2009** to **Prof. Dr. Thorsten Bach, Dean of the Faculty of Chemistry, TECHNISCHE UNIVERSITÄT MÜNCHEN, Lichtenbergstr. 4, D-85747 Garching, Germany.** 

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#### PLANT WATCH

# Cement plant expansion in the Ukraine decreases environmental emissions

August 20, 2009 — ABB Switzerland Ltd. (Zurich, Switzerland; www.abb.com) has won an order from international building materials group CRH to deliver electrical and automation equipment for Podilsky Cement's new production line. Once the project is completed, the cement production line will have a daily output of 7,500 tons. The Podilsky Cement factory, located near Kiev, is one of the biggest cement plants in the Ukraine. The expansion project will help the plant decrease emissions from fossil fuel combustion by changing the technology of cement production from a wet production process to a state-of-the-art dry production process.

# KBR awarded contract for refinery in Angola...

August 20, 2009 — KBR (Houston; www.kbr. com) has been awarded a contract by Sonangol, E.P. to provide license and engineering services for fluid-catalytic-cracking (FCC) and hydroprocessing technologies for the Sonaref Refinery to be located in Lobito, Angola. The 200,000-bbl/d grassroots refinery is being built to reduce the country's dependence on imported products.

#### ...And a FEED contract by VCNG

August 5, 2009 — KBR has been awarded a contract by Verkhnechonskneftegas (VCNG) to provide front-end engineering and design (FEED) services for the VC FFD Project located in the Eastern Siberia region of Russia. KBR will provide FEED services for a new, 140,000-bbl/d oil facility, which will be tied back, via a new 85-kilometer pipeline, to the existing East Siberian Pacific Ocean (ESPO) pipeline.

#### Diageo USVI enters contract for rumdistillery washwater-treatment unit

July 21, 2009 — Diageo USVI (London; www. diageo.com) has awarded a contract to Veolia Water Solutions & Technologies (VWS; Saint Maurice, France; www.veoliawaterst.com) for the turnkey design, build, and startup of the washwater treatment plant that will support its planned Captain Morgan rum distillery on St. Croix, U.S. Virgin Islands. The washwater treatment plant will be located in the western half of the 25-acre building site at the St. Croix Renaissance Industrial Park.VWS, through its U.S. businesses Biothane and N.A. Water Systems, will

### **BUSINESS NEWS**

construct a treatment plant with capacity to process approximately 150-million gal/yr of washwater. The treatment process will take byproducts from the distillation process and turn them into clean water and biogas for green energy. This process enables Diageo to recycle water, provide a clean source of energy to its distillery, and create a rich fertilizer that can be used by public/private organizations. Diageo is already in talks with organizations that are interested in using the fertilizer. Once in operation in 2010, the distillery will have the capacity to distill up to 20-million gal/yr of rum.

#### **MERGERS AND ACQUISITIONS**

### Solvay increases investment in innovative printed electronics

August 20, 2009 — By investing \$12 million, Solvay (Brussels, Belgium; www.solvay.com) has become the largest minority shareholder in Plextronics, Inc. (Pittsburgh, Pa.; www. plextronics.com). Plextronics specializes in the development and commercialization of polymer-based technologies for printed electronics, such as organic solar cell and OLED (organic light-emitting diode) lighting.

### SABIC and Mitsubishi Rayon form a joint venture

August 10, 2009 — Saudi Basic Industries Corp. (SABIC; Riyadh, Saudi Arabia; www. sabic.com) and Mitsubishi Rayon Co. (MRC; Tokyo; www.mrc.co.jp) have signed a letter of intent (LoI) to establish a 50/50 joint venture (JV) in Saudi Arabia. The Lol outlines the principal terms of the proposed \$1-billion JV including the structure, technology, marketing and feedstock supply, with startup targeted for 2013. Under the LoI, the JV will utilize the ethylene-based Alpha process commercialized by Lucite (a wholly owned subsidiary of MRC) to manufacture methyl methacrylate (MMA) monomer, with a design capacity of 250,000 metric tons per year (m.t./yr). Also, the JV company will manufacture polymethyl methacrylate (PMMA), with a design capacity of 30,000 m.t./yr.

#### Oxea completes acquisition of production plant in the Netherlands

August 3, 2009 — Oxea (Oberhausen, Germany; www.oxea-chemicals.com), the global chemical company, has completed its acquisition of assets of the Amsterdam Esters Plant from ExxonMobil Chemical Holland B.V. Details of the transaction were not disclosed.

# Teijin Nestex textile dyeing company will dissolve and liquidate

August 3, 2009 — Teijin Fibers Ltd. (Osaka, Japan; www.teijinfiber.com) has announced plans to withdraw from the operations of Teijin Group's core textile-yarns dyeing plant, Teijin Nestex Ltd., based in Ishikawa, Japan, and to dissolve and liquidate the company at the end of March 2010.Teijin Nestex's predecessor Daishojiseren Ltd. joined the Teijin Group in 1951 and the company has functioned as the Group's core textile-yarns dyeing plant for approximately 50 years. During this time, the increasing shift of textile manufacturing offshore has significantly hampered the company's profitability.

#### Arkema to buy certain assets from Dow

August 3, 2009 — Arkema (Colombes, France; www.arkema.com) and The Dow Chemical Co. (Midland, Mich.; www.dow. com) have entered into an agreement for Dow to meet U.S. Federal Trade Commission (FTC)-required divestitures related to its acquisition of Rohm and Haas. This comes ahead of the November 27, 2009 deadline. Arkema will buy a Clear Lake, Tex., acrylic acid and esters plant and the UCAR Emulsion Systems specialty-latex businesses in North America for a fairvalue consideration of \$50 million (2009 estimated revenue for these businesses is approximately \$450 million). The proceeds from the sale are accretive to Dow's shareholders and will be used for further deleveraging. The selection of Arkema as the buyer must be approved by the FTC, and the two companies will be shortly reviewing the proposed transaction with FTC authorities. The deal is expected to close in the 4th quarter of 2009.

# Dow to divest ownership in Optimal Group of Companies to Petronas

July 31, 2009 — The Dow Chemical Co. (Dow; Midland Michigan; www.dow.com) and Petroliam Nasional Berhad (Petronas) have announced that they have reached an agreement for Dow's Union Carbide Corp. subsidiary to sell its entire shares of ownership in the Optimal Group of Companies (Optimal) to Petronas for \$660 million. Petronas would fund this acquisition through internally generated funds. The transaction, subject to customary conditions and approvals, is expected to close by the end of the 3rd quarter of 2009.

Dorothy Lozowski

#### FOR ADDITIONAL NEWS AS IT DEVELOPS, PLEASE VISIT WWW.CHE.COM

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### **Economic Indicators**

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#### **CHEMICAL ENGINEERING PLANT COST INDEX (CEPCI)**

/1057_50	- 100
(175/-57	= 100)

(1057.50 - 100)	lun 100	May 100	lun 109	
(1957-59 = 100)	Prelim.	Final	Final	Annual Index:
CE Index	508.9	509.1	597.1	2001 = 394.3
Equipment	596.8	596.8	729.7	0000 005 0
Heat exchangers & tanks	529.9	529.9	738.2	2002 = 395.0
Process machinery	583.0	583.0	658.7	2003 = 402.0
Pipe, valves & fittings	748.1	748.1	858.8	2004 - 444 2
Process instruments	388.9	389.0	452.8	2007 - 777.2
Pumps & compressors	896.7	896.7	865.9	2005 = 468.2
Electrical equipment	458.9	458.9	459.0	2006 = 499.6
Structural supports & misc	602.4	602.4	793.1	2000 - 40010
Construction labor	326.0	326.6	319.4	2007 = 525.4
Buildings	485.2	485.4	515.3	2008 = 575.4
Engineering & supervision	347.3	347.9	353.9	



Starting with the April 2007 Final numbers, several of the data series for labor and compressors have been converted to accommodate series IDs that were discontinued by the U.S. Bureau of Labor Statistics

#### **CURRENT BUSINESS INDICATORS**

CPI output index (2000 = 100)	— Ju
CPI value of output, \$ billions	Jun
CPI operating rate, %	— Ju
Producer prices, industrial chemicals (1982 = 100)	— Jul
Industrial Production in Manufacturing (2002=100)*	— Jul
Hourly earnings index, chemical & allied products (1992 = 100) -	— Jul
Productivity index, chemicals & allied products (1992 = 100)	— Ju

CPI OUTPUT INDEX (2000 = 100)



### **CPI OUTPUT VALUE (\$ BILLIONS)**

LATEST

89.8

66.0

94.8

234.6

149.1

128.5

= 1.480.4

Jun.'09 =

May.'09 =

Jun.'09 =

Jun.'09 =

Jun.'09 =

Jun.'09 =

Jun.'09 =

.'09 =

.'09

.'09 =

.'09

.'09

.'09

.'09

=

=

=

=



128.8 **CPI OPERATING RATE (%)** 

89.1

65.2

218.8

94.4

147.2

PREVIOUS

May. '09 =

May. '09

May. '09

May.'09 =

May.'09 =

May.'09 =

Apr.'09 = 1,394.1

=

=

89.1

65.4

93.9

147.6

128.6

229.8

1.424.8



\*Due to discontinuance, the Index of Industrial Activity has been replaced by the Industrial Production in Manufacturing index from the U.S. Federal Reserve Board. Current business indicators provided by Global insight, Inc., Lexington, Mass.

MARSHALL & SWIFT EQUIPMENT COST INDEX												
(1026 - 100)	2nd Q	1et Q	4th Q	3rd Q	2nd Q	1500	Т				1	
(1920 = 100)	2009	2009	2008	2008	2008	1485						
M & S INDEX	1,462.9	1,477.7	1,487.2	1,469.5	1,431.7							
Process industries, average —	1,534.2	1,553.2	2 1,561.2	1,538.2	1,491.7	1470						
Cement	1,532.5	1,551.1	1,553.4	1,522.2	1,473.5	1455						
Chemicals	1,504.8	1,523.8	1,533.7	1,511.5	1,464.8							
Clay products	1,512.9	1,526.4	1,524.4	1,495.6	1,453.5	1440						
Glass	1,420.1	1,439.8	1,448.1	1,432.4	1,385.1	1425						
Paint	1,535.9	1,554.1	1,564.2	1,543.9	1,494.8	1.20	П.				1	
Paper	1,435.6	1,453.3	1,462.9	1,443.1	1,400.0	1410						
Petroleum products	1,643.5	1,663.6	1,668.9	1,644.4	1,594.4	1005						
Rubber	1,581.1	1,600.3	1,604.6	1,575.6	1,537.5	1395	Ш.				1	
Related industries						1380						
Electrical power	1,394.7	1,425.0	1,454.2	1,454.4	1,412.8							
Mining, milling	1,562.9	1,573.0	1,567.5	1,546.2	1,498.9	1365						
Refrigeration	1,789.0	1,807.3	1,818.1	1,793.1	1,741.4	1350						
Steam power	1,490.8	1,509.3	1,521.9	1,499.3	1,453.2							
						1335						
	Anr	iual Inde	ex:			1220						
2001 = 1,093.9	2003 = 1,123.6	i	2005 = 1,244.5	2	007 = 1,373.3	1320	st 2	nd	3rd	4th	-	
2002 = 1,104.2	2004 = 1,178.5	i	2006 = 1,302.3	2	008 = 1,449.3		C	Qua	rter			

#### **CURRENT TRENDS**

Final estimates for May and preliminary estimates for the June CEPCI indicate that there was a very slight decrease in equipment prices from month to month. Meanwhile, estimates for the May, June (both revised) and July operating rates confirm that slowly but surely, shuttered facilities and process units are coming back on-stream, and widespread capacity corrections are behind us.

Visit www.che.com/pci for more on capital cost trends and methodology.

# May. '09

2009

2008

YEAR AGO Jul.'08 =

Jun.'08 =

Jul.'08 =

Jul.'08 =

Jul.'08 =

=

=

Jul. '08

Jul. '08

106.1

77.7

315.6

110.8

141.7

130.6

2.073.9



### **PROCESS INSIGHT**

### Selecting the Best Solvent for Gas Treating

Selecting the best amine/solvent for gas treating is not a trivial task. There are a number of amines available to remove contaminants such as  $CO_2$ ,  $H_2S$  and organic sulfur compounds from sour gas streams. The most commonly used amines are methanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA). Other amines include diglycolamine<sup>®</sup> (DGA), diisopropanolamine (DIPA), and triethanolamine (TEA). Mixtures of amines can also be used to customize or optimize the acid gas recovery. Temperature, pressure, sour gas composition, and purity requirements for the treated gas must all be considered when choosing the most appropriate amine for a given application.



#### **Primary Amines**

The primary amine MEA removes both CO<sub>2</sub> and H<sub>2</sub>S from sour gas and is effective at low pressure. Depending on the conditions, MEA can remove H<sub>2</sub>S to less than 4 ppmv while removing CO<sub>2</sub> to less than 100 ppmv. MEA systems generally require a reclaimer to remove degraded products from circulation. Typical solution strength ranges from 10 to 20 weight % with a maximum rich loading of 0.35 mole acid gas/mole MEA. DGA<sup>®</sup> is another primary amine that removes CO<sub>2</sub>, H<sub>2</sub>S, COS, and mercaptans. Typical solution strengths are 50-60 weight %, which result in lower circulation rates and less energy required for stripping as compared with MEA. DGA also requires reclaiming to remove the degradation products.

#### **Secondary Amines**

The secondary amine DEA removes both CO<sub>2</sub> and H<sub>2</sub>S but generally requires higher pressure than MEA to meet overhead specifications. Because DEA is a weaker amine than MEA, it requires less energy for stripping. Typical solution strength ranges from 25 to 35 weight % with a maximum rich loading of 0.35 mole/mole. DIPA is a secondary amine that exhibits some selectivity for H<sub>2</sub>S although it is not as pronounced as for tertiary amines. DIPA also removes COS. Solutions are low in corrosion and require relatively low energy for regeneration. The most common applications for DIPA are in the ADIP<sup>®</sup> and SULFINOL<sup>®</sup> processes.

#### **Tertiary Amines**

A tertiary amine such as MDEA is often used to selectively remove  $H_2S$ , especially for cases with a high  $CO_2$  to  $H_2S$  ratio in the sour gas. One benefit of selective absorption of  $H_2S$  is a Claus feed rich in  $H_2S$ . MDEA can remove  $H_2S$  to 4 ppm while maintaining 2% or less  $CO_2$  in the treated gas using relatively less energy for regeneration than that for DEA. Higher weight percent amine and less  $CO_2$  absorbed results in lower circulation rates as well. Typical solution strengths are 40-50 weight % with a maximum rich loading of 0.55 mole/mole. Because MDEA is not prone to degradation, corrosion is low and a reclaimer is unnecessary. Operating pressure can range from atmospheric, typical of tail gas treating units, to over 1,000 psia.

#### **Mixed Solvents**

In certain situations, the solvent can be "customized" to optimize the sweetening process. For example, adding a primary or secondary amine to MDEA can increase the rate of  $CO_2$  absorption without compromising the advantages of MDEA. Another less obvious application is adding MDEA to an existing DEA unit to increase the effective weight % amine to absorb more acid gas without increasing circulation rate or reboiler duty. Many plants utilize a mixture of amine with physical solvents. SULFINOL is a licensed product from Shell Oil Products that combines an amine with a physical solvent. Advantages of this solvent are increased mercaptan pickup, lower regeneration energy, and selectivity to H<sub>2</sub>S.

#### **Choosing the Best Alternative**

Given the wide variety of gas treating options, a process simulator that can accurately predict sweetening results is a necessity when attempting to determine the best option. ProMax® has been proven to accurately predict results for numerous process schemes. Additionally, ProMax can utilize a scenario tool to perform feasibility studies. The scenario tool may be used to systematically vary selected parameters in an effort to determine the



optimum operating conditions and the appropriate solvent. These studies can determine rich loading, reboiler duty, acid gas content of the sweet gas, amine losses, required circulation rate, type of amine or physical solvent, weight percent of amine, and other parameters. ProMax can model virtually any flow process or configuration including multiple columns, liquid hydrocarbon treating, and split flow processes. In addition, ProMax can accurately model caustic treating applications as well as physical solvent sweetening with solvents such as Coastal AGR<sup>®</sup>, methanol, and NMP. For more information about ProMax and its ability to determine the appropriate solvent for a given set of conditions, contact Bryan Research & Engineering.



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