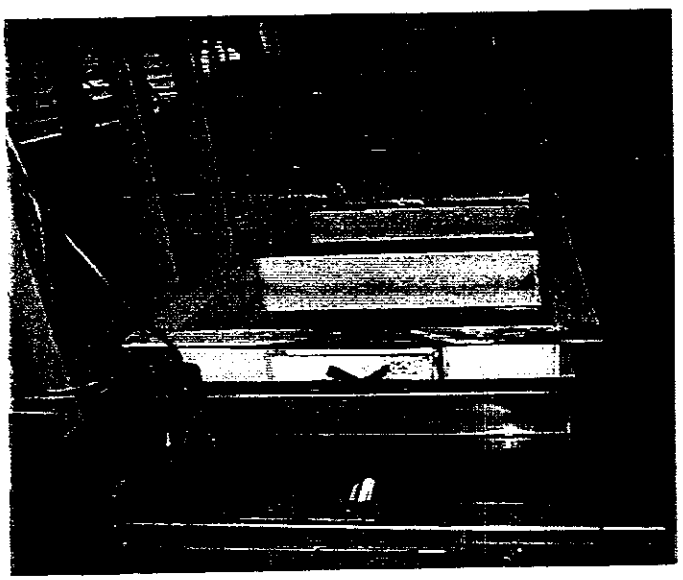
CP 18

PN-ACQ-607

Industrial Initiatives for a Sustainable Environment
IISE

Pollution Prevention (P2)
Cleaner Production (CP) Assessment
Training Course

Cebu, Philippines
February 14 – 18, 2000



Industrial Initiatives for a Sustainable Environment
A USAID Funded Project Managed by Chemonics International
Implemented by the DENR, DTI, PCG

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Industrial Initiatives for a Sustainable Environment
Republic of the Philippines

POLLUTION PREVENTION / CLEANER PRODUCTION ASSESSMENT COURSE

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Vice President
Millennium Science & Engineering, Inc.
IISE P2/CP Program Consultant

Cebu, Philippines
14 - 18 February, 2000

Course Participant Introductions

- Name
- Organization
- Technical Background
- Pollution Prevention Experience
- Sector Experience

Curriculum Overview - Day 1

- Morning
  - Introduction
  - Course Overview
  - Course Schedule
  - Introduction to P2
- Afternoon
  - Introduction to P2 (Cont.)
  - Industry Refresher

Curriculum Overview - Day 1

- Morning
  - Introduction
  - Course Overview
  - Course Schedule
  - Introduction to P2
- Afternoon
  - Introduction to P2 (Cont.)
  - Industry Refresher

Curriculum Overview - Day 2

- Morning
  - P2 Mass Tracking Model Protocol
- Afternoon
  - R2M2 Assessment Protocol

Curriculum Overview - Day 3

- Morning
  - Mass Tracking vs. R2M2 Approach
  - Cost Alternatives Analysis
- Afternoon
  - Process Assessment I (Field Visit)

Curriculum Overview - Day 4

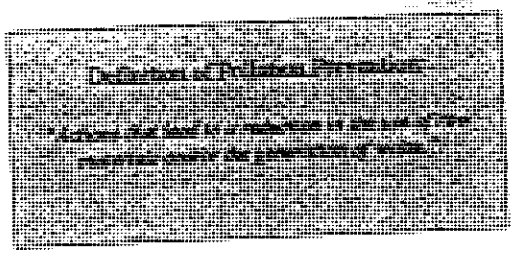
- Morning
  - Process Assessment I - Discussion
- Afternoon
  - Process Assessment II (Field Visit)

Curriculum Overview - Day 5

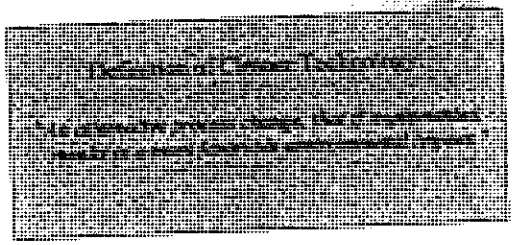
- Morning
  - Process Assessment II - Discussion
- Afternoon
  - Course Review
  - Exam

Pollution Prevention (P2) Overview

P2 Overview



P2 Overview



P2 Regulatory Drivers

- In the U.S.:
  - HSWA (1984): Requires Waste Reduction Certification on Manifests
  - Emergency Planning and Community Right-to-Know Act (1986): Public Access to Waste Data
  - Pollution Prevention Act (1990): Promotes P2 Through Government Involvement (e.g., State Assistance Grants)
  - Clean Air Act Amendments (1990): P2 Mandate
- No P2 regulations in RP now, but …

P2 Hierarchy: P2 Act of 1990

1 - Source Reduction
2 - Reuse / Recycle
3 - Treatment
4 - Disposal

Source reduction - Elimination

Pollution Prevention vs. "Prevention of Pollution"

- ISO Standards Development Process
- U.S. Delegation Position with Regard to P2
- Importance of the Difference to IISE

P2 Success Stories: Dow Chemical (Midland, MI)

- 17 Projects, Capital Investment $3 MM
- Eliminated 6.5 Million Pounds Waste / Yr
- Reduced Emissions 453,000 Pounds / Yr
- Savings of $5.3 MM /Yr
- Involved Committee of Dow Engineers & NGOs

From: *Chemical & Engineering News*, 9/13/99

P2 Success Stories: Cascade Cabinet (WA)

- Wooden Cabinet Manufacturer
- SME – Only 200 Employees
- 6,000 Wood Scrap / Day
- Wood Waste – Land-filled (Hauling Costs, Landfill Charge, Lost Product)
- Grinder Purchased - $60K
- Only Disposal Cost – Chipping Time

From: *Green Ledgers: Case Studies in Corporate Environmental Accounting*, WRI (1995), p.168.

P2 Success Stories: Ravenswood Aluminum (WV)

- Large Aluminum Manufacturer
- Conducted Water Use Reduction Study
- Reduced Water Loss By 10% Through Eliminating Valve, Pump Leakage

From: Author's Experience

P2 Methodology: Generalized Approach

- Identify Processes
- Prioritize Processes
- Select Processes
- Develop Process Flow Diagrams

P2 Methodology: Generalized Approach (Cont.)

- Identify Input and Output Streams
- Determine Baseline / Material Balance
- Identify Potential P2 Alternatives
- Evaluate Alternatives

P2 Methodology: Generalized Approach (Cont.)

- Implement Alternative(s)
- Measure Against the Baseline

P2 Issue No. 1: Participant Prioritization

How will we prioritize the potential candidates for where we conduct the assessments?

Key Filipino Industrial Sectors

- Mining / Quarrying
- Food / Beverage Manufacturing
- Textiles
- Agriculture*
- Leather Tanning / Manufacture
- Wood / Furniture Products
- Pulp and Paper*

(* Not Significant in IISE Selected Sites)

Key Filipino Industrial Sectors (Cont.)

- Electroplating
- Power Generation
- Industrial Chemicals
- Petrochemicals*
- Petroleum, Products*
- Rubber Products
- Iron / Steel

(* Not Significant in IISE Selected Sites)

P2 / CP Assessments - Intended Participants

- Highest Priority Participants: those industrial members which have the greatest potential to reduce their impact on the environment accompanied by a high level of interest in participation
- Previously completed IER process

P2 Issue No. 2: Process Prioritization

How will we prioritize and select the key processes to evaluate?

Selected Industrial Processes

- Anodizing
- Annealing
- Assembly
- Bleaching
- Bottling
- Canning
- Cement Production
- Chemical Distillation
- Chemical Synthesis
- Conversion Coating
- Cracking
- Degreasing
- Dyeing
- Electroplating
- Extruding
- Forming
- Fermentation
- Food Processing
- Forging
- Fuel Storage
- Galvanizing
- Gluing
- Injection Molding
- Metal Casting
- Metal Refining
- Mixing
- Packaging
- Painting
- Pharmaceuticals
- Photo Processing
- Pickling
- Powder Coating
- Pressing / Stamping
- Printing
- Pulping
- Refining
- Semiconductor Mfg
- Ship Building
- Ship Recycling
- Ship Repair
- Smelting
- Steel Fabrication
- Stripping
- Tanning
- Wood Preserving

P2 Issue No. 2: Process Prioritization

Key Factors

- Use of Target Chemicals
- Use of Other Toxic Chemicals
- Release of Wastes to One or More Media
- Immediate Worker Health Threat to Worker

P2 Issue No. 3: Baseline Determination

What are the issues we will encounter with baseline determination?

P2 Issue No. 3: Baseline Determination

estimate - approximations
[illegible] "do not know"

Key Factors

- Estimating Material Quantities
- Determining Chemical Content and Concentrations in Materials Used / Wastes
- Normalization to Account for Production Levels

P2 Issue No. 4: Alternative Selection

How do we know which alternatives to evaluate for potential implementation?

P2 Issue No. 4: Alternatives Evaluation

Key Factors

- Cost
- Implementability
  - Equipment Availability
  - Technical Feasibility
  - Compatibility with Current Operations

P2 Issue No. 5: Measuring Pollution Reduction

How will we be able to measure pollution reduction?

P2 Issue No. 5: Measuring Pollution Reduction

Key Issues

- IISE 20% Reduction Goal
- Which Organizations?
- Which Processes?
- Which Parameters?
- Mass Reduction vs. Risk Reduction

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POLLUTION PREVENTION CASE STUDIES - FROM EPA'S WEB SITE

Dry Cleaning Firm Shows 80% Waste Reduction

The Problem

Perchloroethylene (PERC) is used as a cleaning solvent in the dry cleaning industry. In the 1980s, PERC was considered to be a potential cancer-causing agent. (The carcinogenic effects of PERC are currently being studied). The dry cleaning industry made operational changes to reduce environmental discharges and employee exposures. Then the Clean Air Act Amendments of 1990 required the industry to develop pollution prevention plans to reduce emissions by 1995, to strictly monitor current consumption, and to report PERC emissions to the air and transfers to hazardous waste landfills (adsorbed on filters from dry cleaning machines).

Approach Selected

Rather than just plan for future pollution prevention, Leff-Marvins Cleaners took a proactive approach and looked to immediately replace all its old dry cleaning machines with new equipment that could condense, distill, filter, and recycle the PERC within a self-contained unit. By reducing its emissions earlier than required, Leff-Marvins Cleaners realized that it would have to deal with less stringent control requirements and less recordkeeping than would be imposed in 1995.

Approach Implemented

Leff-Marvins Cleaners spoke with a number of equipment vendors to find machines that could provide closed-loop handling of PERC. They sought to replace a transfer dry cleaning unit and two reclaimer units that handled 150 pounds of dry cleaning. The units had significant PERC fugitive emissions and generated two disposable filters that were treated as hazardous wastes because of the nearly 200 gallons (per month) of trapped PERC.

The old equipment was replaced with two new dry cleaning units that had a combined capacity of 110 pounds of dry cleaning. The new units used a cold water, closed loop, chiller process to capture and recycle the PERC. Nylon, reusable filters for capturing lint replaced the disposable hazardous waste filters. The permanent filters were stripped of lint by distillation through the system, reducing the hazardous wastestream to 35 gallons per month of still bottoms. Four dye-clarifying, activated carbon filters are replaced annually and disposed as hazardous waste.

Operating Results

Since installation of the new equipment, Leff-Marvins' purchases of PERC have dropped from 200 gallons per month to less than 40 gallons per month, a reduction of 80 percent. Annual hazardous waste disposal volumes have dropped from 1,600 gallons of spent PERC and lint to 420 gallons of still residues (also an 80 percent decrease) plus the number of hazardous waste filters requiring disposal was reduced to four from 24 per year.

Cost, Savings, and Tradeoffs

The changeover to new equipment produced a net annual savings of about $17,000. The environmental and hazardous material savings were actually $2,000 per month, but this was offset by an increase in the electric power bill of $500. The additional power requirements reflected electrical needs for condensation/distillation and an increase in business.
Leff-Marvins Cleaners estimated that payback of the $81,400 in new equipment would be achieved in 4 years through reduced PERC purchases, waste disposal savings, and fewer returns of clothing for recleaning, because the new equipment proved to clean better than the old dry cleaning machines. In addition, the new equipment had lower maintenance costs.

Environmental Benefits

Leff-Marvins Cleaners achieved other benefits in addition to decreasing PERC emissions well before the mandated deadline and reducing waste disposal by 80 percent. The new equipment brought an increase in business, a reduction in clothing returns for recleaning, and lower downtime with less maintenance. Also, employees expressed a greater satisfaction with their working environment.

Contact For Further Information

Pennsylvania Department of Environmental Resources, P.O. Box 8472, Harrisburg, PA 17105-8472. Telephone: (717) 787-7382

Case Study: Carpet Manufacturers Reduce Pollution via Automated Dyebath Reuse

In a conventional batch dyeing process, water is pumped into a dyeing machine, and fabric is placed in a bath and saturated with water. Chemicals and dye are then added to the water.
The bath is heated to dyeing temperature and held at that temperature until dyeing is complete. When complete, the dyebath is emptied, the machine is refilled, and the process is repeated for the next load. When a dyebath is emptied, large quantities of energy, water, and useful chemicals are sent to treatment and subsequently discharged.

A more efficient procedure would be to analyze the spent dyebath for remaining dye, add make-up chemicals to the bath to bring it to the

required strength, and then reuse it for subsequent dyeings (i.e., closed loop recycling). The technical and economic viability of reusing dyebaths has been demonstrated in the past; however, applying the process requires skills that were not always available to the textile manufacturer. For example, this procedure usually requires chemical analysis of the dyebath to determine what chemicals need to be added for reuse. If a chemist is not available to analyze each bath, automation of the process can be accomplished with an analytical system that will simply, accurately, and economically determine the concentration of the remaining dyebath, and add the proper amount of make-up chemicals.

Implemented Approach

Through a grant from the NICE3 program, several innovative techniques were investigated and evaluated that could allow full automation of the dyeing process. With a fully automated process, low-cost precision pumping systems allow a small volume of dyebath chemicals to be used for numerous dyeing operations. Using innovative monitoring insturments, a system is being developed that can analyze the dyebath and communicate the results to a computer for calculation of what chemicals need to be added for the next dyeing operation.

Operating Results

The waste reduction in the automated dyebath reuse process is straightforward; approximately 6 percent of the dyes, 60 percent of the auxiliary chemicals, and 42 percent of the water are directly reused in the manufacturing process and removed from the wastestream. Nationwide, waste would be reduced by 36-million pounds (16.3-million kg) of chemicals each year.

Widespread implementation of the automated dyebath reuse process would enhance U.S. industrial competitiveness by lowering costs. In addition to applications in the carpet industry, this technology could prove useful in the dyeing and finishing sectors of the textile industry.

Cost, Savings, and Tradeoffs

The cost to implement the program was $832,741 (Industry share: $432,741). By implementing this program, the savings at the test facility (Shaw Industries) were $1.6-million per year. Based on the industry share of $432,741, the payback period for this project was less than 3 months. Cost projects indicated that implementation of the dyebath reuse process could save money in terms of carpet production at almost all carpet plants.

Energy Benefits

The project has energy savings that are derived from three sources: (1) the reduction in direct thermal and electrical energy to heat dyebaths; (2) the elimination of energy to produce additional dyes, auxiliary chemicals, and water; all of which are reused with the new technology; and (3) reduction in energy associated with treatment of wastewater. If fully implemented throughout the carpet industry, dyebath reuse technology could save up to 3.6-trillion

Btu per year. On a national scale, and including the textile industry, full implementation would produce energy savings of up to 7-trillion Btu (7.4-quadrillion joules) each year by the year 2010. Based on the national average, residential energy consumption of 7-trillion Btu could supply all of the energy needs for about 70,000 homes for 1 year.

Contact For Further Information

Eric Hass, (MATEC), U.S. Department of Energy, Golden Field Office
Telephone: (303) 275-4728
Charlie Pike, State of California,
Telephone: (916) 327-1649
Greg Andrews, State of Georgia,
Telephone: (404) 651-5120

Sources

NICE3 Project Summary: "Automated Reuse of Dyebaths in Carpet Manufacturing."
(DOE/CH10093-235; DE93017075) Revised September 1994.

NICE3 Program Summary: "Wouldn't it be NICE ..." (DOE/CH10093-349; DE94011821)
September 1994.

Furniture Manufacturer Assembles More With Lower Emissions

New England Woodcraft, Inc. manufactures household and institutional furniture at its factory in Forestdale, Vermont. The plant determined that it was emitting significant amounts of volatile organic compounds (VOCs) on the order of 6 to 7 pounds per gallon of finish. (VOCs can result in the formulation of smog in reaction to ozone.) The nitrocellulose coatings being used contained toxic and carcinogenic ingredients such as formaldehyde. Significant amounts of solid and hazardous waste were generated at the plant as well.

Nitrocellulose coatings have been used by many furniture manufacturers to produce high quality coatings. However, New England Woodcraft sought to reduce worker exposure to toxics and reduce the emissions and hazardous waste generated from the use of nitrocellulose coatings.

Approach Implemented

In 1988, this company, began testing water-based coatings as a replacement for the traditional nitrocellulose coatings. In 1990, New England Woodcraft, in a joint effort with C.E. Bradley Laboratories, formulated a successful water-based coating and the necessary application equipment to replace the old nitrocellulose coatings.

Operating Results

The pre-mixed water-based emulsion finishes now used at New England Woodcraft contain only 1.67 pounds of VOCs per gallon of finish, a 75

percent reduction when compared to nitrocellulose finishes. Also, the new formulation contains no formaldehyde. Moreover, the high solids, water-based finish covers more area with less material. These factors have combined to reduce VOC emissions at the facility from 90 tons to 9 tons annually (90 percent reduction). Also, hazardous waste generation was reduced by over 90 percent, from greater than 2,200 pounds per month to less than 220 pounds per month.

Cost, Savings, and Tradeoffs

Significant cost reductions were realized in waste management, waste disposal, and taxes associated with hazardous waste generation. As a result of a 90 percent decrease in hazardous waste generation, the facility's regulatory status changed from a large quantity generator to a small quantity generator. Hence, the facility is conditionally exempt from some reporting and regulatory requirements under the Resource Conservation and Recovery Act (RCRA). Additionally, the facility received a 25 percent decrease in insurance rates due to decreased fire hazards.

Other Benefits

Reduced employee exposure to toxics and hazardous waste has improved the employee's work environment and subsequently their health and safety.

Contact For Further Information

Mr. Harmon Thurston
New England Woodcraft, Inc.
Route 53, Box 165
Forestdale, VT 05745
Telephone: (802) 247-8211

Newspaper Recycles Waste Ink

The Hartford Courant is a regional newspaper with a daily circulation of 225,000 and a Sunday circulation of 320,000. Approximately 175 gallons of waste ink are generated each week. The lithographic presses produce waste ink that is a mixture of mostly black ink blended with other colors and press cleaning solvents. During printing, excess ink contaminated with the blanket wash solvent, fountain solution (mostly water), and paper dust is collected in trays under the presses. In general, the ink and solvent wastestreams generated by a printing operation are considered hazardous wastes, especially if they contain chromium or lead or have a low flash point. Prior to implementing pollution prevention actions, the waste is shipped offsite for reuse as a supplemental fuel.

Approach Selected

The newspaper set out to essentially eliminate the generation of hazardous waste inks by cleaning and recycling waste ink. A study was performed under the U.S. Environmental Protection Agency's (EPA) Waste Reduction and Innovative Technology Evaluation (WRITE) Program to evaluate a technology that could be used to recycle waste printing ink for reuse inlithographic printing operations.

Approach Implemented

The Hartford Courant now collects the waste, recycles the solvent, and blends the waste ink back into virgin black ink for reuse. The facility has decreased both the toxicity and quantity of its hazardous waste from 9,100 gallons of waste ink and solvent to 46 gallons of paper dust and 3,050 gallons of water, a significant reduction that has allowed the facility to report its emissions as a small quantity generator.

The major components of the recycling unit at the The Hartford Courant were purchased on a skid, and other equipment was added as required. The waste ink goes to a large waste ink storage tank; when enough ink is collected in this tank, a batch is processed through a recycling unit back into a reusable black ink product. The recycling process primarily involves vacuum distillation, filtration, and blending.

After solvent and water from the waste ink are separated tests are performed to determine the amount of virgin black ink required for blending. The ratio of virgin ink to processed ink can vary from about 3:1 to 5:1. The virgin ink is added to improve the color, consistency, and other functional properties of the processed ink to an acceptable range. After blending, the recycled ink is transferred to a clean holding tank. The recycled ink is then drawn by a pump through a final filter to the presses.

Operating Results

Product quality of the spent, recycled, and virgin inks was evaluated by conducting selected performance tests and comparisons of the printed material by qualified professionals. The recycled ink fared well in laboratory performance tests such as viscosity, grind, residue, tinting strength, water content, and water pickup. In addition, there was no significant difference in print quality between the virgin and recycled inks in the opinion of experienced readers.

The waste volume reduction potential of this technology involves the amount of waste ink prevented from being disposed into the environment (by landfilling, waste incineration, or as a supplemental fuel). The facility generates approximately 175 gallons per week or 9,100 gallons per year of waste ink. The waste ink contains about 40 percent water and solvent (mostly water)and 60 percent ink. By recycling, the ink is recovered. The recycling wastestreams consist of water (wastewater) from the separator and the paper-dust paste residue from the filters. Any solvent that distills off is reused in the printing process. The facility plans to discharge the wastewater to the municipal sewer, but is considering installing an activated carbon filter for removing organics in the wastewater, so that the water can be reused. The paper-dust residue(about 1 gallon for every 200 gallons of waste ink processed) is disposed of by an offsite contractor for incineration or use as a supplemental fuel.

Cost, Savings, and Tradeoffs

The company has eliminated the disposal costs for the hazardous waste that they no longer generate. The disposal cost was $38,000/year. The major cost of the recycling option is for utilities (energy), labor, and disposal of wastewater and paper-dust residue, which is $7,100/year. The value of the recycled product is almost $20,000/year. When this is added to the difference in operating costs, the total "savings" are $50,000/year. With a purchase and installation cost of $318,000, a rough estimate of the payback period is about 6.25 years, based upon the current rates of items such as labor and utilities. When inflation and taxation are taken into account, the payback period is more accurately calculated as 10 years.

Environmental Benefits

By recycling virtually all of the potential pollutants in the waste ink (chromium, lead, barium,organics, etc.) are reused and, thus, prevented from entering the environment. In addition, the recycling unit was easy to install and operate. At The Hartford Courant, no additional labor was needed to operate the recycling equipment. Current employees were utilized to perform tasks similar to their previous job descriptions.

Contact For Further Information

The Hartford Courant; 285 Broad Street, Hartford, CT 06115
Telephone: (203) 275-1917

Sources

Final Report; On-site Waste Ink Recycling. Technology Evaluation Report; WRITE Program.
Risk Reduction Engineering Laboratory, Office of Research and Development, U.S.
Environmental Protection Agency. Cincinnati, Ohio. August 1992.

"Connecticut WRITE Today" ConnTAP Quarterly, 1993, 6(1):4.

Motorola Goes Solder-less

Traditionally, soldering methods use chemical fluxes to remove oxides from metal surfaces prior to soldering. Unfortunately, these fluxes leave corrosive residues, which must be removed with chemical rinses. Freon 113 and trichloroethane (TCA), both known ozone depleting chemicals (ODCs), were commonly used as part of these chemical rinse activities.

Approach Selected

Motorola Government Systems and Technology Group, in an effort to eliminate ODCs from its manufacturing processes, entered into a Cooperative Research and Development
Agreement (CRADA) with the Department of Energy's National Laboratories at Sandia and Los Alamos. Motorola provided manufacturing technology

while the labs provided analytical expertise and reliability predictions. Successful approaches were likely to either eliminate production of oxides or eliminate corrosive residues requiring rinses. Ultimately, the team developed a soldering process that is so clean that no chemical rinses are needed.

Approach Implemented

The new soldering process replaces flux with a preparation fluid that is lightly sprayed onto the bottom side of circuit boards. The fluid is a 2 percent mixture of adipic acid in isopropyl alcohol. Adipic acid is a safe, nontoxic, organic acid that is used in various commercial food products as a neutralizer and flavoring agent.

The circuit boards travel into an inert gas section of a wave soldering machine. The inert atmosphere in the chamber prevents oxide formation while the board is heated to soldering temperatures. When the board passes onto the liquid wave of solder metal, the adipic acid breaks down to scavenge oxides from the metal surfaces being soldered. A small amount of formic acid can be introduced into the atmosphere to assist in oxide removal. The acid is almost totally decomposed to carbon dioxide and water vapor. The boards do not require cleaning. Residues left after soldering were noncorrosive in the normal life cycle of electronics hardware.

Operating Results

Typical old-style soldering machines use up to 8,000 pounds of cleaners per month, or 48 tons of cleaners per year. The use of the new soldering process has eliminated the need for a rinsing stage and, therefore, has eliminated the use of Freon 113 and TCA cleaners and their associated air emissions.

Cost, Savings, and Tradeoffs

Costs for the cleaning solvents ranged from 52 cents to $2.55 a pound. Each machine that employs the new soldering process now saves between $50,000 and $245,000 per year in chemical use alone. The machines used in the development effort cost from $300,000 to $400,000 each. However, conventional wave solder machines can be retrofitted with nitrogen inert capability for $40,000 to $100,000, depending on the degree of mechanical and computer control modification required.

Environmental Benefits

As a result of the new soldering process, Motorola has helped eliminate the chemical air emissions of Freon 113 and TCA. For its efforts, Motorola has received the U.S. Environmental Protection Agency's Stratospheric Ozone Protection Award for the second time in 3 years.

Contact For Further Information

Jim Landers, Motorola Government Space and Technology Group,
Scottsdale, AZ Telephone: (602) 441-3600

Source

Arizona Pollution Prevention, Arizona Department of Environmental Quality APPLE+
Newsletter.

Biodiesel: "Not Blowing Smoke"

The combustion of diesel fuel in mass transit vehicles generates emissions such as particulate matter (PM), hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides(NOx), and sulfur oxides (SOx). The Clean Air Act Amendments of 1990 (CAAA) and the corresponding U.S. Environmental Protection Agency (EPA) regulations specify the reduction of these pollutants by imposing requirements such as stricter emission standards for newer vehicles and limiting the sulfur content in the fuels.

To meet the requirements of the new CAAA, and potential, tougher diesel regulations in the future, transit authorities across the country have begun to consider the use of alternate fuels for their mass transit vehicles. In 1993, more than 30 transit authorities participated in a program, sponsored by the biodiesel industry, to evaluate biodiesel as an alternative fuel. Biodiesel (methyl esters) is a cleaner-burning fuel made from natural,renewable resources such as vegetable oils.

Approach Implemented

In 1993, the biodiesel industry distributed enough fuel to log nearly 7-million road miles in more than 100 demonstrations involving more than 1,500 vehicles. During that time,transit authorities and school districts recorded information on emissions, performance, and oil contaminants. The practical road demonstrations included million-mile tests with transit authorities in Baltimore, Cincinnati, and Oakland, as well as more than 30 50,000-mile tests. For this program, mass transit authorities used a mix of 20 percent biodiesel and 80 percent petroleum diesel. However, some municipalities have used a blend of up to 40 percent biodiesel without experiencing any operational problems.

Operating Results

When biodiesel was used in place of conventional diesel fuel, transit managers noticed a reduction in smoke, odor, and diesel engine emissions. Some operators reported a 20 to 30 percent reduction of smoke. In tests conducted by independent researchers comparing emissions from vehicles using biodiesel vs. conventional diesel fuel, PM was reduced by 31 percent, HC was reduced by 47 percent, CO was reduced by 21 percent, and NOx was reduced by 3 percent. SOx emissions were not quantified, but would also be reduced,compared to conventional fuels, because biodiesel contains no sulfur, while diesel fuel contains about 0.05 percent sulfur.

Biodiesel performs similarily to petroleum diesel in terms of torque, horsepower, and miles per gallon but provides about 2 percent fewer Btus/gallon than conventional diesel. Also, maintenance shop supervisors have noted that biodiesel appears to provide slightly better lubrication to engine parts than standard diesel fuel.

Cost, Savings, and Tradeoffs

The cost of biodiesel depends on the cost of its components, diesel, and vegetable oil. In general, a 20/80 blend can cost up to 40 cents per gallon more than petroleum diesel. However, not all of the costs of meeting tougher emission standards have been quantified. Therefore, an emission management system based on biodiesel could be an inexpensive option for meeting these standards. According to an April 1994 study commissioned by the National SoyDiesel Development Board, the cost of biodiesel can range from about 18 cents per mile for a commercial medium-duty truck fleet to 28 cents per mile for a transit fleet. The study also found that a truck or bus fleet using 20 percent biodiesel blended with conventional diesel would experience lower total annual costs than with other alternatives.

Other Benefits

Biodiesel is made from natural, renewable resources such as soybean and vegetable oils.(Based on the Institute for Local Self-Reliance, one unit of energy used to produce biodiesel can supply a minimum of 2.5 units of fuel energy.) The primary by-product of the biodiesel production process is glycerine, which has more than 1,600 commercial applications. A principal feedstock source of biodiesel is soybeans, a major crop produced by nearly 400,000 farmers in 29 States across the Nation. The supply (equivalent) of 40-million gallons/year is nearly equal to projected demand if biodiesel use is implemented in all urban transportation buses. The use of biodiesel requires no expensive engine modifications. Because it has a higher flash point, offers low-pressure storage at ambient temperatures, handles like diesel, and is nontoxic and biodegradable, biodiesel is safer to transport and safer for the environment than conventional diesel fuel.

Contact For Further Information

National SoyDiesel Development Board
1907 Williams Street
P.O. Box 104898
Jefferson City, MO 65110-4898
Telephone: (800) 769-3437

Sources

Passenger Transport, APTA, May 16, 1994.

Instructions for Completion of IISE P2/CP Assessment Form

Nine worksheets have been prepared to assist the P2/CP Assessment Teams in performing facility assessments and collecting and reducing the necessary information. Worksheets 1-5 should be completed using the IER forms (previously completed) and for the P2/CP assessment while on-site. Completing these should provide the necessary information for the team to complete worksheets 6-9 following the in-plant assessment. Instructions to complete each worksheet are presented below, and examples for each entry are shown in parentheses after some of the descriptions.

Worksheet 1 - Overview

Worksheet 1 provides a general overview of the facility and the assessment. The following specific information should be referenced for answering the specific questions on the sheet.

1. Facility Name – Enter the name of the facility/company where the assessment is being conducted (e.g., Halsangz Plating Cebu Corp.).
2. Location – Enter the town/city name or industrial zone name, if appropriate (e.g., Mactan Export Processing Zone).
3. Sector – Enter the sector of industry (and PSIC number if known) under which the facility falls (e.g., electroplating).
4. Date – Enter the date during which the assessment is being conducted.
5. Time – Enter the start and end times of the assessment.
6. Date IER Completed – Enter the date when the Initial Environmental Review was completed.
7. IER Report Attached? – Place an "X" in the appropriate box indicating whether a copy of the Initial Environmental Review is attached to the completed P2/CP Assessment Worksheets.
8. P2/CP Assessment Team Members – Enter the names and affiliations of the assessment team members including both IISE and host facility team members.
9. Facility Contact Information – Provide name, address, telephone, fax, and e-mail contact information to whom all future environmental correspondence should be addressed.
10. Process Name – Enter the name of the particular process that is being described. It is preferable that the subprocesses be entered on the worksheet in the same sequence as they take place in the facility (e.g., 1. Receiving Raw Materials, 2. Transferring Raw Materials into Metering Devices, 3. Specific Manufacturing Steps, etc.)
11. Description – Provide a brief description of the process: what is performed, whether it is batch or continuous, automated or manual, etc.
12. Wet Process? – Place an "X" in the appropriate box indicating whether water is used or transferred in the process.
13. RP 28 / POPs Chems? - Place an "X" in the appropriate box indicating whether chemicals included in the DENR's list of 28 hazardous chemicals or UNEP's POPs are used in the process.

Worksheet 2 - Input Material Information

Worksheet 2 is designed to aid the Team in documenting the chemicals/products used in a process at the facility. These materials may be used as inputs ("building blocks") of the actual product or may be used for other activities in the facility, e.g., cleaning. You may want to use separate sheets for each process. It may be helpful to gather this information from a receiving department, where all of the materials received at the facility are documented and/or from various process areas. The following specific information should be referenced for answering the specific questions on the sheet.

1. Product Name – Enter the name of each major and/or hazardous/toxic product used at the facility. It is not intended that every product received at the facility should be included; only large quantity and/or hazardous/toxic products (e.g., table salt for the cafeteria does not need to be included but toluene for the process does).

2. Annual Use – Enter the quantity in kilograms of the amount of material purchased/used each year. Some materials (e.g., liquids or gases) may be presented in other units (e.g., liters or cubic meters), but the annual use should be normalized to kilograms so that further analyses may be consistent.
3. Chemical Components – Enter the names of the chemicals that are components of the product, especially those that are hazardous and/or toxic.
4. RP 28 / POPs Chems. Present – Enter names of the chemicals that are components of the product and are included in ISSE's list of hazardous 37 chemicals.
5. Mass % - Enter the percent (by mass) for each RP 28/ POPs chemical present in the product.
6. Annual RP 28 / POPs Use – Enter the annual mass in kilograms of each RP 28 /POPs chemical used in the facility as a result of use of the product.

Worksheet 3 - Process Waste Stream Analysis

Worksheet 3 is designed to aid the Team in documenting the wastes discharged from the facility. These materials may be discharged as gaseous, solid, or liquid wastes that are either emitted from the facility or stored on-site. The following specific information should be referenced for answering the specific questions on the sheet.

1. Process – Because there will be wastes from many different processes, enter each process and its wastes on a separate worksheet (e.g., "pickling" and its associated wastes are entered on one worksheet and "rinse" and its associated wastes are entered on another).
2. Operation – To properly determine the annual waste loading, the typical hours per day, days per week, and weeks per year of operation should be entered in the correct spaces (e.g., the operation is run 8 hrs/day, 5 days/wk, 48 wks/yr). Also, record the production rate in terms of units processed per unit time (e.g., 300 pieces/hr or 2,000 sq. m /week). This production level for the baseline will be used in the normalization process for comparison following P2 implementation.
3. Waste Stream – Several waste streams may be discharged from one process. Enter the name of each waste stream, followed by the information requested in the subsequent areas of the worksheet (e.g., from a phase split there would be a waste organic solvent, gaseous emissions, tank washdown, and possibly sludge cleanout).
4. Waste Phase – Enter the primary phase of the waste (e.g., gas for air emissions; liquid for wastewaters, waste solvents, etc.; solid for sludges, possibly for off-spec. material, waste containers, etc.).
5. Waste Stream Flowrate – Enter the wastestream flowrate in kilograms per hour for average operations so that this flowrate (kg/hr) may be multiplied by the operation schedule (hrs/day * days/wk * wks/yr) to determine the total annual mass of waste.
6. Chemical Components – Enter the major and/or important chemical components of the waste stream in the lines provided, using more as necessary. The major/important chemical components include those that are hazardous and/or those that constitute a major percentage of the waste stream (i.e., >5%).
7. RP 28 / POPs? – Mark an "X" in the appropriate box ("Y" for yes and "N" for no) indicating whether the chemical component listed previously is a chemical contained in IISE's list of 37 hazardous chemicals.
8. Mass % - Enter the percent (by mass) of the entire waste stream for each chemical component listed previously.
9. RP 28 / POPs Flowrate – For each or the RP 28 / POPs chemicals, determine the flowrate (in kg/hr) by multiplying the Waste stream Flowrate by the Mass %; and enter it on the appropriate line.
10. Fate – Describe the fate of the waste stream in the area provided. It may be emitted/discharged untreated, stored on- or off-site, or treated on- or off-site. If it is emitted/discharged untreated, indicate how it is emitted/discharged (e.g., as fugitive, stack, area, etc. emissions for gaseous/volatile wastes; discharged to water bodies, ground (water), the air by evaporation, etc. for wastewaters; disposed in an unregulated manner on the ground, in water bodies, open-burned, etc. for solid waste). If it is treated, indicate where and how

(e.g., on- or off-site; air: oxidizers, incinerators, activated carbon, water curtains, recycle, etc.; water: activated sludge wastewater treatment, aerated or facultative lagoons, incinerator, activated carbon, distillation, separation, recycle, etc.; solid waste: landfill, incinerator, recycle, land application (for sludges), composting, etc.). If it is stored, indicate where and how (e.g., in barrels on-site, in a tank, in a pile, at a storage facility, etc.). If it is stored on-site, indicate the quantity stored on-site.

Worksheet 4 - Initial Process Flow Diagram

Worksheet 4 is intended to aid the Team in gaining a better understanding of the process that is being assessed. In sketching a process flow diagram (PFD) during the assessment with the assistance of facility personnel, the team should be able to complete a mass balance around the process, indicating all inputs and outputs from the process. The process will be represented by individual (named) blocks for each step. Each input will be represented by an arrow pointing into the step into which it is introduced and named accordingly. Inputs can include raw materials, solvents, catalysts, wash streams, etc. Each output will be represented by an arrow pointing out of the step that indicates where it is being sent. Outputs can include intermediate or finished products, recycle streams, wastewaters, solid waste, air emissions, etc. All inputs and outputs (aside from intermediate and final products) presented in the PFD should also be presented in Worksheets 2 and 3.

Worksheet 5 - Pollution Prevention Options

Worksheet 5 is intended to capture pollution prevention options identified during the assessment along with a description of the location for implementation. For example, if a separation process splits an intermediate product from toluene and toluene is sent directly to the sewer, a recommendation for recycling toluene back into the process may be presented here along with recommendations of where the toluene could be reintroduced.

The remaining worksheets (6-9) are to be completed upon return to the office.

Worksheet 6 - Final Process Flow Diagram

Upon return to the office, the Team will prepare a final PFD based upon the complete information gathered during the facility assessment. The final PFD will be based upon the initial PFD, along with any modifications that were a result of further information collected after sketching the initial PFD.

Worksheet 7 – Mass Balance Summary

Worksheet 7 is intended to assist the team in constructing mass balances for hazardous material use in individual processes. Its goal is to aid the team in determining the fate of hazardous materials. For each input chemical, the annual use must be entered in either of the two input columns (RP 28 / POPs or Other HM) and its outputs, which should be a combination of the six possible outputs stated (HW Gen., WW Gen., Air Emis., SW Gen., Recover) should total the input. The following specific information should be referenced for answering the specific questions on the sheet.

1. Process Name – Enter the name of the process around which the mass balance is being constructed (e.g., the process line for a specific product or a specific step if need be [a tank cleanout, for instance]).
2. Chemical Name – The mass balance should be individually completed for each hazardous material used in the process. Enter the name of each hazardous chemical for the process on a separate line.
3. RP 28 / POPs – If the input chemical is an RP 28 or POPs chemical, enter the annual quantity used in kilograms per year on this line (e.g., 10,000 kg/yr benzene or 5,000 kg/yr 1,1,1-TCA).
4. Other HMs – Because the mass balance is intended only for hazardous materials and if the chemical is not an RP 28 / POPs chemical, enter the annual quantity used in kilograms per year on this line (e.g., 8,000 kg/yr acetone, 13,000 kg/yr toluene, or 16,000 kg/yr Cl_2).

5. Cons. In Proc. – Because matter is conserved, the fate of all input chemicals/ materials must be able to be tracked. Usually at least some input chemical is consumed in the process. This could be a "direct" consumption such as is the case for chemicals that are the building blocks of products or "indirect" consumption such as is the case for carrier chemicals like solvents that may partially remain with the chemical of interest after the separation. Alternatively, the chemical may be totally changed in the process such as is the case where an acid is added to neutralize a process and it forms salt and water. Enter the annual quantity in kilograms per year of the chemical that is consumed in the process.
6. HW Gen. – Many hazardous materials or combinations of several non-hazardous materials become hazardous wastes once they can no longer be used for their intended or another beneficial purpose. Enter the annual quantity in kilograms per year of the chemical that becomes a hazardous waste after use in the process.
7. WW Gen. – Many hazardous materials are discharged from processes in the form of wastewater. Enter the annual quantity in kilograms per year of the chemical that is discharged as wastewater after use in the process.
8. Air Emis. – Chemicals may be emitted to the air either as fugitive emissions emitted to the area through volatilization or as stack emissions. Enter the annual quantity in kilograms per year of the chemical that is emitted to the air after use in the process.
9. SW Gen. – The input chemical may be rendered non-hazardous through some physical change or chemical reaction and may be discharged as solid waste. Enter the annual quantity in kilograms per year of the chemical that is discharged as a solid waste after use in the process.
10. Recover – Many chemicals may be reused or recovered after use in a process. A process may require a certain level of chemical purity that another process does not require and can therefore use the "waste" chemical directly. Alternatively, a chemical may be able to be recovered and used again through a cleaning process such as scrubbing, distillation, electrolysis, etc. Enter the annual quantity in kilograms per year of the chemical that is recovered or reused off-site, in another process, or in this process after recovery elsewhere. Do not enter values for any recycle streams internal to the process.
11. MB? – Enter "Y" for "yes" or "N" for "no" to indicate whether the mass input balances with the mass output. The team may need to make reasonable assumptions to complete the balance. For example, If a certain process uses 10,000 kg/yr toluene and 5,000 kg/yr are recovered and another 3,000 kg/yr are discharged in the wastewater. It is reasonable to assume that 2,000 kg/yr are lost to air emissions if no toluene is consumed in the process or disposed as hazardous or solid wastes.
12. Comments – If assumptions are made to complete the mass balance or there is anything of note concerning the specific chemical in the process described, state them here.

Worksheet 8 - P2/CP Option Description

Worksheet 8 is to be filled out for each cleaner production and/or pollution prevention option identified for the various processes in the facility and serves as a brief summary describing the option to personnel unfamiliar with the option. The following specific information should be referenced for answering the specific questions on the sheet.

1. Option Name – Provide a brief (a few word) project name that uniquely identifies the option (e.g., Closed loop recycle system).
2. Option Description – Briefly describe the option and how it differs from the current process, materials, etc.
3. Source and Contact – Provide the contact information for the option (e.g., company, contact person, phone, address, e-mail, etc.).
4. Option Goal or Purpose – Briefly explain the goal or purpose of the option (e.g., eliminate VOC area emissions, reduce hazardous waste generation, reduce hazardous chemical usage and exposure, reduce wastewater generation, etc.).
5. Specific Estimate of Hazmat, Haz. Waste, Air Emission, and/or Wastewater Reduction by Option – Estimate the extent of reduction in hazardous material usage, hazardous waste

generation, or other emissions that would be a result of this option (e.g., This option will reduce solvent usage by 20% and air emissions by 40%).

6. Type of P2/CP Option – Mark an "X" in the appropriate box indicating whether the type of option is source reduction, recycling, treatment, or disposal.
7. Nature of P2/CP Option - Mark an "X" in the appropriate box indicating whether the nature of the option is personnel/procedural related, material related, or equipment related.
8. Specific Materials or Equipment Needed – List the specific materials and equipment needed to implement the option (e.g., decanter, 1 m^3 FRP tank, 10 lps centrifugal pump, 50 m of 10 mm PVC piping, metering valve, etc.).
9. Qualitative Assessment for Implementation – Mark an "X" in the appropriate box indicating whether the implementation cost is high, medium, or low and the ease of implementation is very difficult, moderate, or easy. This should be a qualitative assessment compared to the range of P2/CP options.

Worksheet 9 - P2/CP Option Evaluation

Worksheet 9 is designed to identify the relevance of implementing the option and also potential issues that could make implementation infeasible. Answering "yes" to any of the first 10 questions would help identify how the option would contribute to P2/CP. Answering "yes" to any of the last five questions would indicate where there might be areas that could cause the option to be infeasible. If "yes" is answered on any of the last five questions, please comment how the option impacts what is asked in the question.

Worksheet 10 - Option Cost Identification

Worksheet 10 is used to identify the cost factors associated with each P2/CP option. For each cost factor listed, mark an "X" in the "yes" box if the option would require changes with respect to that cost factor. Provide a brief description of the change and the annual savings or cost associated with each. Provided below are brief descriptions for each of the cost factors.

1. Process Equipment – New equipment or modifications to existing equipment are required to implement the option (e.g., purchasing a new heat exchanger or solvent distillation unit or retrofitting an existing wastewater treatment plant or air scrubber).
2. Personnel Training – Personnel training is needed to use new equipment materials or less training is required, as the materials are less hazardous and don't require the same precautions.
3. Installation / Site Preparation – Capital expenditures are required to install new equipment or prepare a site.
4. Utility Connections / Systems – New wiring/piping is necessary for the new equipment/materials or annual utility costs are increased/reduced.
5. Permitting – Additional or less stringent permits are required for new materials/processes.
6. Input Materials – New or additional materials are required as a result of material/process changes or fewer materials are required as a result of recycling, etc.
7. Disposal / Treatment – Changes in disposal and/or treatment are required as a result of material/process changes (e.g., conventional wastewater treatment rather than hazardous waste disposal is required as a result of changing a hazardous solvent for an aqueous cleaner).
8. O&M Labor and/or Supplies – Operation and maintenance labor and/or supplies increase or decrease as a result of the material/process change.

IISE P2/CP ASSESSMENT

Worksheet 1

Facility Name: _____

Location: _____ Sector: _____

Date: _____ Time: _____ Date IER Completed: _____

IER Report Attached? Yes ☐ No ☐

CP/P2 Assessment Team Members:
(Include both IISE and Facility Personnel)

1. _____
2. _____
3. _____
4. _____
5. _____

Facility Contact Information

Name: _____ Phone: _____

Address: _____ Fax: _____

_____ E-mail: _____

_____

Process Overview

Process Name	Description	Wet Process?	RP 28/ POPs Chems?
1.		Y ☐ N ☐	Y ☐ N ☐
2.		Y ☐ N ☐	Y ☐ N ☐
3.		Y ☐ N ☐	Y ☐ N ☐
4.		Y ☐ N ☐	Y ☐ N ☐

IISE P2/CP ASSESSMENT

Facility Name: _____

Process Name	Description	Wet Process?	RP 28/ POPs Chems?
5.		Y ☐ N ☐	Y ☐ N ☐
6.		Y ☐ N ☐	Y ☐ N ☐
7.		Y ☐ N ☐	Y ☐ N ☐
8.		Y ☐ N ☐	Y ☐ N ☐
9.		Y ☐ N ☐	Y ☐ N ☐
10.		Y ☐ N ☐	Y ☐ N ☐

HSE P2/CP ASSESSMENT

Facility Name: _____ Process Name: _____

Input Material Information

Product Name	Annual Use (kg)	Chemical Components	RP 28 / POPs Chems. Present	Mass %	Annual RP 28/ POPs Use (kg)
1.					
2.					
3.					
4.					
5.					
6.					
7.					
8.					

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IISE P2/CP AS. .SMENT

Facility Name: _____

Process Wastestream Analysis

Process: _____

Operation: _____ Hrs/day _____ Days/wk

_____ Wks/yr _____ Production Rate

Wastestream	Waste Phase	Wastestream Flowrate	Chemical Components	RP 28 / POPs ? Y	N	Mass %	RP 28 / POPs Flowrate	Fate
1.				☐	☐			
				☐	☐			
				☐	☐			
				☐	☐			
				☐	☐			
2.				☐	☐			
				☐	☐			
				☐	☐			
				☐	☐			
3.				☐	☐			
				☐	☐			
				☐	☐			
				☐	☐			
				☐	☐			

Facility Name: _____

Initial Process Flow Diagram

Process: _____

IISE P2/CP ASSESSMENT

Facility Name: _____

Pollution Prevention Options

Process: _____

Note: List Options Identified During Assessment and Location for Implementation
1.
2.
3.
4.
5.

Facility Name: _____

Final Process Flow Diagram

Process: _____

Facility Name: _____

Mass Balance Summary

Process Name: _____

Chemical Name	Inputs: RP 28 / POPs (kg/yr)	Inputs: Other HM (kg/yr)	Cons. In Proc. (kg/yr)	Outputs: HW Gen. (kg/yr)	Outputs: WW Gen. (kg/yr)	Outputs: Air Emis. (kg/yr)	Outputs: SW Gen. (kg/yr)	Outputs: Recover (kg/yr)	MB? (Y/N)	Comments:

Note: Attach sheet with all back-up calculations and assumptions.

Facility Name: _____

CP/P2 Option Description

Process: _____

Option Name	
Option Description	
Source and Contact	
Option Goal or Purpose	
Specific Estimate of Hazmat, Haz. Waste, Air Emission, and/or Wastewater Reduction by Option	
Type of CP/P2 Option	☐ Source Reduction ☐ Treatment ☐ Recycling ☐ Disposal
Nature of CP/P2 Option	☐ Personnel/Procedural ☐ Equipment ☐ Material
Specific Materials or Equipment Needed	
Qualitative Assessment for Implementation	Cost of Implementation: ☐ High Cost ☐ Low Cost ☐ No Cost Ease of Implementation: ☐ Very Difficult ☐ Moderate ☐ Easy

IISE P2/CP ASSESSMENT

Facility Name: _____

CP/P2 Option Evaluation

Option Name: _____ Process: _____

Y	N	
☐	☐	Does the option reduce ozone depletion potential?
☐	☐	Does the option reduce global warming potential?
☐	☐	Does the option reduce acid rain potential?
☐	☐	Does the option reduce photochemical oxidation or smog-forming potential?
☐	☐	Does the option reduce human toxicity potential by ingestion?
☐	☐	Does the option reduce human toxicity potential by inhalation or dermal exposure?
☐	☐	Does the option reduce aquatic toxicity potential?
☐	☐	Does the option reduce terrestrial toxicity potential?
☐	☐	Does the option reduce the use of RP 28 / POPs chemicals?
☐	☐	Does the option reduce the use of other hazardous materials?
☐	☐	Are there any anticipated problems with the option's compatibility with production? If yes, comment:
☐	☐	Is it anticipated that implementing this option would have a negative impact on compliance? If yes, comment:
☐	☐	Would there be added health and safety (industrial hygiene) concerns by implementing the option? If yes, comment:
☐	☐	Does the option require additional labor/expertise or other resources? If yes, comment:
☐	☐	Are there space or utility limitations in the buildings where the option might be implemented? If yes, comment:

Facility Name: _____

Option Cost Identification

Process: _____

Option Name: _____

Does the option require or change the requirement for any of the following?

Y	N		Description	Savings / (Cost)
☐	☐	Process Equipment		
☐	☐	Personnel Training		
☐	☐	Installation / Site Preparation		
☐	☐	Utility Connections / Systems		
☐	☐	Permitting		
☐	☐	Input Materials		
☐	☐	Disposal / Treatment		
☐	☐	O&M Labor and/or Supplies		

Note: Please attach all unit cost assumptions and calculations.

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IISE P2/CP ASSESSMENT

Facility Name: _____

P2 Option – Cost Evaluation Worksheet

Process: _____

Option Name: _____

Capital Costs

Item	Cost	Comments
Equipment		
Materials		
Installation		
Utilities		
Engineering		
Start-up / Training		
Other Costs		
TOTAL CAPITAL COSTS		

Facility Name: _____

P2 Option – Cost Evaluation Worksheet

Process: _____

Option Name: _____

Incremental Operating Costs

Item	Savings (+) / Cost (-)	Comments
Change in Disposal / Treatment Costs		
Change in Raw Material Costs		
Change in Labor		
Change in Other Costs		
Annual Net Operating Savings / Costs		

Calculating Project Payback

Payback Period (in years) = Total Capital Costs / Annual Net Operating Cost Savings

Total Capital Costs	
Annual Net Operating Savings	
Payback Period (Years)	

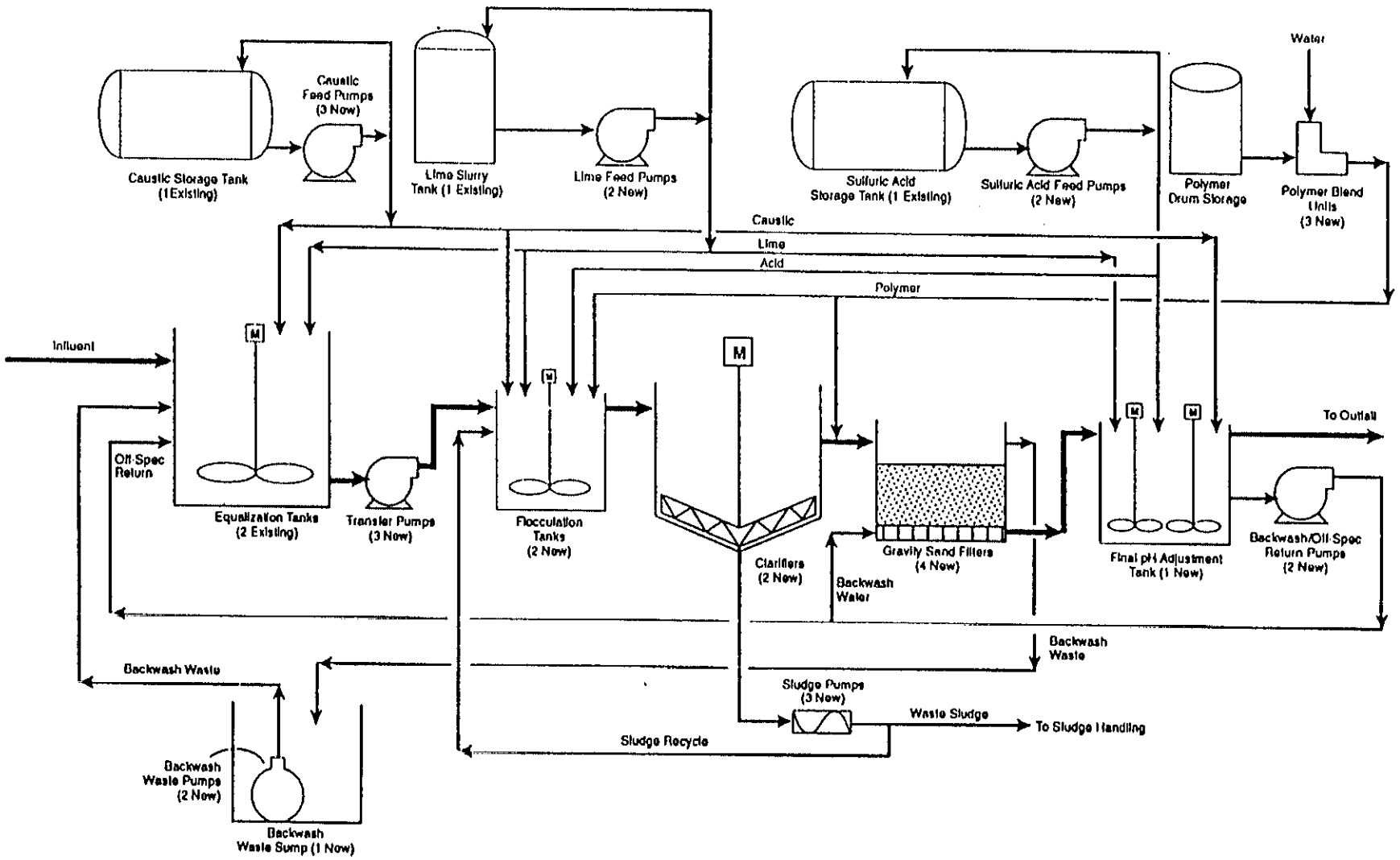


Figure 18.3. Liquid process flow diagram.

43

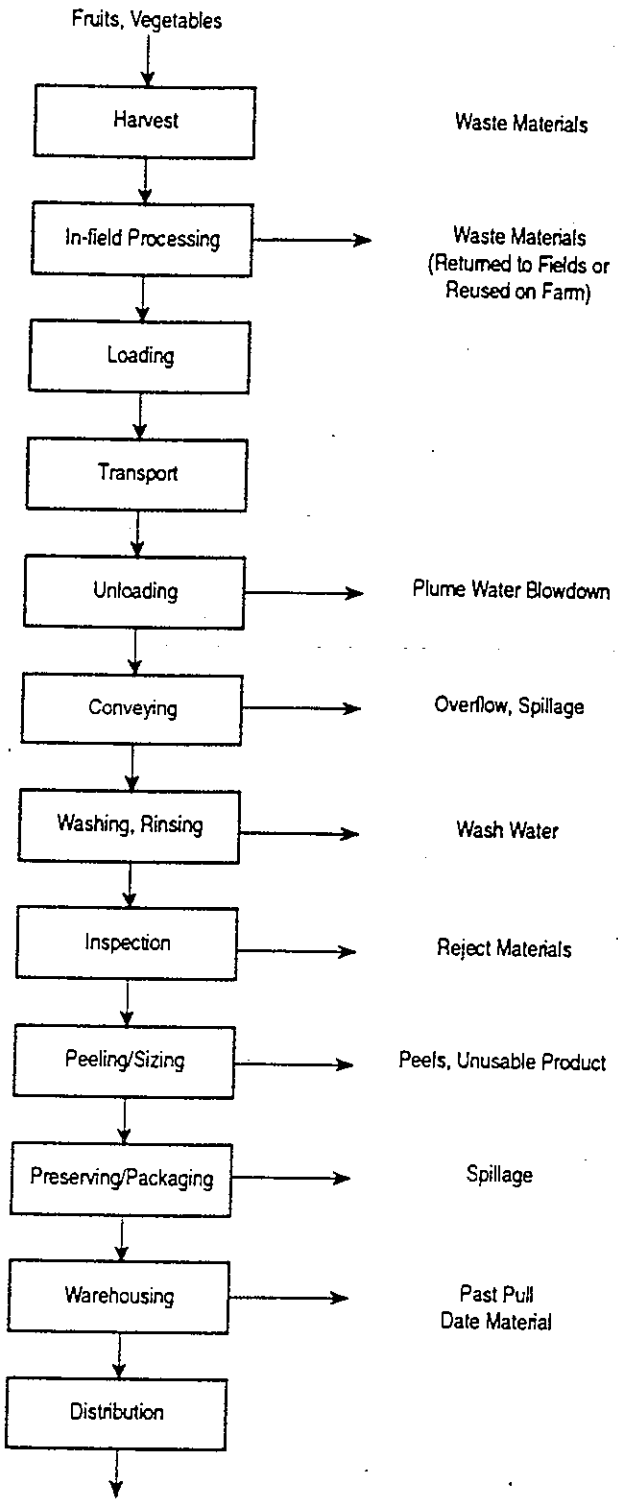


Figure 19.2. Generalized fruit and vegetable processing sequence.

44

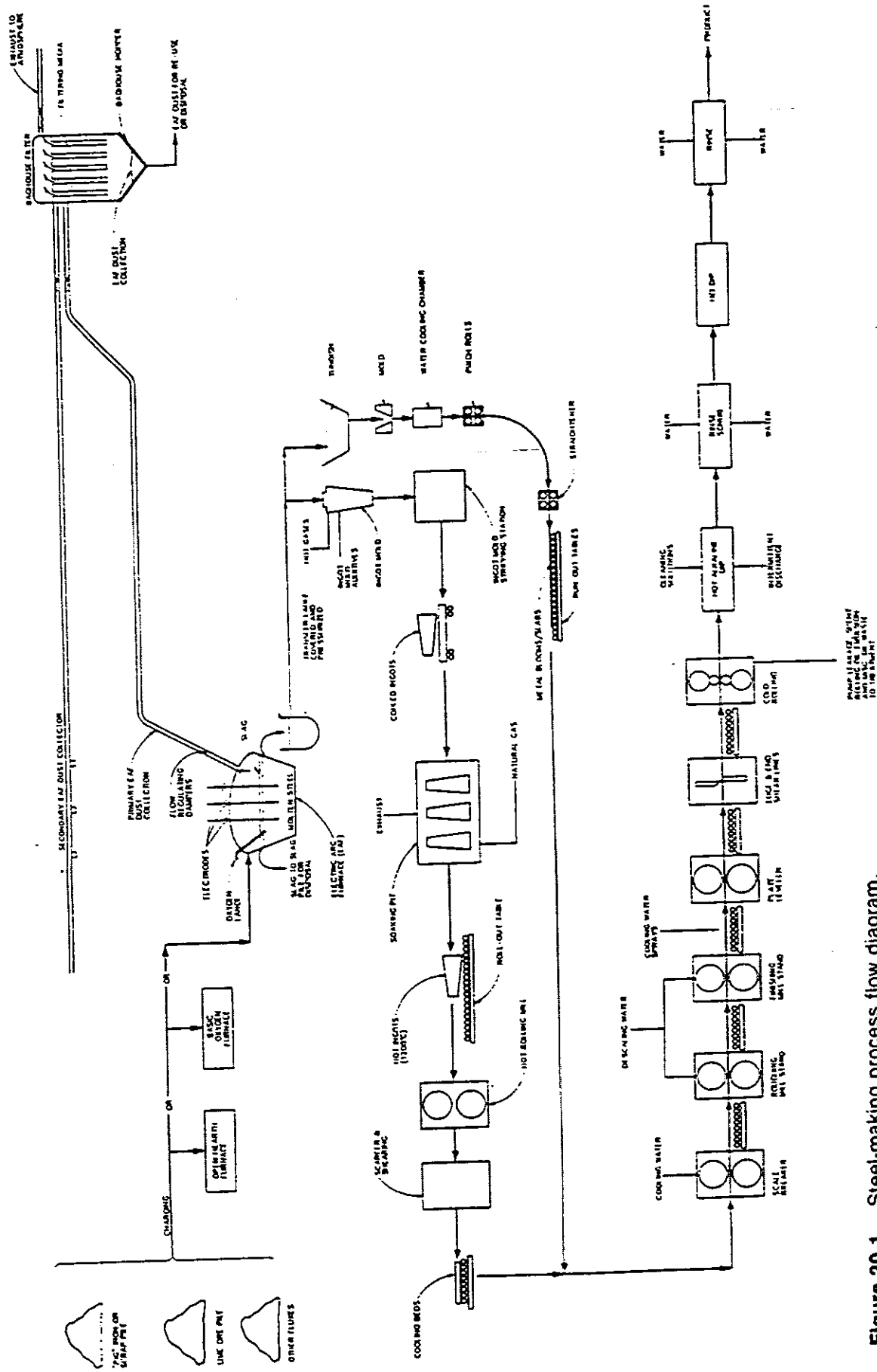


Figure 20.1. Steel-making process flow diagram.

question and of how it fits into the overall facility operation. This perspective is a prerequisite for thorough assessment of options in later phases of the pollution prevention plan development cycle. If consultants are on the assessment team, the site review enables them to become familiar enough with the facility to utilize their expertise effectively.

The site review should not be performed perfunctorily, even though the assessment team members who are employed at the facility will all be familiar to some extent with the work-site being reviewed. Those who are not involved in the day-to-day operation in that area will see factors that otherwise would be overlooked. Furthermore, personnel assigned to that specific site will often see it in a new light when performing a pollution prevention assessment. Some of the information that can be gathered through site reviews is summarized in Box 14.

Typical questions to ask during site reviews include:

- What is the composition of the waste streams and emissions generated in the company? What is their quantity?
- From which production processes or treatments do these waste streams and emissions originate?
- Which waste materials and emissions fall under environmental regulations?
- What raw materials and input materials in the company or production process generate these waste streams and emissions?
- How much of a specific raw or input material is found in each waste stream?
- What quantity of materials are lost in the form of volatile emissions?
- How efficient is the production process and the various steps of that process?
- Are any unnecessary waste materials or emissions produced by mixing materials — which could otherwise be reused with other waste materials?
- Which good housekeeping practices are already in force in the company to limit the generation of waste materials?
- What process controls are already in use to improve process efficiency?

Box 14

Site visits should be well-planned to ensure that maximum benefit is obtained without excessive expenditures of time. While multiple visits to check or supplement data will usually be required, good planning can minimize such repetitions. Several suggestions for preparing for site visits are given below.

Good planning is essential for efficient site reviews.

Review existing documentation, such as operators' manuals and purchasing and shipping records. This will enable the team to focus on the topics to be investigated.

Decide on data sources and collection procedures.

Decide on data collection formats to ensure that the data collection will be rigorous and compatible with the compilation and analysis stage described on the following page. In particular,

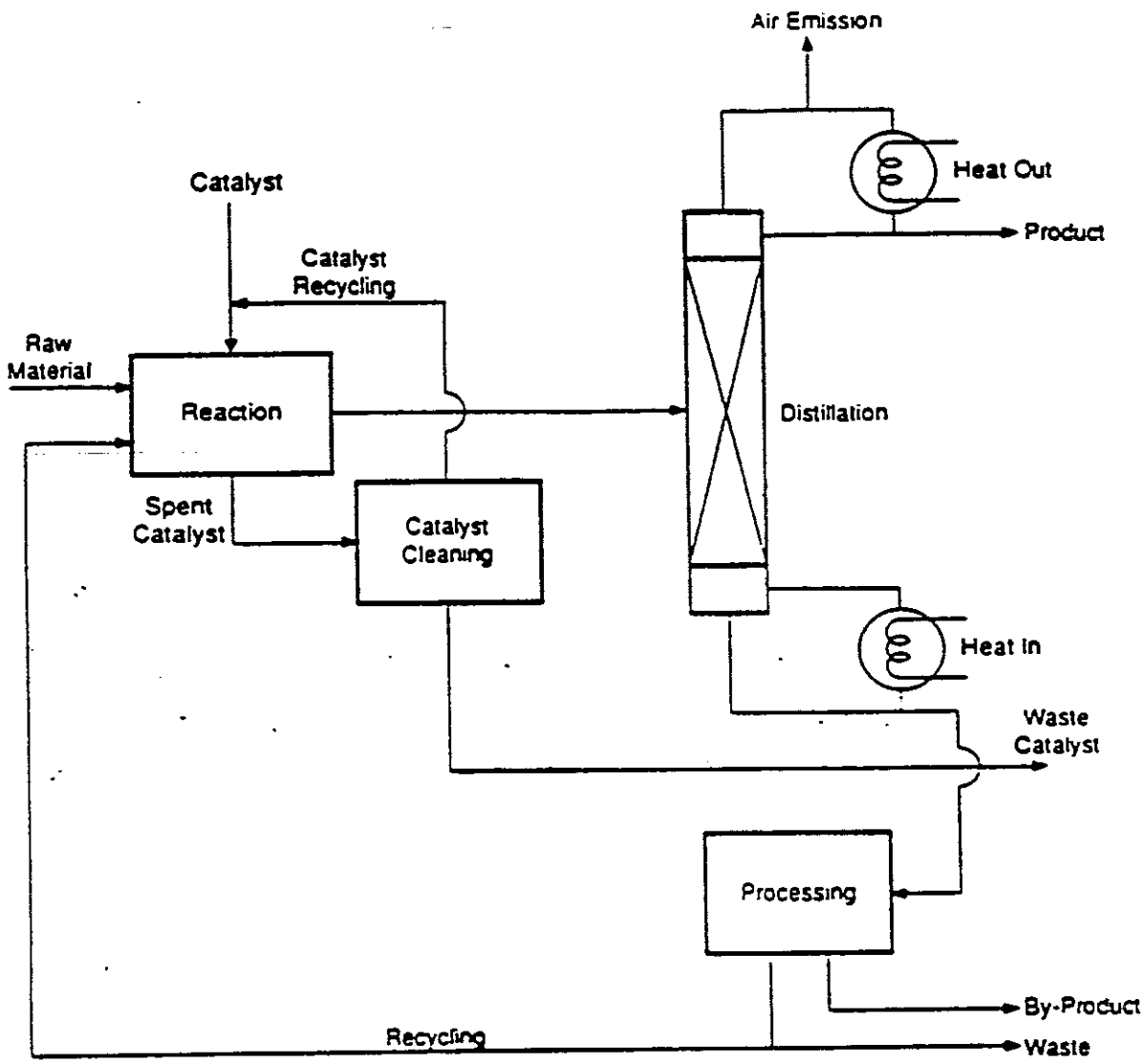


Figure 4. Example Flow Diagram

Boundaries should be selected according to the factors that are important for measuring the type and quantity of pollution prevented, the quality of the product, and the economics of the process. The amount of material input should equal the amount exiting, corrected for accumulation and creation or destruction.

Option screening should consider these questions:

- Which options will best achieve the goal of waste reduction?
- What are the main benefits to be gained by implementing this option (e.g., financial, compliance, liability, workplace safety, etc.)?
- Does the necessary technology exist to develop the option?
- How much does it cost? Does it appear to be cost-effective, meriting in-depth economic feasibility assessment?
- Can the option be implemented within a reasonable amount of time without disrupting production?
- Does the option have a good "track record"? If not, is there convincing evidence that the option will work as required?
- What other areas will be affected?

Box 15

Depending on the resources currently available, it may be necessary to postpone feasibility assessments for some options. However, all options should be evaluated eventually.

Technical Evaluation

The assessment team will perform a technical evaluation to determine whether a proposed pollution prevention option is likely to work in a specific application. Technical evaluation for a given option may be relatively quick or it may require extensive investigation. The list in Box 16 suggests some criteria that could be used in a technical evaluation. Some of these are more detailed versions of questions asked during the option screening phase.

Technical evaluations require the expertise of a variety of people.

All groups in the facility that will be affected directly if the option is adopted should contribute to the technical evaluation. This might include people from production, maintenance, QC/QA, and purchasing. In some cases, customers may need to be consulted and their requirements verified. Prior consultation and review with these groups will ensure the viability and acceptance of an option. If the option calls for a change in production methods or input materials, carefully assess the likely effects on the quality of the final product. If after the technical evaluation the option appears impractical or can be expected to lower product quality, drop it.

Some options can be implemented right away.

For options that do not involve a significant capital expenditure, the team can use a "fast-track" approach. For example, procedural or housekeeping changes can often be implemented quickly, after the appropriate review, approvals, and training have been accomplished. Material substitutions also can be accomplished relatively quickly if there are no major production rate, product quality, or equipment changes involved.

Typical technical evaluation criteria:

- Will it reduce waste?
- Is the system safe for our workers?
- Will our product quality be improved or maintained?
- Do we have space available in our facility?
- Are the new equipment, materials, or procedures compatible with our production operating procedures, work flow, and production rates?
- Will we need to hire additional labor to implement the option?
- Will we need to train or hire personnel with special expertise to operate or maintain the new system?
- Do we have the utilities needed to run the equipment? Or, must they be installed at increased capital cost?
- How long will production be stopped during system installation?
- Will the vendor provide acceptable service?
- Will the system create other environmental problems?

Box 16

Options that can affect production or quality need careful study.

Equipment-related options or process changes are more expensive and may affect production rate or product quality. Therefore, such options require more study. The assessment team will want to determine whether the option will perform in the field under conditions similar to the planned application. In some cases, they can arrange, through equipment vendors and industry contacts, visits to existing installations. Experienced operators' comments are especially important and should be compared with vendors' claims. A bench-scale or pilot-scale demonstration may be needed. It may also be possible to obtain scale-up data using a rental test unit for bench-scale or pilot-scale experiments. Some vendors will install equipment on a trial basis, with acceptance and payment after a prescribed time, if the user is satisfied.

Environmental Evaluation

Environmental considerations:

- *effect on number and toxicity of waste streams*
- *risk of transfer to other media*
- *environmental impact of alternate input materials*
- *energy consumption*

In this step, the pollution prevention assessment team will weigh the advantages and disadvantages of each option with regard to the environment. Often the environmental advantage is obvious — the toxicity of a waste stream will be reduced without generating a new waste stream. Most housekeeping and direct efficiency improvements have this advantage. With such options, the environmental situation in the company improves without new environmental problems arising.

Unfortunately, the environmental evaluation is not always so clearcut. Some options require a thorough environmental evaluation, especially if they involve product or process changes or the substitution of raw materials.

MASS TRACKING MODEL

Introduction

The key model proposed for the measurement of pollution reduction in the Philippines under the Industrial Initiatives for a Sustainable Environment (IISE) project has been developed. The Risk Management Reduction Model (R2M2) approach is based on the relative risk of a process in comparison to alternatives. This ensures that all the environmental pollution pathways are considered, implementing multi-media pollution reduction. The model measures Potential Environmental Impact (PEI) of the output streams of the process.

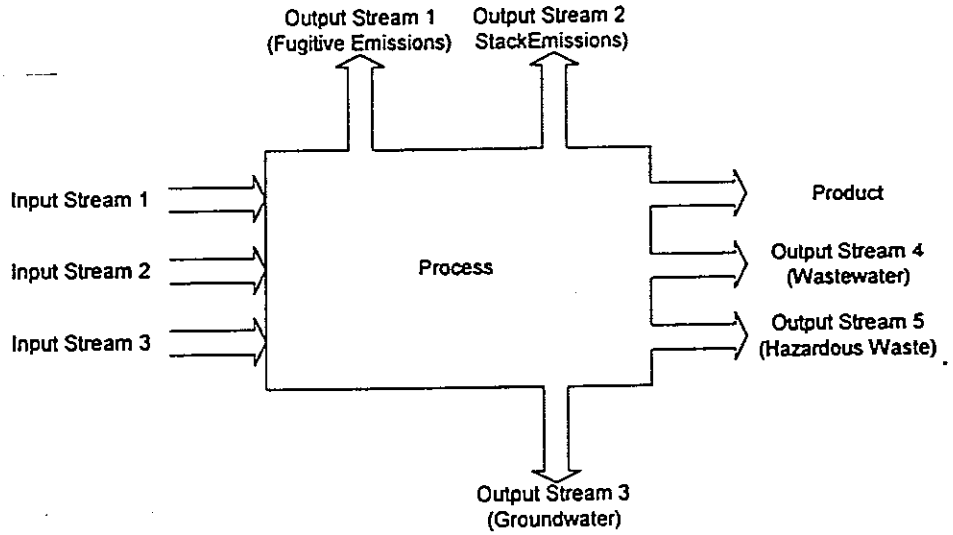
The Mass Tracking Model (MTM) is proposed for tracking pollution reduction for processes where the R2M2 would not be particularly useful. The MTM can be used to address either a gross parameter, such as biological oxygen demand (BOD), or a specific chemical(s). The MTM would only be used when the process does not contain targeted chemicals in the any of the waste streams, or does not contain any chemicals likely to be added to the list of targeted chemicals in the any of the waste streams. MTM is designed as a less rigorous approach (but still valuable) to measuring pollution reduction than R2M2.

Description of MTM

A fundamental task of the project is to conduct in-plant P2/CP assessments. Similar to R2M2, a baseline scenario would be established for each process evaluated at a facility. These data and information will be gathered by teams of appropriately trained personnel including those familiar with the processes being evaluated and P2 engineers, at a minimum. After gathering facility information, the P2 engineer will evaluate the data, establish the pollution baseline, and prepare an "alternatives evaluation." Following implementation of P2/CP alternatives, the updated process would be compared to the baseline level.

The MTM is proposed for use in measuring reduction of mass loading to the environment of selected parameters. A mass balance approach considering inputs and outputs to a process is used (Figure 1). For waste outputs, the concentration of a chemical in the waste stream multiplied by the flow rate would determine the mass loading for that chemical in the waste stream. Summing the mass loading from each waste stream yields the mass loading from the process. Non-chemical specific parameters that could be used for the MTM include BOD, total organic carbon (TOC), and chemical oxygen demand (COD). These chemicals would not generally include IISE-targeted chemicals, since the R2M2 would be utilized for targeted chemicals.

Figure 1—Process Flow Diagram



Risk Reduction Measurement Model (R2M2)

Dale A. Rice, P.E.
Vice President
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IISE P2/CP Program Consultant

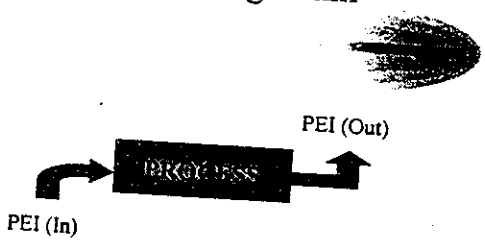
R2M2 Based on EPA's "WAR" Algorithm

- WAste Reduction Algorithm
- Developed by USEPA's National Risk Management Research Laboratory
- Available to General Public - Spring 2000
- EPA Positioned to Assist the Technical Team of IISE
- Designed for Use in the Chemical Industry

"WAR" and R2M2 Algorithms

- Risk-based
- Process-oriented
- Key Assumption: Industrial Streams Entering and Leaving a Process Have Potential Environmental Impact (PEI)
- Makes Use of Matrix of 1600 Chemicals

R2M2 Algorithm



R2M2 Chemical Matrix

- RP Priority Chemical List (RP 28)
- Priority Organic Pollutants (POPs)
- Other Hazardous Chemicals As Appropriate

RP 28 Chemicals

Non-Organics

- Asbestos
- Selenium
- Tributyltin
- Arsenic
- Beryllium
- Cadmium
- Chromium
- Cyanide
- Lead
- Mercury

RP 28 Chemicals

Organics

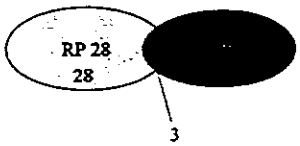
- Benzene
- Carbon Tetrachloride
- Chlorofluorocarbons
- Chloroform
- Chlorinated Ethers
- Ethylene Dibromide
- Ethylene Oxide
- Halons
- Hexachlorobenzene
- Hexachloroethane
- Mirex
- Polychlorinated Biphenyls
- Phosgene
- Pentachlorophenol
- Polybrominated biphenyls
- Vinyl Chloride
- 1,1,1-Trichloroethane
- 1,2-Diphenylhydrazine

"POPs" Chemicals

- DDT
- Aldrin
- Dieldrin
- Endrin
- Chlordane
- Heptachlor
- Hexachlorobenzene
- Mirex
- Toxaphene
- PCBs
- Dioxins
- Furans

RP 28 / POPs Chemicals

TOTAL NUMBER OF
"IISE CHEMICALS" = 37



War Algorithm: Potential Environmental Impact Equation

$$I = \sum M_i^{(in)} \sum \chi_{ij} \sum \alpha_k \Psi_{jk}$$

where:

I = rate of input of PEI
M_i = mass flowrate of chemical stream,i
χ_{ij} = chemical fraction in each in each input stream
α_k = weighting factor for each impact category
Ψ_{jk} = PEI of chemical component

R2M2 Health / Environmental Impact Categories

- Ozone-Depletion Potential
- Global-Warming Potential
- Acid-Rain Potential
- Photo-chemical-Oxidation Potential

R2M2 Health / Environmental Impact Categories (Cont.)

- Human-Toxicity Potential (Ingestion)
- Human-Toxicity Potential (Inhalation / Dermal Exposure)
- Aquatic-Toxicity Potential
- Terrestrial-Toxicity Potential

R2M2 Algorithm

- R2M2 Includes RP 28 / POPs Chemicals in Matrix
- User-friendly IISE Version Under Construction
- EPA Consulted 10/99 – Concurrence Obtained
- R2M2 to Be Tested, Further Developed Before Widespread Use
- Similar to WAR, But Has Probability Coefficient

R2M2 Modified PEI Equation

$$I = \sum M_i^{(out)} \sum \chi_{ij} \sum \alpha_k \beta_{jk} \Psi_{jk}$$

where:

I = rate of output of PEI

M_i = mass flowrate of chemical stream, i

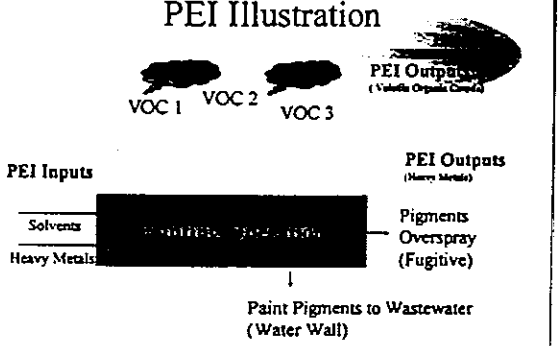
χ_{ij} = chemical fraction in each output stream

α_k = weighting factor for each impact category k

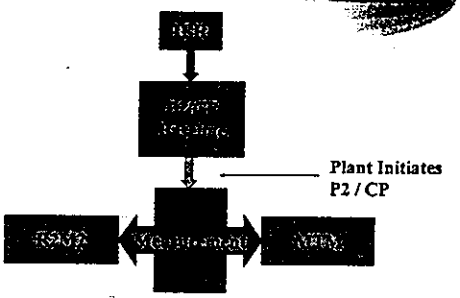
Ψ_{jk} = PEI of chemical component

β_{jk} = probability factor

PEI Illustration



IISE P2/CP Work Flow



R2M2 v. MTM

[redacted]

R2M2 v. MTM

R2M2	MTM
• RP28 / POPs • Other HMs (To Be Defined)	• BOD • COD • Other Non Haz Chemicals • Solid Waste

RISK REDUCTION MEASUREMENT MODEL

Introduction

Chemonics was awarded the Municipal Coastal Environmental Initiative (MCEI) contract by the United States Agency for International Development on 24 July 1998. This contract, subsequently renamed IISE (Industrial Initiatives for a Sustainable Environment), will operate in the Visayas and Mindanao regions of the Philippines, with support from the project field headquarters in Manila. To accomplish the objectives of the project, the IISE team will work closely with its partners to create a self-sustaining, multi-stakeholder program that will encourage adoption of environmental management systems and application of pollution prevention / cleaner production (P2/CP) technologies.

A fundamental task of the project is to conduct in-plant P2/CP assessments. The IISE project will result in the conduct of P2/CP assessments at 400 firms and a 20% reduction in pollution. To accomplish this, a "baseline" must be established at each facility that documents the current characteristics and flow of its hazardous waste streams. These data and information will be gathered by teams of appropriately trained personnel including those familiar with the processes being evaluated and P2 engineers, at a minimum. After gathering facility information, the P2 engineer will evaluate the data, establish the pollution baseline, and prepare an "alternatives evaluation." Following implementation of P2/CP alternatives, the updated potential risk would be compared to the baseline level.

Proposed Use of Models

A proposed method for establishing the baseline and measuring progress was conceptualized. The basic approach is to "measure" the level of potential risk for each chemical appearing in any of a facility's waste streams. Two models are proposed for utilization. The first model, the Risk Reduction Measurement Model (R2M2), would be used where the waste streams of the process contain IISE-targeted chemicals. All processes would be investigated using the R2M2 unless the waste streams in the process do not contain target chemicals or chemicals likely to be added to the list of targeted compounds. Targeted chemicals are currently those on the Philippines list of 28 chemicals (RP 28) from RA 6969 and the Priority Organic Pollutants (POPs) list. Additional chemicals may be added to the target list later as needed to expand the use of the risk reduction model.

The second model that is proposed is the Mass Tracking Model (MTM). This model would be used to measure reduction of chemicals contained in waste streams of a process that do not contain targeted chemicals. This model accounts for sheer reduction in mass flow rates of waste streams. The MTM would be used when the process does not contain targeted chemicals in any of the waste streams, or does not contain chemicals likely

to be added to the list of targeted chemicals in any of the waste streams.

Purpose of the Model

A model is proposed for quantification of pollution-related risk reduction as a function of environmental impact for the chemicals of concern. Use of an algorithm ensures consistent application of the parameters selected for measurement. Given the number of facilities and processes that are to be investigated, consistency in the assignment of relative risk is critical to successful measurement. The model proposed for the IISE P2/CP project is based on the WAR algorithm.

Description of the WAR Algorithm

EPA's WAR algorithm has been designed to evaluate the relationship of competing process alternatives. The WAR algorithm considers input and output streams of a process. Figure 1 illustrates typical streams to and from a generic process. For a given process, several input streams (which may be comprised of material in the solid, liquid, or gaseous phase) are used in an effort to generate a product. The process typically also will have several non-product streams (which may be comprised of material in the solid, liquid, or gaseous phase) that result from the process. The portion of the WAR algorithm discussed below deals with the product stream and non-product output streams.

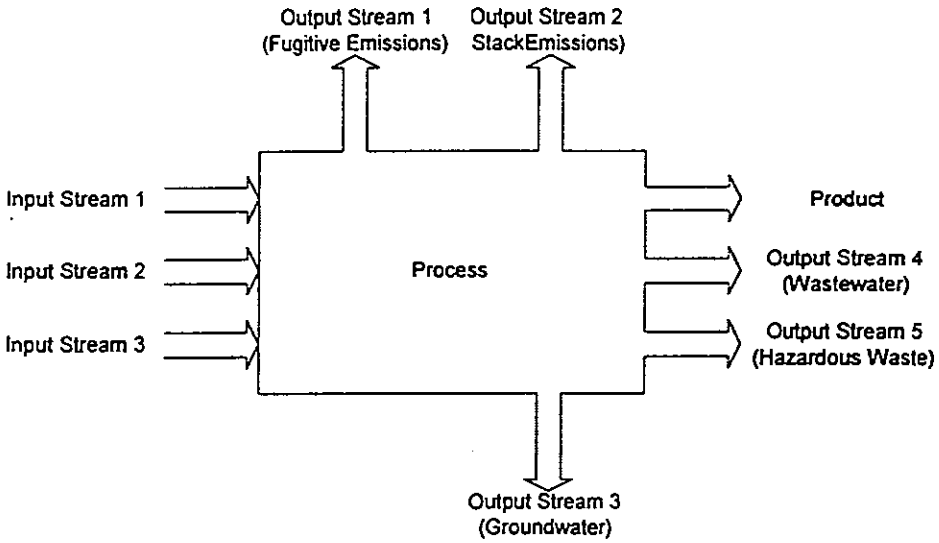
The WAR algorithm was developed primarily for comparison of process alternatives; however, one can apply the concepts of the WAR algorithm to establish an impact baseline and measure improvement over time. The algorithm assumes that each chemical stream entering and exiting a process possesses an inherent property, its potential environmental impact (PEI). The impact of chemicals found in industrial processes and in their associated waste streams is evaluated for several different impact categories. These include:

1. Global warming potential,
2. Acid rain potential,
3. Photochemical oxidation potential,
4. Ozone depletion potential,
5. Aquatic toxicity potential,
6. Terrestrial toxicity potential,
7. Human toxicity potential by ingestion, and
8. Human toxicity potential by inhalation or dermal exposure.

The first four categories represent atmospheric impact categories. The remaining four represent local toxicological impact categories.

The PEIs for input and output streams are evaluated separately. For example, the PEI associated with the output streams of a process is calculated by analyzing each of the waste streams generated from the process. Each of the specific chemicals for each waste stream are evaluated. Based upon the impact category values associated with each

Figure 1—Process Flow Diagram



chemical, the concentration of the chemical in the waste stream, and the mass flow rate of the waste stream, the PEI is determined for each chemical in each waste stream. The PEI of the process is the sum of the PEI for all the chemicals in all the waste streams of the process.

The PEI for each chemical is based upon a specific score for each of the eight impact categories. Table 1 provides the methodology for determining scores for each category. For example, the human toxicity potential by ingestion is based upon the lethal-dose that produced death in 50% of rats by oral ingestion (LD_{50}). The human toxicity potential by inhalation or dermal exposure is based on the time-weighted average of the threshold limit value. Scores for atmospheric categories are based upon the ratio of the chemical's adsorption/release/reaction rate compared to the reaction/release/adsorption rate of a chemical standard.

After the scores for each chemical are determined, they are normalized within each category. Normalization ensures that, on average, the impact potential for different categories will have equivalent values. The normalized values are represented by the parameter Ψ. Ψ is calculated by dividing each chemical score by the average of all the chemical scores within that category. (The database currently contains chemical scores for over 1600 chemicals.) Therefore, it is not the absolute Ψ value for each chemical that is important, but rather, the chemical's Ψ value relative to other chemicals' Ψ values. Without normalization, implicit weighting could be present in the chemical database causing unintentional bias in the calculation of the PEI indexes. Normalizing each category by the average value of entries in that category insures that the average value in that category will be unity. The units of Ψ are potential environmental impact (PEI) per kilogram (kg) of chemical.

The WAR algorithm also allows the user to weigh each of the eight impact categories above in order of importance. This weighting factor, represented by the parameter α, is a value between zero and ten. The parameter α is dimensionless. For purposes of the IISE, α is proposed to have a value of 1 for all categories.

The overall PEI per kg of chemical j, Ψ_j, is calculated using the following equation:

$$\Psi_j = \sum_k \alpha_k \Psi_{jk} \tag{1}$$

where the summation k is taken over all impact categories.

The overall PEI of the process, I_{out}, is given by the following equation:

$$I_{out} = \sum_i I_i^{(out)} = \sum_i \dot{M}_i^{(out)} \sum_j x_{ij} \Psi_j \tag{2}$$

where the summation i and j are taken over all waste streams and chemicals, respectively, $I_i^{(out)}$ is the PEI of waste stream i, $\dot{M}_i^{(out)}$ is the mass flow rate of the waste stream i in units of kg per time, and x_{ij} is the mass fraction of component j in waste stream i. The units of I_{out} are PEI/time.

Table 1—Description of Parameters Used to Develop Ψ Values

Category	Description
Global Warming Potential	Ratio of the extent to which a unit of mass of a chemical adsorbs infrared radiation to the extent that CO_2 adsorbs infrared over a base time frame of 100 years.
Acidification Potential	Ratio of the release of a hydrogen ion in the atmosphere as promoted by a chemical to the rate of release of a hydrogen ion as promoted by SO_2.
Photochemcial Oxidation Potential	Ratio of the rate at which a unit mass of chemical reacts with a hydroxyl radical to the rate at which a unit mass of ethylene reacts with a hydroxyl radical.
Ozone Depletion Potential	Ratio of the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen. The chemical must contain a chlorine or bromine atom.
Aquatic Toxicity Potential	The inverse of the lethal concentration that produced death in 50% of a representative species of fish.†
Terrestrial Toxicity Potential	The inverse of the lethal-dose that produced death in 50% of rats by oral ingestion.††
Human Toxicity Potential by Ingestion	The inverse of the lethal-dose that produced death in 50% of rats by oral ingestion.††
Human Toxicity Potential by Inhalation or Dermal Exposure	The inverse of the time-weighted average (TWA) of the threshold limit value (TLV).‡

TABLE 1

Notes:

† The source of the lethal concentration that produced death in 50% of a representative species of fish, fathead minnows, (LC_{50}) is AQUIRE, ECOSAR, Parger's *Environmental Contaminant Reference Handbook*, 1995, and *Handbook of Environmental Data on Organic Chemicals*, by Karel Verschueren.

†† The source of lethal-dose that produced death in 50% of rats by oral ingestion (LD_{50}) is *Sax's Dangerous Properties of Industrial Materials*, by Richard J. Lewis, 3rd Edition, the *Hazardous Substance Data Bank*, and the *Registry of Toxic Effects of Chemical Substances*, edited by Doris V. Sweet.

‡ The source of the time-weighted average (TWA) of the threshold limit value (TLV) is the Occupational Safety and Health Administration, the American Conference of Governmental Industrial Hygienists, and the National Institute for Occupational Safety and Health.

R2M2 Description

One of the limitations of the WAR algorithm is that the relative risk or probability of environmental impact is not addressed. For example, consideration is not given between the scenario where a waste stream enters the environment uncontrolled and another where proper waste management practices are in place. The former situation represents a higher risk than the latter. For the IISE project, risk reduction is a key objective for the P2/CP program; progress measurements, therefore, should be a function in terms of risk reduction.

The Risk Reduction Measurement Model is proposed as a useful variation of the WAR algorithm to accommodate the need to account for risk reduction. A modification to the WAR algorithm for this project incorporates a new parameter accounting for the probability of the waste stream being released to the environment in certain cases. The disposition of the waste stream is important because, for example, the environmental impact of the discharge of a liquid waste stream to the site soil and groundwater is much greater than the impact of the same liquid stream captured in drums and treated at an approved facility. Thus, the relative risk posed by PEI in a process can be reduced if a waste stream can be more effectively managed.

The introduction of a risk coefficient, β, is proposed to modify the WAR equation. Incorporation of β modifies the result of the WAR algorithm to yield a term PEI*, which can be called "risk-reduced potential environmental impact." The overall PEI* of a chemical is given by the equation:

$$\Psi_j^* = \sum_k \beta_k \alpha_k \Psi_{jk} \tag{3}$$

The PEI* of the process is calculated using Equation 2. An example of the usefulness of the risk coefficient is illustrated in the case of personnel protective equipment (PPE) that is implemented in a painting process. Appropriate PPE reduces the human toxicity potential by inhalation or dermal exposure; β can be used to distinguish the relative risk of a hazardous solvent and/or metallic pigment in the breathing zone of the worker versus the case where the worker wears PPE. Thus in this case, a β value less than 1 (assumed for PPE usage in that the risk of exposure to the user is reduced) would reduce the net PEI* level. A value of β can be assumed for each relevant environmental impact category.

In general, β would be assigned a value of 1 in the baseline scenario. If a process change (or housekeeping change) is made, the value of β would be adjusted to a value less than 1 as appropriate. The parameter is meant to be more of a "fine tune" adjustment to PEI*, and is not expected to have as much significance as, for example, those processes where highly toxic chemicals are replaced with those less toxic. Rather, it will serve as a tool to accommodate reduction in risk where changes in housekeeping or disposition of wastes may be the only possible alternatives available at a facility. Preliminary examples of β values are shown in Table 2.

The model logic is shown in Figure 2. This logic is a necessary preliminary design step prior to construction of the program that will be used to calculate the PEI* of the process. The logic of the model begins by identification of the process. Next, a waste

Table 2

Determining Beta

Input Questions

1. Does the potential (or implemented) P2 alternative result in an actual chemical waste reduction?

2. Does potential (or implemented) P2 alternatives result in lower probability of a chemical waste stream release to the environment?

3. For each of the four exposure categories, check the box which best describes the change to the chemical waste stream release following implementation of of the P2 alternative:

	Air	Water	Soils	Human
Confirmed Release Eliminated				
Confirmed Release Substantially Reduced				
Potential Release Eliminated				
Confirmed Release Partially Reduced				
Potential Release Unlikely				

Results

If Yes: Beta = 1.0 and Exit
If No: Continue

If Yes: Continue
If No: Beta = 1.0 and Exit

Assume the following Beta Values for the boxes checked by user. Note - only Psi values shown in ( ) will be modified.

Air (1,2,3,4)	Water (5)	Soils (6)	Human (7,8)
0.5	0.5	0.5	0.5
0.6	0.6	0.6	0.6
0.7	0.7	0.7	0.7
0.7	0.7	0.7	0.7
0.8	0.8	0.8	0.8

Potential Release Probability Significantly Reduced				
No Change				

0.9	0.9	0.9	0.9
1	1	1	1

Code to Psi Values Above:

1. Global warming potential
2. Acid rain potential
3. Photochemical oxidation potential
4. Ozone depletion potential
5. Aquatic toxicity potential
6. Terrestrial toxicity potential
7. Human toxicity potential by ingestion
8. Human toxicity potential by inhalation or dermal exposure

65

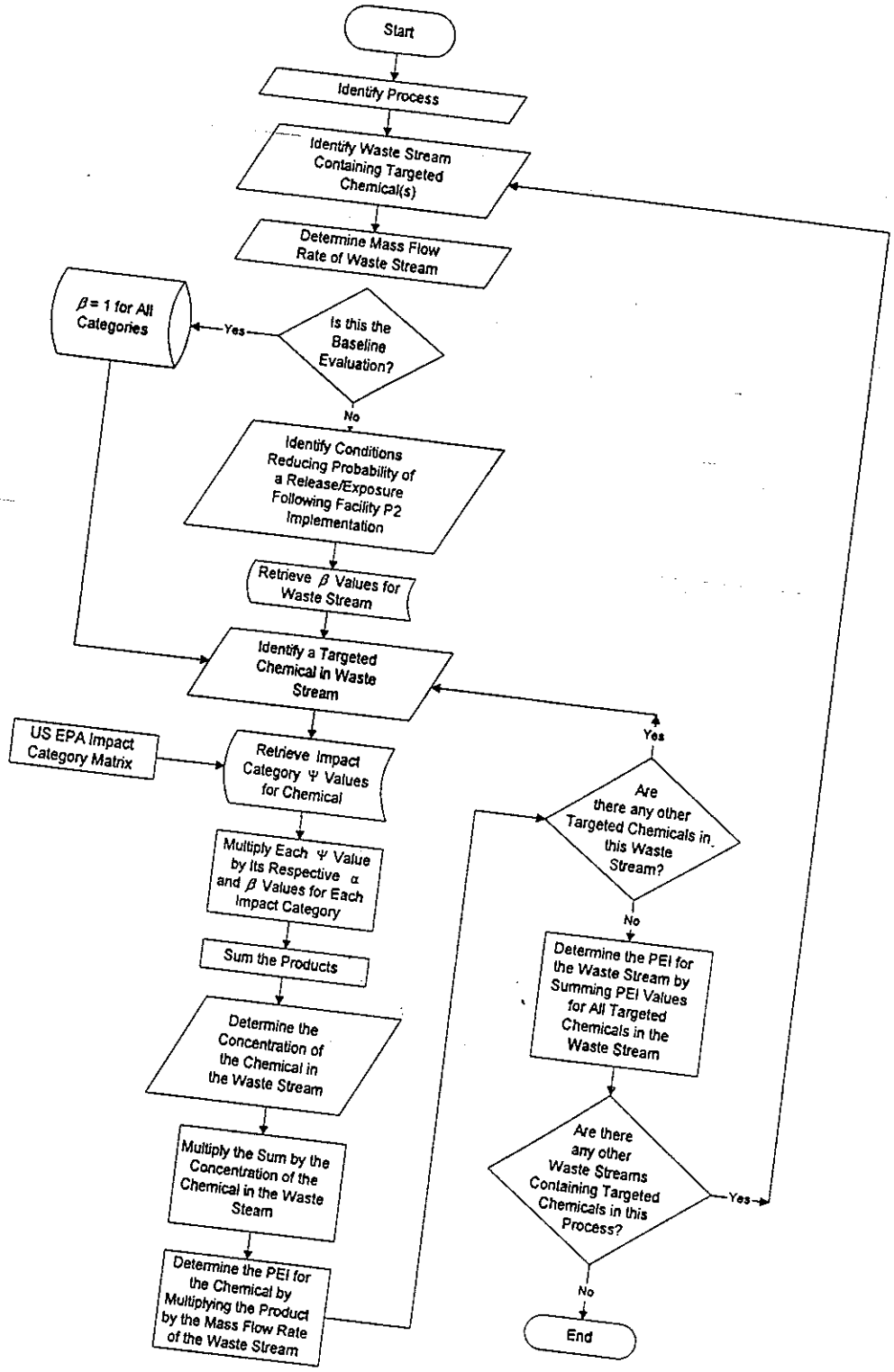
Example Template
IIER Philippines P2/CP

Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical)							Alpha Values (dimensionless)								Beta Values (dimensionless)								ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
		HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP					
BENZENE	y	0.118	0.092	0.090	0.118			0.388		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.8		0		0
CARBON TETRACHLORIDE	y	0.166	0.008	0.053	0.166	0.413	0.453	.		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.3		0		0
CHLOROFORM	y	0.430	0.001	0.017	0.430	0.008				1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.9		0		0
ETHYLENE OXIDE	y	5.427	0.328	0.026	5.427					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	11		0		0
HEXACHLOROBENZENE	y	0.039	11.812	0.100	0.039					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	12		0		0
HEXACHLOROETHANE	y	0.088	0.030	1.445	0.088					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.6		0		0
PHOSGENE	y	0.520	0.738	0.002	0.520					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.8		0		0
VINYL CHLORIDE	y	0.781	0.227	0.004	0.781					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.8		0		0
1,1,1-TRICHLOROETHANE	y	0.038	0.000	0.042	0.038	0.032	0.050	0.002		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.2		0		0
ARSENIC	y	0.512	59.061	0.223	0.512					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	60		0		0
POTASSIUM CYANIDE	y	78.147	0.024	8.501	78.147			1.219		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	163		0		0
ETHYLBENZENE	n	0.1116	0.0007	0.04869	0.112			0.253		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.5		0		0
METHANOL	n	0.0694	0.0011	7.5E-05	0.069			0.972		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.4		0		0
METHYL ETHYL KETONE	n	0.1428	0.0005	0.00069	0.143					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.3		0		0
METHYL ISOBUTYL KETONE	n	0.1879	0.0007	0.00421	0.188			0.021		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.4		0		0
DICHLOROMETHANE	n	0.2442	0.0067	0.00713	0.244	0.0046				1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.5		0		0
STYRENE	n	0.0781	0.0007	0.05498	0.078			1.167		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	0.2		0		0
TOLUENE	n	0.0781	0.0004	0.0645	0.078			2.466		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.4		0		0
1,2,4-TRIMETHYLBENZENE	n	0.0781	0.0024	0.28631	0.078			1.369		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2.9		0		0
o-XYLENE	n	0.1744	0.0007	0.13477	0.174			2.041		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.9		0		0
m-XYLENE	n	0.0781	0.0007	0.13814	0.078			1.825		1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2.3		0		0
p-XYLENE	n	0.0781	0.0007	0.07622	0.078					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	2.1		0		0
ZINC OXIDE	n	0.7632	0.0591	0.00098	0.763					1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1.6				

Notes:

HTPI = Human toxicity potential by injection
HTPE = Human toxicity potential by inhalation or demeral exposure
ATP = Aquatic toxicity potential
TTP = Terrestrial toxicity potential (same method as HTPI)
GWP = Global warming potential
ODP = Ozone depletion potential
PCO = Photochemical oxidation potential
AP = Acid rain potential

Figure 2—R2M2 Logic Diagram



stream and its characteristics, such as mass flow rate and management/disposition of the waste, are identified. The appropriate β value for the disposition/exposure is retrieved. Then, each chemical is identified, and its Ψ values are retrieved. The concentration of the chemical in the waste stream is input, and the PEI* of the chemical is calculated. This is repeated for any additional chemicals. The PEI* value of all chemicals is summed to determine the waste stream PEI*. This procedure is repeated for each waste stream from the process. The PEI* of the waste streams is summed to determine the overall PEI* of the process.

R2M2 Inputs

PEI* must be calculated for each process in which R2M2 is employed. Each process may be comprised of several waste streams, and several chemicals may be found in each waste stream. Figure 3 illustrates the flow logic of identifying all the information inputs required for the algorithm.

After the processes at the facility have been identified and chosen for evaluation in the R2M2, the process must be looked at in detail in an effort to identify all the waste streams in the process and the waste stream flow rates. Each waste stream is then investigated to determine the chemicals in the waste stream and their concentrations. Only chemicals on the target list (or those that are likely to be added to the target list) will be investigated.

Examples of Use of R2M2

Painting Process

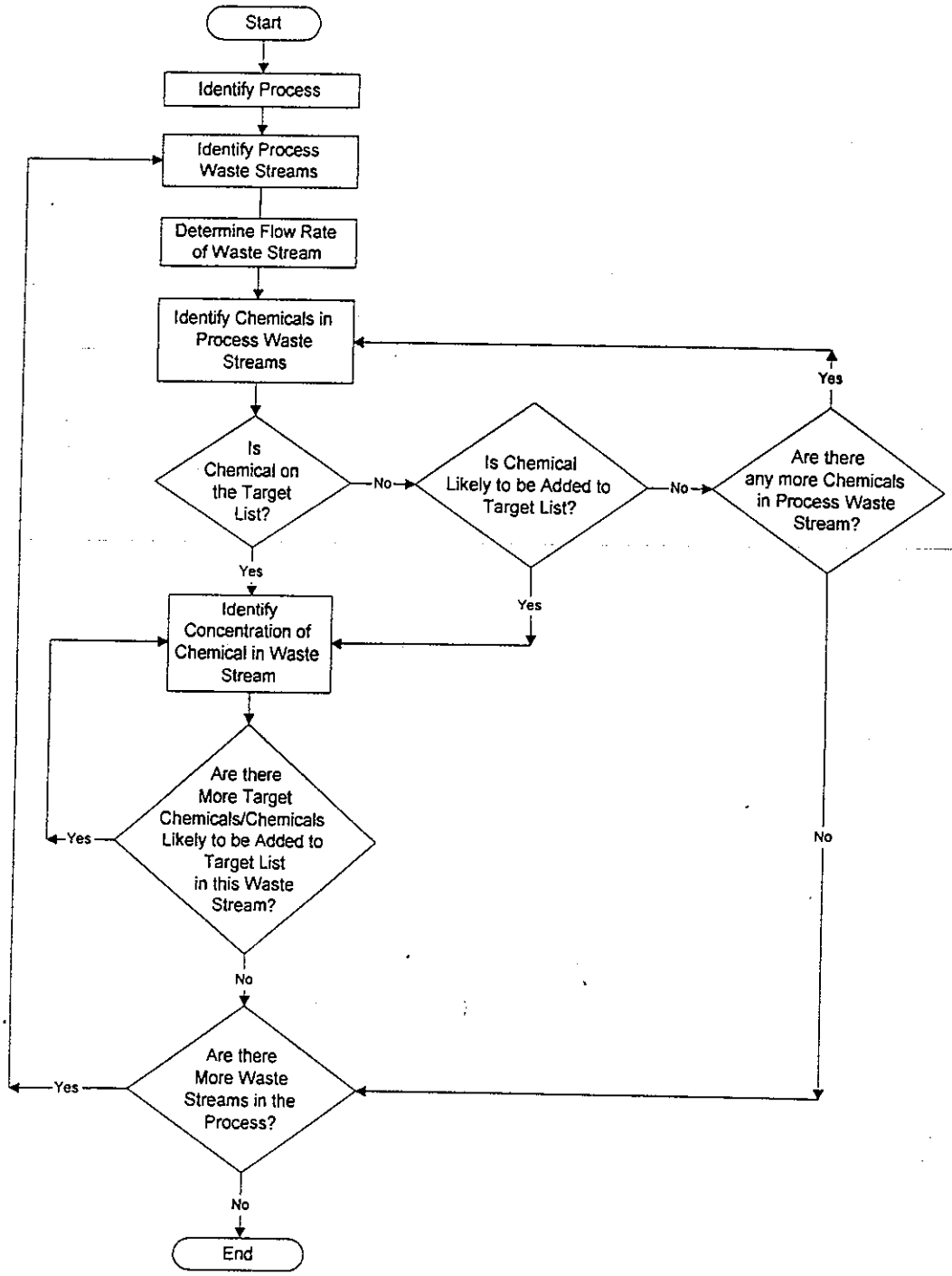
In this first example, a painting process uses a paint containing toluene, 1,2,4-trimethylbenzene, and zinc oxide. All the VOCs in the paint are assumed to act as carriers and volatize to the atmosphere. Output streams for this process are the VOC stream (to the atmosphere) and paint overspray. The amount of paint overspray depends on the efficiency of the paint gun and the experience of the painter. The overspray contains the pigment in the paint.

Table 3 shows a summary table of the calculations used in determining the process PEI*. While the concentration of toluene and 1,2,4-trimethylbenzene in the paint is 9 percent and 1 percent, respectfully, the concentrations increase to 19.6 percent and 2.2 percent in the VOC stream. The concentration of zinc oxide increases from 3 percent in the paint to 5.3 percent in the pigment waste stream.

Similarly, the mass of paint used by the process in a year is 235.8 kg. The mass of the VOC waste stream is 101.4 kg per year, and the mass of the pigment waste stream is 67.2 kg per year. The material applied to the product accounts for the balance of the pigment.

In the baseline case, the values of beta are set to a value of 1. The PEI* of each chemical is calculated, and then the PEI* of all the chemicals in all the waste streams is

Figure 3— R2M2 Baseline Data Collection Flow Sheet



Process: Painting Process at Facility ABC
IIER Philippines P2/CP

Baseline

Waste Stream	Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical) HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	Beta Values (dimensionless) HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
VOC	TOLUENE	n	0.0781	0.0004	0.0645	0.078			1.157		1	1	1	1	1	1	1	1	1.4	19.6%	0.270	101.4	27
VOC	1,2,4-TRIMETHYLBENZENE	n	0.0781	0.0024	0.28631	0.078			2.466		1	1	1	1	1	1	1	1	2.9	2.2%	0.064	101.4	6.5
Pigment	ZINC OXIDE	n	0.7632	0.0591	0.00098	0.763					1	1	1	1	1	1	1	1	1.6	5.3%	0.084	67.2	5.6
																							40

Risk Reduction alernatives implemented: Use of a High Acrylic Coating that does not contain targeted compounds

Alternative

Waste Stream	Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical) HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	Beta Values (dimensionless) HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
	None																						0
																							0

PEI Reduction = 100.0%

Notes:

HTPI = Human toxicity potential by ingestion
HTPE = Human toxicity potential by inhalation or demeral exposure
ATP = Aquatic toxicity potential
TTP = Terrestrial toxicity potential (same method as HTPI)
GWP = Global warming potential
ODP = Ozone depletion potential
PCO = Photochemcial oxidation potential
AP = Acid rain potential

TABLE 3

summed to give the process PEI*. The annual process PEI* for this process is calculated to be 40.

The alternative case utilizes a paint that does not contain any targeted chemicals. Therefore, the PEI* of the alternative is 0, and the PEI* reduction is 100 percent.

Kerosene Bath

Kerosene is often used to keep away insects in furniture manufacturing in the Philippines. Bamboo stock may be submersed in a kerosene bath for preservation. In this example, a 450 gallon bath is used to submerse the bamboo until needed in the process. Currently, the bath is emptied and refilled with kerosene every thirty days. The recommendations to reduce pollution are to cover the bath and ensure it is located out of direct sunlight in effort to reduce evaporative losses. These methods are expected to allow the bath to be emptied and refilled every 40 days. The calculated annual PEI*s of 4,500 and 3,400 for the Baseline and P2 Alternative 1, respectively, are shown in Table 4.

The second P2 alternative for this process is for the workers to wear PPE. Wearing of gloves when handling the bath and treated bamboo would reduce the value of β to 0.5. The annual PEI for Alternative 2 is 3,800.

The third alternative is to combine Alternatives 1 and 2. The annual PEI* for Alternative 3 is 2,900. This represents a 36 percent reduction in annual PEI from the baseline case.

Process: Kerosene Bath for Bamboo for pesticide purposes (bath is current;y changed every 30 days).
IIER Philippines P2/CP

Baseline

Waste Stream	Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical)								Beta Values (dimensionless)								ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
			HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP					
	Kerosene	n									1	1	1	1	1	1	1	1	0.0	99.0%	0.000	16,158	0
																							0

Alternative 1: Covering Bath, Moving out of direct Sunlight, extends life of Kerosene and maintins volume such that bath is replaced every 40 days instead of 30 days.

Waste Stream	Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical)								Beta Values (dimensionless)								ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
			HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP					
	Kerosene	n	0	0	0	0	0	0	0	0	1	1	1	1	1	1	1	1	0.0	99.0%	0.000	12,119	0
																							0

Alternative 2: Workers begin wearing PPE (gloves and respirators) when handling material in bath and treated Bamboo.

Waste Stream	Chemical Name	RP28/ POPs	Psi Values (impact/kg chemical)								Beta Values (dimensionless)								ΣβαΨ (impact/kg chemical)	χ (%)	χ ΣβαΨ (impact/kg)	M (kg/year)	PEI (impact/year)
			HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP	HTPI	HTPE	ATP	TTP	GWP	ODP	PCO	AP					
	Kerosene	n	0	0	0	0	0	0	0	0	0.5	0.5	1	1	1	1	1	1	0.0	99.0%	0.000	12,119	0
																							0

PEI Reduction = #DIV/0!

TABLE 7

Notes:
HTPI = Human toxicity potential by ingestion
HTPE = Human toxicity potential by inhalation or demeral exposure
ATP = Aquatic toxicity potential
TTP = Terrestrial toxicity potential (same method as HTPI)
GWP = Global warming potential
ODP = Ozone depletion potential
PCO = Photochemcial oxidation potential
AP = Acid rain potential

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The following conclusions are presented with respect to P2/CP measurement model development:

1. The IISE Project assumes that environmental risk is an appropriate parameter for measuring P2/CP progress.
2. Reduction of environmental risk can be quantified in a relative sense by comparing baseline risk to the risk determined following implementation of P2 alternatives. The proposed methodology for measurement is based on research conducted by the US EPA.
3. US EPA's "WAR" algorithm is suitable for use in the IISE project and can be enhanced by incorporating a probability factor. The proposed R2M2 algorithm allows the user to insert a coefficient that reduces the calculated potential environmental impact for cases in which probability of environmental impact is reduced.
4. Not all of P2/CP assessments will use the R2M2. Where IISE-targeted chemicals are not present, a waste loading model, MTM, will be used.
5. The R2M2 conceptual model will be fully developed into a user-friendly tool that can be used by the P2/CP personnel of the IISE team. Specifically, Visual Basic or other commonly available software can be used to write the R2M2 program that walks the user through the P2/CP evaluation process. This task should be authorized by Chemonics International prior to the conduct of further P2/CP training. MSE is prepared to lead the model preparation.
6. Further expansion of the beta table, consulting with the IISE team in Cebu will be conducted.

Designing Sustainable Processes with Simulation: The Waste Reduction (WAR) Algorithm

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1. INTRODUCTION

The concept of implementing pollution prevention techniques into process design is not new; although, it has received more attention in recent years. The premise of which is to attack the environmental concerns of a process in the design stage instead of relying on end-of-pipe treatment or remediation. This concept was first introduced in the 1970s by way of heat exchange networks (HENs). They were employed to minimize energy consumption of manufacturing processes. A great deal of research has been spawned from this innovation as discussed by Shenoy (1995) and Gundersen (1988) in their reviews of the subject matter.

Heat exchange networks led to the creation of mass exchange networks (MENs) which were introduced by El-Halwagi and Manousiouthakis (1989). The idea behind MENs is to concentrate pollutants in desired waste streams while removing them from other streams. This technique minimizes the volume of waste generated within a manufacturing process. Within both HENs and MENs, a number of optimization routines

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have been employed to maximize the efficiency of these pollution prevention techniques (El-Halwagi, 1997).

Both of these techniques help reduce the quantity of pollution or waste generated during the operation of a manufacturing process. However, neither technique addresses the impact of the pollution generated within a process. For example, process design option A may produce 100 kg/hr of pollutants while process design option B may produce 200 kg/hr. However, the pollutants generated during option A may be much more environmentally unfriendly than those generated during option B. This difference in impact may be such that it may be more desirable to produce 200 kg/hr of pollutants in option B than producing 100 kg/hr of pollutants in option A.

To address this idea of including environmental impact considerations into process design, Cabezas et al. (1997) introduced a potential environmental impact (PEI) balance as an amendment of the Waste Reduction (WAR) algorithm. The WAR algorithm was first introduced by Hilaly and Sikdar (1994). They introduced the concept of a pollution balance which was the precursor to the PEI balance. The pollution balance, basically, was a methodology that allowed the user to track the pollutants throughout a process. The PEI balance quantifies the impact of those pollutants in a process. Ultimately, the PEI balance is a quantitative indicator of the environmental friendliness or unfriendliness of a manufacturing process.

Cano-Ruiz and McRae (1998) provide a comprehensive review of the different techniques used to incorporate environmental considerations into process design. Most commonly, environmental concerns are treated as constraints in an economic optimization problem where the constraints are designated by regulations. Minimizing the amount of waste or pollutants generated within a process is another common method to incorporate environmental considerations into process design (Cano-Ruiz and McRae, 1998). A number of index type methods have been implemented to evaluate the environmental impact of the emissions of chemical processes: Houghton et al. (1996) proposed an index for global warming defined as the emissions rate multiplied by the global warming potential of that chemical relative to CO_2, Grossman et al. (1982) proposed a toxicity index by multiplying the effluent flow rate of a chemical by the inverse of its LD_{50} value, Fathi-Afshar and Yang (1985) proposed an index for gaseous emissions by dividing the effluent flow rates of the chemicals by their threshold limit values as defined by the ACGIH and then multiplied by their specific vapor pressures, and Heinzle et al. (1998) and Koller et al. (1998) proposed ecological indices based on a classification approach to assess the environmental impact of a process. Pistikopoulos et al. (1994) proposed relative environmental impact indices for multiple categories, i.e. air pollution, water pollution, global warming, ozone depletion, photochemical oxidation, and solid wastes, and optimized the process for each impact category. The PEC/PNEC (predicted environmental concentation/predicted no effect concentration) ratio has also been used to evaluate the environmental impact of a process design (Cano-Ruiz and McRae, 1998). King et al.(1999) used case base reasoning to evaluate the environmental impact of a process design which relies on past experience.

This paper presents an illustrative case study that exemplifies the intended use of the WAR algorithm, which is to aid in the environmental evaluation of a process design. It also presents modifications to the WAR algorithm and the PEI balance, such as the inclusion of energy into the balance, from their previous descriptions (Cabezas, et al., 1997). Also, the database containing the potential environmental impacts of the chemicals is detailed. ChemCad 4.0 ((Chemstations, 1997)) was used as the chemical process simulator in this case study. (Use of ChemCad 4.0 as the chemical process simulator does not imply United States Environmental Protection Agency, USEPA,endorsement of that product.)

The function of the WAR algorithm is best depicted in Figure 1. This figure displays a schematic of the steps of a product's life. These steps include the acquisition of the raw materials, the manufacturing of these raw materials into desirable products, the distribution and use of these products, and the product disposal or recycle. The WAR algorithm is designed to evaluate the environmental friendliness of only the manufacturing step within this overall framework. The WAR algorithm does not represent a complete life cycle analysis (LCA). The WAR algorithm is simply a tool to be used by design engineers to aid in evaluating the environmental friendliness of a process. This methodology can be used in either the design stage of a future process or in the retrofitting of a current process.

[insert Figure 1 here]

For this purpose, the WAR algorithm is to be used in conjunction with chemical process simulators. There are on-going efforts at the National Risk Management Research Laboratory to incorporate the WAR algorithm into a number of chemical process simulators under Cooperative Research and Development Agreements authorized under the Federal Technology Transfer Act of 1986. A version of ChemCad is scheduled for release in 1999 that will have the WAR algorithm incorporated into it.

2. POTENTIAL ENVIRONMENTAL IMPACT THEORY

The potential environmental impact of a given quantity of material and energy can be generally defined as the effect that this material and energy would have on the environment if they were to be emitted into the environment. Since the definition implies that the impact is an unrealized quantity, i.e., something that has yet to happen, potential environmental impact is, therefore, probabilistic in nature. That is, that the potential environmental impact of a particular emission of material and energy into the environment is an estimate of the effect that this emission is likely to have on average. Consequently, one should realize and expect that deviations from this average expected impact would manifest themselves for particular situations. Further, potential environmental impact is a conceptual quantity that can not be directly measured. One can, however, construct a theory to relate potential environmental impact to measurable quantities as will be discussed below.

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2.1 Impact Balance: Products, Non-Products, and Energy

As has already been discussed in a previous publication (Mallick, *et al.*, 1996), traditional chemical process design relies on the application of mass and energy balances along with thermodynamics, chemical reaction engineering, and engineering economics. Cabezas et al. (1997) and Cabezas et al. (1999) have previously proposed that to properly incorporate environmental effects into process design, a balance equation describing the potential environmental impact of the process must be considered. Since one of the purposes of this paper is to extend this analysis to include the environmental consequences of the energy consumed by chemical processes, the PEI balance equation is extended to include the energy generation process. The energy generation process can be considered to be simply an electric power generation facility. This is shown schematically in Figure 2. The PEI balance is derived by drawing a boundary around the chemical process (denoted by superscript *cp*) and the energy generation process (denoted by superscript *ep*) and then writing a general balance expression. The PEI balance simply states that potential environmental impact can enter the system, exit the system, be generated within the system, and accumulate within the system. The actual expression is:

$$\frac{\partial I_{syst}}{\partial t} = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(syst)} \qquad (1)$$

where I_{syst} is the amount of potential environmental impact inside the system (chemical process plus energy generation process), $\dot{I}_{in}^{(cp)}$ and $\dot{I}_{out}^{(cp)}$ are the input and output rates of potential environmental impact to the chemical process, $\dot{I}_{in}^{(ep)}$ and $\dot{I}_{out}^{(ep)}$ are the input and output rates of potential environmental impact to the energy generation process, $\dot{I}_{we}^{(cp)}$ and

$\dot{I}_{we}^{(ep)}$ are the outputs of potential environmental impact associated with waste energy (denoted by the subscript *we*) lost from the chemical process and the energy generation process, and where $\dot{I}_{gen}^{(syst)}$ is the rate of generation of potential environmental impact inside the system. For chemical processes, $\dot{I}_{gen}$ represents the creation and consumption of potential environmental impact by chemical reactions inside the process. For steady state processes, the balance expression reduces to:

$$0 = \dot{I}_{in}^{(cp)} + \dot{I}_{in}^{(ep)} - \dot{I}_{out}^{(cp)} - \dot{I}_{out}^{(ep)} - \dot{I}_{we}^{(cp)} - \dot{I}_{we}^{(ep)} + \dot{I}_{gen}^{(syst)} \qquad (2)$$

which simply states that at steady state the amount of potential environmental impact inside the system does not change with time. This expression can be used to generate a series of indexes characterizing the internal and external environmental efficiency of the system as will be further discussed later. Equation (2) represents a more accurate depiction of the potential environmental impact of a chemical process than previous versions of the WAR algorithm (Cabezas, et al., 1997; Cabezas, et al., 1999) that neglected the consumption of energy by the process. The case study discussed in this paper will be assumed to be processes operating at steady state, and, therefore, all further analysis will be based on Equation (2) above. The very interesting case of non-steady state processes will be the subject of a future paper.

[insert Figure 2 here]

2.2 Chemical Processes: Products, Non-Products, and Energy

In order to make use of Equation (2) in chemical process design, it is necessary to relate the conceptual potential environmental impact to measurable quantities. A generalized

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linear theory has been constructed (Cabezas, et al., 1997; Cabezas, et al., 1999; Mallick, et al., 1996) which relates potential environmental impact to measurable quantities such as stream flow rates and compositions and chemical specific overall environmental impacts (ψ_k). This theory is extended here to include the energy generation process. The expressions for the chemical process are:

$$\dot{I}_{in}^{(cp)} = \sum_{j}^{cp} \dot{I}_j^{(in)} = \sum_{j}^{cp} \dot{M}_j^{(in)} \sum_k x_{kj} \psi_k + \ldots \tag{3}$$

$$\dot{I}_{out}^{(cp)} = \sum_{j}^{cp} \dot{I}_j^{(out)} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj} \psi_k + \ldots \tag{4}$$

$$\dot{I}_{we}^{(cp)} = \sum_{j}^{cp} \dot{E}_j^{(cp)} \psi_{we} \approx 0 \tag{5}$$

where $\dot{I}_i^{(cp)}$ is the rate of potential environmental impact *in* (*i=in*) or *out* (*i=out*) of the chemical process, $\dot{I}_j^{(i)}$ is the potential environmental impact flow rate with stream *j* which may be an input or an output stream, $\dot{M}_j^{(i)}$ is the mass flow rate of stream *j* which again may be an input or an output stream, x_{kj} is the mass fraction of component *k* is stream *j*, ψ_k is the potential environmental impact for chemical *k*, $\dot{I}_{we}^{(cp)}$ is the rate of potential environmental impact output due to the emission of waste energy from the chemical process, $\dot{E}_j^{(cp)}$ is the rate of waste energy emission from the chemical process, and ψ_{we} is the potential environmental impact for energy emission. Equations (3) and (4) contain only the potential environmental impacts associated with the pure chemicals. For now, they ignore the combinatorial impacts that could be associated with mixtures of chemicals which accounts for the additional terms not included into those equations. Although the emission of energy directly into the environment is likely to have some

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impact, for purposes of this article, the impacts due to the emission of waste energy directly into the environment will be neglected, and, therefore, ψ_{we} is assumed to be zero. This is consistent with the fact that: (i) chemical process plants do not generally emit large amounts of waste energy into the environment, and that (ii), at least for chemical process plants, the potential environmental impact associated with the emission of mass is usually much greater than that associated with the emission of energy. The sums for subscripts j and k are, respectively, taken over all input or all output streams and all components k including all products and non-products associated with the chemical process. The expressions for the energy generation process are:

$$\dot{I}_{in}^{(ep)} = \sum_{j}^{ep} \dot{I}_{j}^{(in)} = \sum_{j}^{ep} \dot{M}_{j}^{(in)} \sum_{k} x_{kj} \psi_{k} + \ldots \approx 0 \tag{6}$$

$$\dot{I}_{out}^{(ep)} = \sum_{j}^{ep} \dot{I}_{j}^{(out)} = \sum_{j}^{ep-g} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} + \sum_{j}^{ep-s} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} + \ldots \approx \sum_{j}^{ep-g} \dot{M}_{j}^{(out)} \sum_{k} x_{kj} \psi_{k} + \ldots \tag{7}$$

$$\dot{I}_{we}^{(ep)} = \sum_{j}^{ep} \dot{E}_{j}^{(ep)} \psi_{we} \approx 0 \tag{8}$$

where $\dot{I}_{i}^{(ep)}$ is the rate of potential environmental impact *in* (i=*in*) or *out* (i=*out*) of the energy generation process, $\dot{I}_{we}^{(ep)}$ is the rate of potential environmental impact output due to the emission of waste energy from the energy generation process, $\dot{E}_{j}^{(ep)}$ is the rate of waste energy emission from the energy generation process, and ψ_{we} is the potential environmental impact for the waste energy emission. For the input, $\dot{I}_{in}^{(ep)}$, and the waste energy, $\dot{I}_{we}^{(ep)}$, the sums over j and k are respectively taken over all input or all output streams and all components k associated with the energy generation process. For the output, $\dot{I}_{out}^{(ep)}$, the sum over streams j is broken into a sum over gaseous output streams,

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ep-g, and another sum over solid output streams, *ep-s*. The potential environmental impact of the solid output streams can be assumed to be negligible compared to that of the gaseous output streams. Again, the extra terms in Equations (6) and (7) which represent the potential environmental impacts associated with mixtures of chemicals have been omitted. This will be discussed in detail below. Also, the potential environmental impact associated with the emission of mass is usually much greater than that associated with the emission of waste energy, and, therefore, it is assumed that ψ_{we} is approximately zero similar to the chemical process analysis.

The potential environmental impact of the mass inputs, $\dot{I}_{in}^{(ep)}$, to the energy generation process is also assumed to be approximately zero for reasons that will now be discussed. The energy generation process is assumed to be a coal-fired electrical power plant, and the mass inputs to this process consist mainly of coal and air along with water. Of these input streams, the only one that has a significant potential environmental impact is the coal feed stream. Coal ought to have a significant potential environmental impact because it consists of a very complex solid mixture that includes metals, sulfur, and a wide range of organic compounds. Many of these metals and compounds are known to be hazards to human health and the environment. Fortunately, all of these otherwise hazardous components are locked in a solid matrix which makes them unavailable to cause environmental impacts in the way that liquids and gases could, and, thus, the ψ_k for the components in coal is approximately set to zero. The air and the water have no potential environmental impact so ψ_{air} and ψ_{water} are set to zero and $\dot{I}_{air}^{(in)}$ and $\dot{I}_{water}^{(in)}$ are, consequently, zero. In summary, all of the terms under the summation in Equation (6) can

be approximately set to zero so that the entire term $\dot{I}_{in}^{(ep)}$ is zero or at least very small compared to the output term, $\dot{I}_{out}^{(ep)}$.

The potential environmental impact of the mass outputs, $\dot{I}_{out}^{(ep)}$, from the energy generation process are divided into gaseous and solid streams as already mentioned. The gaseous streams mainly consist of air pollutants, e.g., NO_x, CO_2, SO_2, etc., which are known to have impacts on human health and the environment, and these are included in the analysis. The solid streams consist of coal slag, i.e., non-combustible ashes and residue, and coal impurities such as metals removed in coal pre-treatment. All of these are in solid form which makes them relatively unavailable for causing environmental impacts as compared to gases. In addition, present practice dictates that these residues be carefully sequestered and rendered environmentally harmless. One additional complication is that data for estimating these environmental impacts is highly uncertain, and these would render any analysis fraught with difficulty. For these reasons, it is assumed here that the potential environmental impact of the components in the solid output streams is negligibly small, i.e., $\psi_k \approx 0$, it is further assumed that the potential environmental impact of the mass outputs, $\dot{I}_{out}^{(ep)}$, can be approximated by that of the gaseous component as shown in Equation (7).

Equations (3) to (8) include all products and non-products because they all have potential environmental impacts, and there is in general no reason for presuming that one class of components, say products, should be excluded from the analysis except as previously discussed. In addition, there is significant benefit to conducting a more complete analysis

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that includes all potential environmental impacts associated with a process. For example, if one is interested in comparing two alternative products, e.g., two detergents, and their associated manufacturing processes, then it becomes quite important to include both products and non-products in the analysis. This is particularly important when the products of a process are likely to eventually be emitted into the environment, e.g., consumer products. The objective here is to have processes that emit and generate as little potential environmental impact as possible consistent with the need to have processes that manufacture products that fulfill human needs. It is important to keep in mind is that once new potential environmental impact is generated and embodied in a product or a non-product, it will very likely require money and other resources to keep the potential environmental impact from being realized. It is, thus, prudent to have processes and products that emit, generate, and embody as little potential environmental impact as possible consistent with societal needs.

2.3 Environmental Impact Indexes: Products, Non-Products and Energy

Equations (2) to (8) can be used to generate indexes that characterize the relative environmental efficiency of a process. There are two different classes of indexes: those associated with potential environmental impact output and those associated with potential environmental impact generation. Of the output indexes, the two most important ones are the total rate of impact output, $\dot{I}_{out}^{(t)}$, and the total impact output per mass of products, $\hat{I}_{out}$:

$$\dot{I}_{out}^{(t)} = \dot{I}_{out}^{(cp)} + \dot{I}_{out}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)} = \sum_{j}^{cp} \dot{M}_j^{(out)} \sum_k x_{kj} \psi_k + \sum_{j}^{ep-g} \dot{M}_j^{(out)} \sum_j x_{kj} \psi_k \qquad (9)$$

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$$\hat{I}_{out}^{(t)} = \frac{\dot{I}_{out}^{(cp)} + \dot{I}_{out}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)}}{\sum_p \dot{P}_p} = \frac{\sum_j^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k + \sum_j^{ep-g} \dot{M}_j^{(out)} \sum_j x_{kj}\psi_k}{\sum_p \dot{P}_p} \tag{10}$$

where $\dot{P}_p$ is the mass flow rate of product p and the sum is taken over all product streams p. Of the generation indexes, the two most important ones indexes are, similarly, the total rate of impact generation, $\dot{I}_{gen}^{(t)}$, and the total impact generated per mass of product, $\hat{I}_{gen}^{(t)}$, defined by,

$$\begin{aligned} \dot{I}_{gen}^{(t)} &= \dot{I}_{out}^{(cp)} - \dot{I}_{in}^{(cp)} + \dot{I}_{out}^{(ep)} - \dot{I}_{in}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)} \\ &= \sum_j^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k - \sum_j^{cp} \dot{M}_j^{(in)} \sum_k x_{kj}\psi_k + \sum_j^{ep-g} \dot{M}_j^{(out)} \sum_j x_{kj}\psi_k \end{aligned} \tag{11}$$

$$\begin{aligned} \hat{I}_{gen}^{(t)} &= \frac{\dot{I}_{out}^{(cp)} - \dot{I}_{in}^{(cp)} + \dot{I}_{out}^{(ep)} - \dot{I}_{in}^{(ep)} + \dot{I}_{we}^{(cp)} + \dot{I}_{we}^{(ep)}}{\sum_p \dot{P}_p} \\ &= \frac{\sum_j^{cp} \dot{M}_j^{(out)} \sum_k x_{kj}\psi_k - \sum_j^{cp} \dot{M}_j^{(in)} \sum_k x_{kj}\psi_k + \sum_j^{ep-g} \dot{M}_j^{(out)} \sum_j x_{kj}\psi_k}{\sum_p \dot{P}_p} \end{aligned} \tag{12}$$

In general, the lower the value of these indexes the higher the environmental efficiency of a process, i.e., the less potential impact the process is likely to have on the environment. However, it should be noted that the effort to design processes with lower environmental indexes needs to be constrained by considerations of engineering economics and societal needs. After all, one could conceivably simply shut down the process which would bring all the mass flow rates to zero and all the indexes to zero. This is not the objective here because it ignores the fact that there may be a human need for the products that the process manufactures.

The total rate of potential environmental impact output, $\dot{I}_{out}^{(t)}$, and the potential environmental impact output per mass of product, $\hat{I}_{out}^{(t)}$, define the external environmental efficiency of the process. They allow us to compare alternative processes in terms of their potential effect on the environment external to the process. $\dot{I}_{out}^{(t)}$ is most useful in assessing whether a particular site is or is not able to accommodate a given process plant. For example, if a process has a low rate of impact output, $\dot{I}_{out}^{(t)}$, then the surrounding environment is more likely to be able to dissipate the impact being emitted than would be the case for a process with a high impact output rate. Consequently, a process with a low rate of impact output could be located in a more ecologically sensitive area than would be the case for process with a high rate of impact output. The total potential environmental impact output per mass of products, $\hat{I}_{out}^{(t)}$, can decrease either because the rate of potential environmental impact emitted has decreased or because the mass flow rates of products have increased or both. This means that any measures that improve the material utilization efficiency of the process will also tend to lower the potential environmental impact output per mass of products. $\hat{I}_{out}^{(t)}$ allows us to compare different process alternatives on the basis of the potential environmental impact emitted by the process per unit mass of products. This means that comparisons can be made regardless of manufacturing plant size. For example, one can compare the environmental consequences of having one large plant versus several small ones.

The rate of potential environmental impact generation, $\dot{I}_{gen}^{(t)}$, and the potential environmental impact generated per mass of products, $\hat{I}_{gen}^{(t)}$, define the internal

environmental efficiency of the process. They allow us to compare different process in terms of their generation of new potential environmental impact within the process. As has already been discussed, the generation of potential environmental impact is quite important because once it is created, it will likely take resources to keep the potential environmental impact from becoming actual impacts on the environment. Therefore, the prudent course of action is to generate as little potential environmental impact as possible consistent with engineering economic constraints and societal needs. Because at least some of the potential environmental impact in the output from a process is likely to have come into the process with the input, the generation of new potential environmental impact within a process is the one item that the process designer can most directly control, i.e., one can manipulate the operating conditions to increase or decrease $\dot{I}^{(t)}_{gen}$ and $\hat{I}^{(t)}_{gen}$. The quantity $\dot{I}^{(t)}_{gen}$ is useful in comparing processes based on how fast they generate impact, and $\hat{I}^{(t)}_{gen}$ is useful in comparing processes and products based on the amount of new potential environmental impact generated in producing products. Obviously, the lower the rate of potential environmental impact generated, the better the process will be assuming all other factors are equal.

2.4 Impact Balance and Indexes: Non-Products and Energy

There are cases where inclusion of the products in the potential environmental impact balance and indexes of Equations (3) to (12) may be deemed inappropriate. Three illustrative examples where it could be decided that products would not be included in the analysis are: (i) where the product is an intermediate which is directly fed into another

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3.1 Chemical Impact Expression

The overall potential environmental impact of chemical k, ψ_k, can be determined by summing the specific potential environmental impact of chemical k, ψ^s_{kl}, over all of the possible impact categories (Mallick, et al., 1996):

$$\psi_k = \sum_l \alpha_l \psi^s_{kl} \tag{13}$$

where α_l represents the relative weighting factor of impact category l. The units for equation (1) have been corrected from previous versions of the WAR algorithm (Cabezas, et al., 1997; Cabezas, et al., 1999). The units for both the overall and specific environmental impacts of the individual compounds should be potential environmental impact of chemical k/mass of chemical k. The weighting factor should be, of course, dimensionless.

The relative weighting factors, α_l, are used to express the relative importance of the impact categories. Typically, the weighting factors should range between 0 and 10; however, this is not a steadfast rule. The user should assign the weighting factors according to their specific process conditions. The weighting factors should emphasize or de-emphasize specific concerns that are relevant or irrelevant to their process conditions and locality. Since the primary objective of this algorithm is to determine the relative environmental impact indexes of a process design which ultimately will be compared to alternative designs, the actual values of the weighting factors are not as

important as their relative values. The weighting factors are essential to this methodology in that they permit the combining of the impact categories.

3.2 Classification of Impacts

The classification of impact categories was initially based on a study by Heijungs et al. (1992). The categories were then refined to promote the most useful quantities with respect to process design. The result was a list of eight environmental impact categories. These categories fall into two general areas of concern with four categories in each area: global atmospheric and local toxicological. The four global atmospheric impact categories are global warming potential (GWP), ozone depletion potential (ODP), acidification or acid-rain potential (AP), and photochemical oxidation or smog formation potential (PCOP). The four local toxicological impact categories are human toxicity potential by ingestion (HTPI), human toxicity potential by either inhalation or dermal exposure (HTPE), aquatic toxicity potential (ATP), and terrestrial toxicity potential (TTP). Again, this represents a modification to previous presentations of this material (Cabezas, et al., 1997; Cabezas, et al., 1999). In their presentation, they included separate categories for both inhalation and dermal exposure in the area of human toxicity.

The weighting factors in Equation (13) should be used to emphasize the particular areas of concern for individual process designers. For instance, if a process were to be constructed in a rural, wetland area, the process designer would likely de-emphasize the

photochemical oxidation potential of the process and emphasize the aquatic toxicity potential of the process.

3.3 Chemical Impact Database

To implement the WAR algorithm, the specific potential environmental impacts of each chemical in the database, ψ_{kl}^{s}, needed to be determined. The initial chemical database mimics the ChemCad 4.0 (Chemstations, 1997) chemical database which is comprised of approximately 1600 chemicals. The ψ_{kl}^{s} values are normalized within each impact category. There are two reasons for this. First, normalization will ensure that values of different categories contain the same units to allow for their combination as in Equation (13). Second, a proper normalization will ensure that values from different categories will have on average equivalent scores. Without the second condition, implicit weighting factors could be present in the chemical database causing unintentional bias in the calculation of the PEI indexes.

The scores used in the WAR algorithm will be calculated using the following normalization scheme:

$$\psi_{kl}^{s} = \frac{(Score)_{kl}}{\left\langle (Score)_{k} \right\rangle_{l}} \tag{14}$$

where $(Score)_{kl}$ represents the value of chemical k on some arbitrary scale for category l and $\left\langle (Score)_{k} \right\rangle_{l}$ represents the average value of all chemicals in category l. Normalizing each category by the average value of entries in that category insures that the average

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value in that category will be unity. This normalization eliminates unnecessary bias within the database. Previous versions of WAR Algorithm (Cabezas, et al., 1997; Cabezas, et al., 1999) had indicated that a Chebyshev normalization would be used. However, this type of normalization would have resulted in biases in the database.

The next issue is determining the appropriate mechanisms by which scores can be assessed for each of the 1600 chemicals in each of the impact categories. Data for the four global atmospheric impact categories were taken from values published by Heijungs et al. (1992). A brief summary of their methodology for determining these parameters would be informative and, thus, will be presented here.

The global warming potential (GWP) is determined by comparing the extent to which a unit mass of a chemical absorbs infrared radiation over its atmospheric lifetime to the extent that CO_2 absorbs infrared radiation over its respective lifetimes. The half-lives of each of these chemicals was factored into the calculation for determining the GWP. Since, chemicals have different atmospheric half-lives the length of time over which the comparison is made will change the GWP of a chemical. For this database, 100 years was chosen as the base time frame.

The ozone depletion potential (ODP) is determined by comparing the rate at which a unit mass of chemical reacts with ozone to form molecular oxygen to the rate at which a unit mass of CFC-11 (trichlorofluoromethane) reacts with ozone to form molecular oxygen.

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For a chemical to have ODP it must exist in the atmosphere long enough to reach the stratosphere; it, also, must contain a chlorine or bromine atom.

The photochemical oxidation potential (PCOP) or smog formation potential is determined by comparing the rate at which a unit mass of chemical reacts with a hydroxyl radical ($OH\bullet$) to the rate at which a unit mass of ethylene reacts with $OH\bullet$.

The acidification potential (AP) or acid rain potential is determined by comparing the rate of release of H^+ in the atmosphere as promoted by a chemical to the rate of release of H^+ in the atmosphere as promoted by SO_2.

The values reported by Heijungs et al. (1992) were inserted directly into Equation (14) to determine the chemical potential environmental impacts of these four categories. Note, only a portion of the 1600 chemical database had values for these four global atmospheric impact categories.

Two categories were used to estimate the potential for human toxicity: ingestion and inhalation/dermal exposure. These two categories were used to estimate toxicity potential because they considered all of the primary routes of exposure of a chemical. As a general rule, HTPI were calculated for a chemical if it existed as a liquid or solid at a temperature of 0 °C and atmospheric pressure, and an ingestion potential, HTPI, was determined for that chemical if it existed as a gas at those conditions. Some chemicals, however, were assigned values for both categories if it was warranted.

3.4 Including Energy into the WAR Algorithm

To provide a more accurate representation of the potential environmental impact of a process, energy has been included into the WAR algorithm by considering the emissions of a typical power plant. These emissions are then evaluated according to the impact criteria mentioned above. The result is a value of PEI/MWh of power plant production. This value is then multiplied by the rate of energy input required for the operation of a specific process. For the case study discussed in this work, the predominant emissions from a typical coal-fired power plant were used (SO_2, NO_2, NO, HCl, HF, CO_2, and CO) (USEPA, 1997) to perform PEI calculations.

The energy required to operate a process was calculated by summing all of the energy requirements of the system. Included into the calculation were the energy used by the compressors, the pumps, the reboilers of the distillation columns, and the energy used in heat exchangers to heat streams. Also included into this calculation was the energy required to pump cooling water through the condensers and the coolers (heat exchangers). The energy required to operate refrigeration units was also taken into consideration. The energy produced by a turbine was considered to be directly available to the process and represented a reduction in energy consumption of the process. No effort was made in this case study to minimize energy consumption by the use of heat-exchange networks (HEN). However, in principle this technique could be integrated into the WAR analysis.

4. AN ILLUSTRATIVE CASE STUDY: ACRYLIC ACID PRODUCTION

The case study will be an acrylic acid production process, as shown in Figure 3 (Turton, *et al.*, 1998). The process is designed for the production of 50,000 tonnes of acrylic acid/yr. The process begins with the catalytic oxidation of propylene with air to form acrylic acid, Equation (17), and by-products (acetic acid, hydrogen, water, and carbon dioxide) which are formed through parallel reactions, Equations (18) and (19).

$$C_3H_6 + \frac{3}{2}O_2 \rightarrow C_3H_4O_2 + H_2O \tag{17}$$

$$C_3H_6 + \frac{5}{2}O_2 \rightarrow C_2H_4O_2 + H_2O + CO_2 \tag{18}$$

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3H_2O + 3CO_2 \tag{19}$$

The reactor is assumed to operate isothermally at 310 °C. The effluent from the reactor is quenched in a adiabatic flash drum with a substantial recycle stream. The vapor effluent of the flash drum is then stripped with a deionized water stream to recover the small fraction of acrylic acid that escaped in the vapor stream from the flash drum. The vapor effluent of the stripper is delivered to an incinerator and is considered a waste stream. The liquid effluent of the flash drum is mixed with the liquid effluent of the stripper to form a stream of which 98% is recycled back to the flash drum for the quenching process. The non-recycled, liquid effluent is sent to a liquid-liquid extraction tower and extracted with a solvent mixture of diisopropyl ether (DIPE, 87% mole) and water. The aqueous effluent contains small amounts of acetic acid, acrylic acid, and DIPE. This stream is distilled to recover a pure water stream that is also considered to be a waste stream. The acids and the DIPE are recycled back to the extraction column. The organic effluent of

the extraction tower is sent to solvent recovery column and then to an acrylic acid column. The acrylic acid product is 99.9% (mole) pure. There is no consumption of DIPE in this process design. There is simply an initial charge which is completely recovered within the process, mostly within the solvent recovery column.

[insert Figure 3 here]

Three design scenarios were considered in this case study: a base case (Unit 300) and two, alternative designs (Units 301 and 302). The four input streams were consistent in all three designs; their specifications are given in Table 1 including the potential environmental impacts (PEI) of each. Note, the number of significant figures associated with environmental impact calculations should be restricted to one; however, for the purpose of this illustration two significant figures will be used.

Table 1: The specifications of the feed streams used in the acrylic acid case study

Feed Streams	Propylene	Steam	Air	DI Water
Temperature (°C)	25	159	25	25
Pressure (bar)	11.5	6	1	5
Flow rate (kg/hr)	5,344	17,876	39,047	2,540
PEI (impact/hr)	11,000	0	0	0
Stream Composition in Mass Fractions				
Propylene	1	0	0	0
Water	0	1	0.0117	1
Oxygen	0	0	0.2302	0
Nitrogen	0	0	0.7581	0

The potential environmental impacts were calculated using uniform weighting factors, α_l, equal to unity. Using $\alpha_l = 1$ for all l categories, the potential environmental impacts for each chemical used in this case study were calculated and presented in Table 2. Note,

DIPE does not appear in Table 2 because it is not seen in any of the input or output streams. Using these weighting factors, the potential environmental impact of the energy consumed by this process was calculated as 24 PEI/MWh.

Table 2: Potential environmental impacts of the chemicals used in the acrylic acid case study

Chemical	PEI (Impact/kg)
Propylene	2.1
Water	0
Oxygen	0
Nitrogen	0
Carbon Dioxide	8.6×10^{-4}
Acrylic Acid	23
Acetic Acid	0.24

Table 2 provides a quick reference for determining the relative impact ranking of the chemicals. From this table, it can be seen that the desired product, acrylic acid, is, coincidentally, the most environmentally unfriendly chemical used in this process. Note, the values in this table will vary when different weighting factor schemes are used.

The potential environmental impacts of the effluent streams from this process are shown in Table 3 with the other stream specifications for Unit 300. The acrylic acid stream is considered the only product stream in this case study. The other three, effluent streams are viewed as non-product streams.

The case studies used in previous papers published on the WAR algorithm focused on process modification primarily through the addition of recycle streams. The case study

discussed here will focus on using the WAR algorithm as a decision tool for other types of process modifications.

With the goal in mind of limiting the PEI while maximizing production of the acrylic acid stream, the base case results were examined to identify possible improvement areas. Obviously, from inspection of Table 3, to reduce the PEI of this process the off-gas and acetic acid non-product streams need to be addressed. The off-gas waste stream contains unreacted propylene and a primary by-product, carbon dioxide. To address this issue, the operation of the reactor was examined. The kinetics of the reaction scheme is such that lower temperatures favor the selectivity to acrylic acid.

Table 3: The specifications of the effluent streams used in the acrylic acid case study (Unit 300)

Effluent Streams	Off-gas	Waste Water	Acetic Acid	Acrylic Acid
Stream type	Non-product	Non-product	Non-product	Product
Temperature (°C)	37.6	102	47	40
Pressure (bar)	1	1.1	1.1	1.1
Flow rate (kg/hr)	35,772	21,058	1,055	6,237
PEI/hr	1,300	3	1,700	150,000
Stream Composition in Mass Fractions				
Propylene	0.0173	0	0	0
Water	0.0415	0.9997	0	0
Oxygen	0.0671	0	0	0
Nitrogen	0.8275	0	0	0
Carbon Dioxide	0.0462	0	0	0
Acrylic Acid	0	0	0.0594	0.9992
Acetic Acid	0.0003	0.0003	0.9406	0.0008

The second process improvement involves lowering the PEI of the acetic acid stream. From Tables 2 and 3, it can be seen that the primary contributor to PEI is the excess

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acrylic acid that has been lost in this stream. An obvious process modification is one that improves the separation efficiency of the acrylic and acetic acids while maintaining a product purity of 99.9%. This separation is performed in the acrylic acid column, see Figure 3. An improvement in the separation is achieved by increasing the reflux ratio of that column which results in a purer acetic acid non-product stream and a greater recovery of acrylic acid in the product stream. The cost of this improvement is increased usage of energy.

Both alternative designs employ both of these process modifications: lowered reactor temperatures and increased reflux ratio in the acrylic acid column. The first alternative design, Unit 301, incorporated a 30 °C reduction in reactor temperature to an operating temperature of 280 °C. It also incorporated a 54% increase in the reflux ratio of the acrylic acid column. Interestingly, decreasing the temperature in the reactor resulted in a equivalent conversion of propylene. However, there was a greater selectivity towards acrylic acid.

The second alternative design (Unit 302) consists of lowering the reactor temperature another 20 °C to 260 °C and doubling the reactor volume. Increasing reactor volume is required to maintain an equivalent level of propylene conversion. The reflux ratio in the acrylic acid column was also increased; however, only a 9% increase was required to achieve the same separation as observed in Unit 301.

The performance specifications of the three process designs are summarized in Table 4. The selectivity was determined by comparing the amount acrylic acid (desired product) that was made to the amount of acetic acid and carbon dioxide (undesired by-products) that was produced.

Table 4: A Comparison of the Performance of the Three Process Designs

	Unit 300	Unit 301	Unit 302
Acrylic Acid Selectivity (in moles)	1.58	2.31	3.02
Energy Consumed (MJ/h)	258,000	275,000	291,000
PEI/hr of Energy Consumption	1700	1800	1900
Acrylic Acid Column			
Reflux Ratio	7.37	11.4	8.03
Product Flow Rate (kg/h)	6240	6280	6650
Condenser Duty (MJ/h)	-3610	-3410	-3630
Reboiler Duty (MJ/h)	3550	3360	3570

For this research, PEI indexes are presented in two different analysis. The first one includes the PEI of the product stream into the calculations of the indexes. The second one excludes the PEI of the product stream from the calculations of the indexes. The graphical interpretation of the four, basic potential environmental impact indexes ($\dot{I}_{out}^{(t)}$, $\hat{I}_{out}^{(t)}$, $\dot{I}_{gen}^{(t)}$, and $\hat{I}_{gen}^{(t)}$) are presented in Figures 4 and 5. These indexes are presented for both situations where the product stream was included in the analysis (product analysis, Figure 4) and where the product stream was excluded from the analysis (non-product analysis, Figure 5).

A comparison of the potential environmental impact indexes of all three process designs are shown in Figures 4 and 5. The indexes are plotted in units of impact/h and impact/kg

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of product. They both can provide valuable insight which will be discussed later. From the non-product analysis, both the generation and the output of PEI was found to decrease in each case with Unit 302 presenting the most environmentally friendly design. Further discussions including the all components (product and non-products) will be given later. It is quite apparent that Unit 302 provides the best process design option of the three since it has the lowest PEI and the highest rate of production of acrylic acid. Note, economic considerations have not been included into this analysis.

[insert Figure 4 here]

[insert Figure 5 here]

5. DISCUSSION

The most significant modification to the WAR Algorithm is the inclusion of energy consumption into the potential environmental impact calculations. The energy consumed by a process has been assumed to come directly from a power generating facility. The energy generating by this facility has been directly related to the emissions of the facility. These emissions are the basis for quantifying the PEI of the energy consumed by a process. The inclusion of energy into the WAR Algorithm's calculations provides a more realistic view of the PEI generated by a chemical processing plant.

5.1 An Illustrative Case Study: Acrylic Acid Production

In the case study, the PEI of the energy consumed in the process is approximately equal to PEI of the acetic acid, 1700 PEI/hr, and off-gas, 1300 PEI/hr, non-product streams the

base design case, 1700 PEI/hr. Obviously, including the PEI of energy consumption is vital in this case study because of the significant contribution of energy generation to the creation of PEI. Each of the alternative designs increased the energy consumption of the process, from Table 4, which translates into a greater generation of PEI. Thus, any design modification must reduce the amount of PEI generated within the process by an amount that would offset the increase in PEI due to energy consumption. This represents a minimum reduction in PEI for a process modification. From Figure 5 (non-product analysis), it can be seen that the process modifications accomplish this.

Figure 4 (product analysis) indicate that the process modifications did not achieve the goal of reducing the PEI of the original design. This contradiction presents a good opportunity to discuss the advantages of using both types of analysis to extract useful information.

The PEI calculations which incorporate the PEI of the product into the analysis (product analysis) show that the acrylic acid product stream is, by far, the most significant contributor to PEI in this process. From the viewpoint of this analysis, neither of the process modifications resulted in an improved design. However, both designs resulted in a greater acrylic acid production rate (Table 4). From the view of a process designer, this would be a favorable improvement. The increase in acrylic acid production accounts for the increase in the PEI indexes in Figure 4.

To separate these seemingly competing factors, a second analysis is introduced which calculates the PEI without including the product stream into the calculations, non-product analysis. The non-product analysis, Figure 5, shows that the modifications have reduced the PEI of the process. Since the process designer is usually concerned about the potential environmental impact of only the waste streams, the PEI indexes from the non-product analysis will be the indexes that will most often be used in evaluating process modifications. Indeed, these were the indexes used to evaluate the alternative process designs in this research. However, there is very useful information to be obtained from the product analysis as well. For instance, in this case study the process designer would observe that acrylic acid is the most environmentally unfriendly chemical. This may promote research to find an alternative chemical that would satisfy their end needs and be more environmentally friendly.

In these discussions of PEI indexes, note that the comparisons have been made on a quantitative basis, e.g., one design option had a PEI index that was greater or less than the PEI index of another design option. Due to the uncertainties in the parameters and to the approximations made in the methodology, comparisons of indexes should be restricted to a quantitative nature.

6. CONCLUSIONS

The WAR Algorithm, a methodology for determining the potential environmental impact (PEI) of a chemical process, has been modified to include the PEI of the energy

consumed by that chemical process. This is accomplished by relating the emissions of a typical power plant to the production of energy by that power plant. These emissions, in turn, have an PEI associated with them. The categories over which the PEI are measured have been re-configured to include eight environmental concerns (human toxicity, both by ingestion and inhalation/dermal exposure, aquatic toxicity, terrestrial toxicity, global warming, ozone depletion, acid rain formation, and smog formation). This paper details the method for converting measured values of individual chemicals into PEI values for those chemicals in each category. These chemical PEI values are used to determine four, primary PEI indexes ($\dot{I}_{out}^{(t)}$, $\hat{I}_{out}^{(t)}$, $\dot{I}_{gen}^{(t)}$, and $\hat{I}_{gen}^{(t)}$). These four indexes are used to determine the environmental friendliness of a process design. Two types of analysis are used to calculate the PEI indexes: product and non-product. The product analysis includes the PEI of the product streams into the calculations; whereas, the non-product analysis omits the PEI of the product streams from the calculations. Both analyses are useful which was shown in the case study that was presented in this paper. The product analysis provides global information about the process, such as the PEI impact of the product streams. This raises issues about the environmental friendliness of the products and questions whether more suitable chemicals can replace the current products. The non-product analysis provides more focused information which can be used to optimize the environmental friendliness of a chemical process. The WAR Algorithm is intended to be used in tandem with process simulation.

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NOMENCLATURE

$\dot{E}_j^{(cp)}$ the rate of waste energy emission from a chemical process (units of energy/time)

$\dot{E}_j^{(ep)}$ the rate of waste energy emission from an energy generation process (units of energy/time)

$\dot{I}_{gen}^{(syst)}$ the rate of PEI generated within a system including the energy generation process (units of PEI/time)

$\dot{I}_{gen}^{(t)}$ the total rate of PEI generated within a system (units of PEI/time)

$\hat{I}_{gen}^{(t)}$ the total PEI generated within a system per mass of product stream leaving the system (units of PEI/mass of product streams)

$\dot{I}_{in}^{(cp)}$ the rate of PEI entering a chemical process (units of PEI/time)

$\dot{I}_{in}^{(ep)}$ the rate of PEI entering an energy generation process (units of PEI/time)

$\dot{I}_j^{(in)}$ the rate of PEI entering a process in stream j (units of PEI/time)

$\dot{I}_j^{(out)}$	the rate of PEI leaving a process in stream j (units of PEI/time)
$\dot{I}_{out}^{(cp)}$	the rate of PEI leaving into a chemical process (units of PEI/time)
$\dot{I}_{out}^{(ep)}$	the rate of PEI leaving an energy generation process (units of PEI/time)
$\dot{I}_{out}^{(t)}$	the total rate of PEI leaving a system (units of PEI/time)
$\hat{I}_{out}^{(t)}$	the total PEI leaving a system per mass of product streams leaving the system (PEI/mass of products)
I_{syst}	the PEI of a chemical process system including the energy generation process (units of PEI)
$\dot{I}_{we}^{(cp)}$	the rate of PEI waste energy lost from a chemical process (units of PEI/time)
$\dot{I}_{we}^{(ep)}$	the rate of PEI waste energy lost from an energy generation process (units of PEI/time)
$\dot{M}_j^{(in)}$	the mass flow rate of stream j into a process (units of mass/time)
$\dot{M}_j^{(out)}$	the mass flow rate of stream j leaving a process (units of mass/time)
$\dot{P}_p$	the mass flow rate of product stream p (units of mass/time)
PEI	potential environmental impact
$(Score)_{kl}$	a characteristic quantity of chemical k used to determine a PEI value of that chemical for impact category l (units vary for each category)
$\langle (Score)_k \rangle_l$	the average value of all k chemicals in category l (units vary for each category)

t	time
x_{kj}	the mass fraction of chemical k in stream j (units of mass of chemical k/mass of stream j)

Greek symbols

α_l	the weighting factor for impact category l (dimensionless)
ψ_k	the overall PEI of chemical k (units of PEI/mass of chemical k)
ψ^s_{kl}	the specific PEI of chemical k for impact category l (units of PEI/mass of chemical k)
ψ_{we}	the overall PEI of the waste energy lost from a process (units of PEI/energy)

LIST OF ACRONYMS

ACGIH	American Conference of Governmental Industrial Hygienists
AP	Acidification Potential
ATP	Aquatic Toxicity Potential
GWP	Global Warming Potential
HEN	Heat Exchange Network
HTPE	Human Toxicity Potential by Exposure
HTPI	Human Toxicity Potential by Ingestion
MEN	Mass Exchange Network
NIOSH	National Institute for Occupational Safety and Health
ODP	Ozone Depletion Potential

OSHA	Occupational Safety and Health Administration
PCOP	Photochemical Oxidation Potential
PEI	Potential Environmental Impact
TTP	Terrestrial Toxicity Potential
USEPA	United States Environmental Protection Agency
WAR	Waste Reduction

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FIGURE CAPTIONS

Figure 1: The Waste Reduction (WAR) Algorithm is a methodology that aids in the environmental evaluation of chemical manufacturing processes. This is where the WAR Algorithm fits into the overall life cycle of a product.

Figure 2: The overall mass and energy balance around a chemical process facility including the energy generation facility. The system boundary is designated with a dashed line.

Figure 3: The process flow diagram for Acrylic Acid Production Case Study.

Figure 4: The potential environmental impact (PEI) output and generation indexes for Acrylic Acid Production. Calculations include the PEI of the product stream (product analysis). The units of $\dot{I}_{out}^{(t)}$ and $\dot{I}_{gen}^{(t)}$ are PEI/hr; the units of $\hat{I}_{out}^{(t)}$ and $\hat{I}_{gen}^{(t)}$ are PEI/kg product stream.

Figure 5: The potential environmental impact (PEI) output and generation indexes for Acrylic Acid Production. Calculations do not include the PEI of the product stream (non-product analysis). The units of $\dot{I}_{out}^{(t)}$ and $\dot{I}_{gen}^{(t)}$ are PEI/hr; the units of $\hat{I}_{out}^{(t)}$ and $\hat{I}_{gen}^{(t)}$ are PEI/kg product stream.

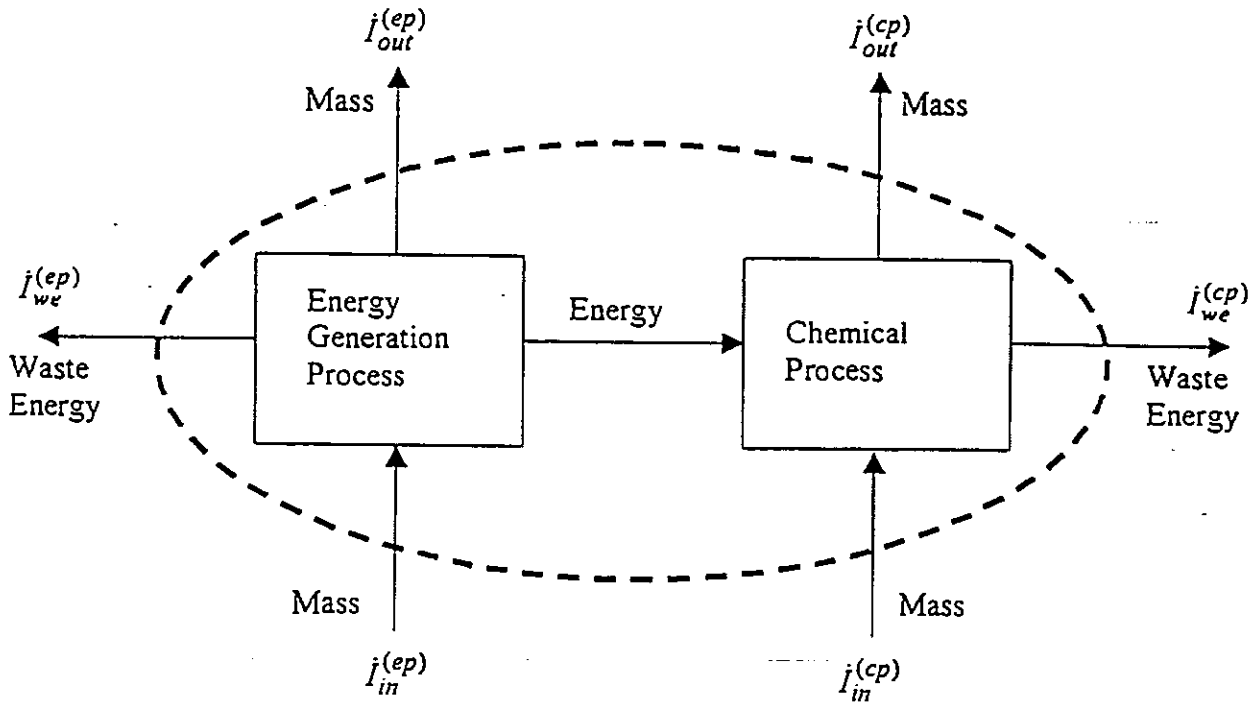

Figure 2: Young and Cabezas

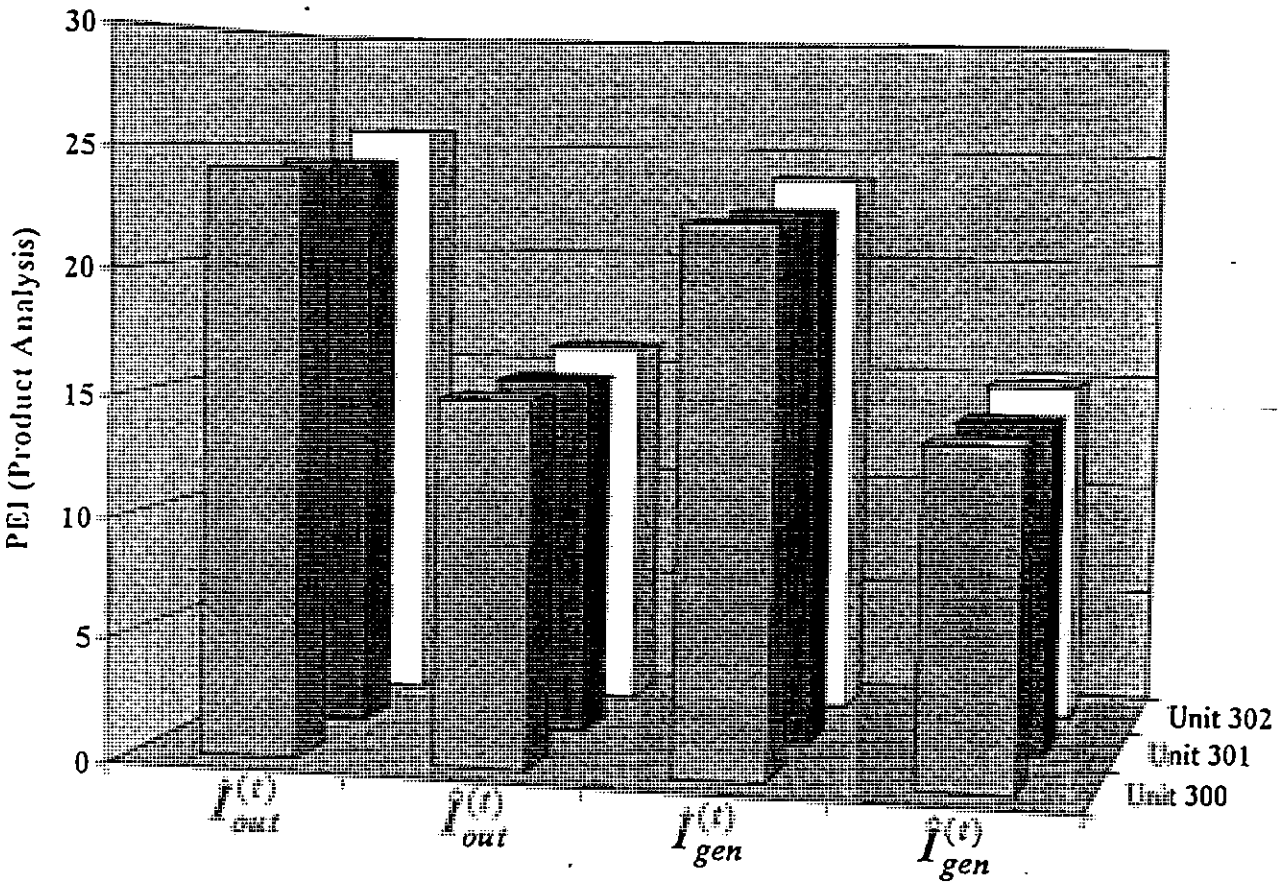

Figure 4: Young and Cabezas

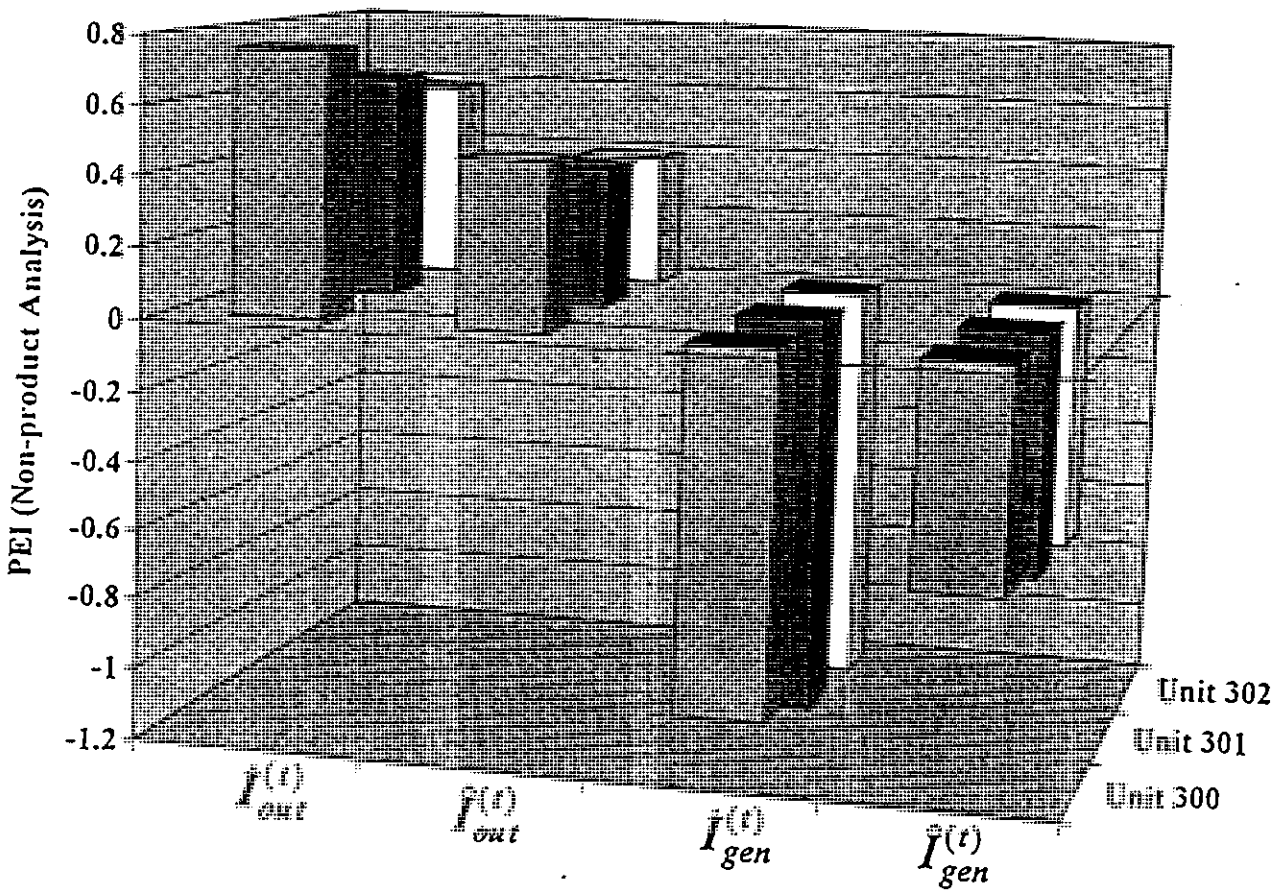

Figure 5: Young and Cabezas

Using Simulation For Pollution Prevention

Heriberto Cabezas and
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U.S. Environmental
Protection Agency,
Sustainable Technology Div.

The goal is to design or modify chemical processes to minimize their environmental impact

The ability to design or modify chemical processes in a way that minimizes the formation of unwanted byproducts is an ongoing goal for process engineers. Two simulation and design methods are discussed here: Process Integration (PI), developed by El-Halwagi and Manousiouthakis [1] at UCLA, and El-Halwagi [2] at Auburn University; and the Waste Reduction (WAR) Algorithm, developed at the U.S. Environmental Protection Agency (Cincinnati, Ohio), and made commercially available through a Cooperative Research and Development Agreement (Crada) under the Federal Technology Transfer Act of 1986.[1]

PI is concerned with improving process efficiency and keeping targeted components from leaving the system. PI is essentially the practical application of the mass-exchange networks (MEN), as detailed in [1,2], which try to remove pollutants from product streams and segregate them into concentrated waste streams.

By comparison, the WAR Algorithm is concerned with evaluating and reducing the potential environmental impact of a process [3] — a key design consideration. Consider Process A, which emits 1 ton/h of a given pollutant, and Process B, which emits 2 tons/h of a different pollutant. When these two processes are compared on the basis of pollutant mass alone, one could logically conclude that Process A is preferable. However, because some pollutants are more toxic than others, the process comparison needs to assess the human-health and environmental impacts.

[1] The Process Integration methodology has been commercialized by Matrix Integration, Inc. (Leesburg, Va.). The initial version of the WAR algorithm is being incorporated into the simulator product ChemCAD IV from Chemstations, Inc. (Houston, Tex.). The authors' discussion here does not endorse either of these commercial products or companies.

Note: For more on simulation, see p. 139.

The WAR Algorithm

This methodology assumes that each stream entering and exiting a process possesses an inherent property, its potential environmental impact (PEI). WAR generates four indexes (discussed below), which can be used to compare the environmental impact of various process alternatives. For a steady-state process, one can write a balance equation for PEI:

$$O = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (1)$$

where:

$\dot{I}_{in}$ = The rate of PEI input, PEI/h (the impact on the environment if all feed streams were to be released at once)

$\dot{I}_{out}$ = The rate of PEI output, PEI/h. (the impact on the environment if all output streams were to be released)

$\dot{I}_{gen}$ = The rate of PEI generation by the process, PEI/h (the difference between $\dot{I}_{out}$ and $\dot{I}_{in}$; $\dot{I}_{gen}$ can be positive or negative, because a given process can either create or consume PEI)

From Equation 1, one can generate two output indexes and two generation indexes, to compare different process alternatives. The lower the value of these indexes, the better the process's environmental performance.

The *output indexes* include the rate of PEI output, $\dot{I}_{out}$, and the amount of PEI output per kilogram of product, $\hat{I}_{out}$. These indexes allow comparison of the potential impact of various output streams on human health and the environment. $\hat{I}_{out}$ is given by:

$$\hat{I}_{out} = \dot{I}_{out} / \dot{P} \qquad (2)$$

where:

$\dot{P}$ = The rate at which the process produces products, kg/h

The *generation indexes* are the rate of PEI generation, $\dot{I}_{gen}$, and the amount of PEI generated per kilogram of product, $\hat{I}_{gen}$. They allow comparison of process alternatives, in terms of the generation of net PEI. $\hat{I}_{gen}$ is given by:

$$\hat{I}_{gen} = \frac{\dot{I}_{out} - \dot{I}_{in}}{\dot{P}} \qquad (3)$$

To compute the four indexes for a

NOMENCLATURE

$\dot{I}_{in}$ = The rate of input of PEI, PEI/h

$\dot{I}_{out}$ = The rate of output of PEI, PEI/h

$\dot{I}_{gen}$ = The rate of PEI generation inside the process, PEI/h (i.e., the difference between $\dot{I}_{in}$ and $\dot{I}_{out}$)

$\hat{I}_{out}$ = The amount of PEI output/kg of product

$\dot{P}$ = The rate at which the process produces product, kg/h

$\hat{I}_{gen}$ = The amount of PEI generated/kg of product

$\hat{I}_i^{in}$ = The PEI input per kg of product, for each individual input stream, i

$\dot{I}_i^{in}, \dot{I}_i^{out}$ = The PEI rate of each individual input and output stream, i, PEI/h

$\dot{M}_i^{in}, \dot{M}_i^{out}$ = Mass flowrate of each input and output for each stream, i, kg/h

x_{ij} = The mass fraction of each non-product chemical component, j, in stream i, kg/kg

ψ_j = The overall environmental impact of chemical component, j, PEI/kg

α_k = A weighting factor that allows one to assign relative importance to each of the eight environmental-impact categories, k, used by the WAR Algorithm

ψ_{jk}^{*} = Specific impact of chemical component, j, in impact category, k, PEI/kg

given process, the rate of PEI of all the input and output streams, $\dot{I}_{in}$ and $\dot{I}_{out}$, respectively, must be calculated. For the input streams, this is done by calculating the PEI rate of each individual input stream, i ($\dot{I}_i^{(in)}$), and then adding the individual values to get $\dot{I}_{in}$. For the output streams, this is done by calculating the PEI rate of each individual input stream, i ($\dot{I}_i^{(out)}$), and then adding them to get $\dot{I}_{out}$. For each stream, i, the PEI rates of the individual input and output streams are calculated from the following:

- The mass flowrate of each input and output, $\dot{M}_i^{(in)}$ and $\dot{M}_i^{(out)}$, respectively
- The stream composition, in terms of the mass fraction, x_{ij}, of each non-product chemical component (pollutant and undesired byproduct), j
- The overall environmental impact, ψ_j, of chemical component j

The overall environmental impact, ψ_j, is calculated by summing the specific impacts, ψ^s_{jk}, of chemical component j over the various impact category k (discussed below), in unit of PEI/kg. This is given by,

$$\dot{I}_{in} = \sum_i \dot{I}_i^{(in)} = \sum_i \dot{M}_i^{(in)} \sum_j x_{ij}\psi_j = \sum_i \dot{M}_i^{(in)} \sum_j x_{ij} \sum_k \alpha_k \psi^s_{jk}$$

$$\dot{I}_{out} = \sum_i \dot{I}_i^{(out)} = \sum_i \dot{M}_i^{(out)} \sum_j x_{ij}\psi_j = \sum_i \dot{M}_i^{(out)} \sum_j x_{ij} \sum_k \alpha_k \psi^s_{jk}$$

where:

α_k = A weighting factor for each impact category k

GOING TO 'WAR' FOR A 'GREENER' ACRYLIC-ACID PROCESS

To illustrate the use of the WAR Algorithm, consider an acrylic-acid-production process designed to produce 50,000 m.t./yr of acrylic acid (Figure 1). The process catalytically oxidizes propylene with air to form acrylic acid, and several byproducts (acetic acid, hydrogen, water and carbon dioxide) [4]. Three alternative design scenarios were considered: a base case (Unit 300) and two alternative designs (Units 301 and 302).

In the base case (Unit 300), the reactor operates at 310°C. The effluent is quenched in an adiabatic flash drum with a substantial recycle stream (98%). The flash-drum vapor effluent is stripped with deionized water to recover any residual acrylic acid.

The vapor effluent from the stripper is delivered to an incinerator. The liquid effluent from the flash drum is mixed with liquid effluent from the stripper; 98% of this mixed stream is recycled to the flash drum for quenching. The non-recycled, liquid effluent is sent to a liquid-liquid extraction unit, where the organics are extracted with a solvent mixture of diisopropyl ether (DIPE; 87 mol%) and water.

The aqueous effluent, which contains small amounts of acetic acid, acrylic acid and DIPE, is distilled to recover pure water, which is considered a waste (since it is not deionized, it cannot be reused in the process). The acids and DIPE are recycled back to the extraction column. The organic effluent from the extraction tower is sent to solvent-recovery column and then to an acrylic-acid distillation column. The final acrylic acid product is 99.9 mol% pure.

In this design, there is no consumption of DIPE. Rather, the initial charge of DIPE is completely recovered within the process.

Acrylic acid is considered the only product in this case study. With the objective of minimizing the potential environmental impact (PEI) of the other three effluent streams and maximizing acrylic acid production, possible improvements were sought. Because the reactor waste gas contains unreacted propylene and byproduct carbon dioxide, the reactor operation was examined.

Seeking improvements

The kinetics of this process are such that lower temperatures favor acrylic acid production. Thus, in the first design alternative, Unit 301, the reactor temperature was reduced by 30°C, to 280°C. This design also incorporated a 54% increase in the reflux ratio of the acrylic acid column. Decreasing the reactor temperature resulted in an equivalent conversion of propylene. However, it produced a greater selectivity toward acrylic acid (from 1.58 to 2.3 mole of acrylic acid per mole of byproduct).

In the second design alternative, Unit 302, the reactor temperature was reduced by another 20°C, to 260°C, and the reactor volume was doubled to maintain an equivalent level of propylene conversion. The reflux ratio in the acrylic acid column was also increased; however, only a 9% increase was required to achieve the same separation as observed in Unit 301.

The four output and generation PEI indexes described above were plotted for the base case and for the the two process modifications. Figure 2 shows the output indexes, $\dot{I}_{out}$ and $\hat{I}_{out}$, and the generation indexes, $\dot{I}_{gen}$ and $\hat{I}_{gen}$.

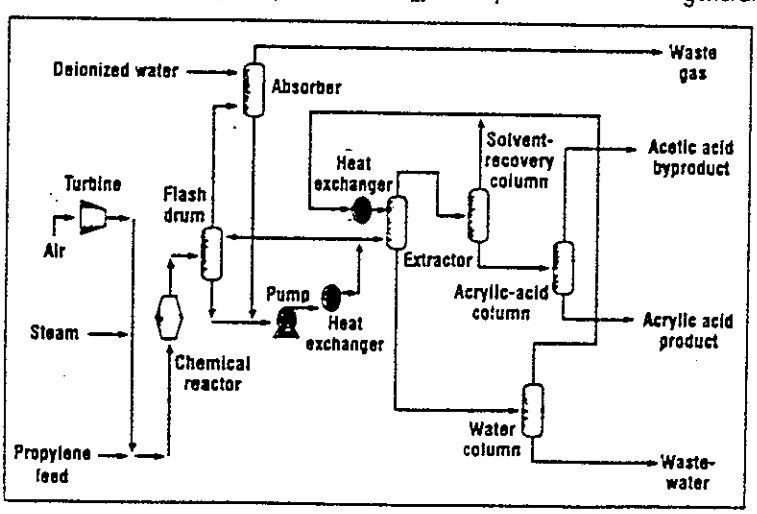

FIGURE 1. The WAR Algorithm was used to identify several waste-minimization routes for the acrylic-acid process shown above

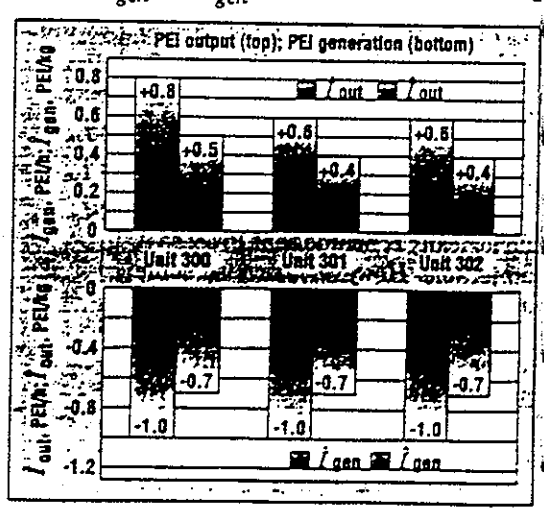

FIGURE 2. The design changes discussed above alter the output and generation PEI, as shown here

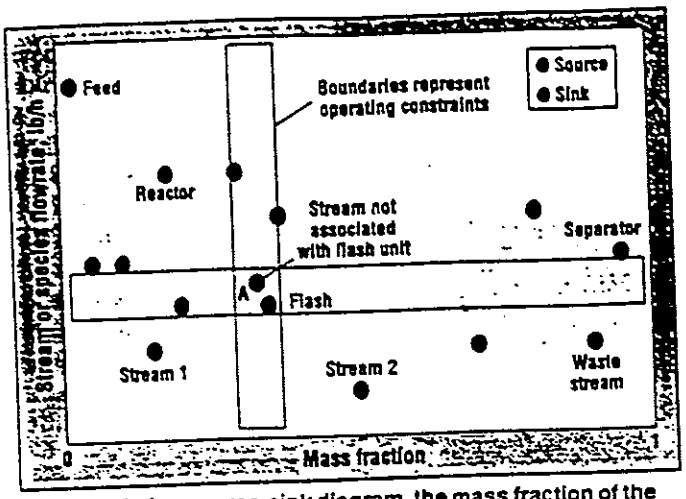

FIGURE 3. In a source-sink diagram, the mass fraction of the target species is plotted against flowrate. As shown, Stream A can be recycled directly back to the flash unit

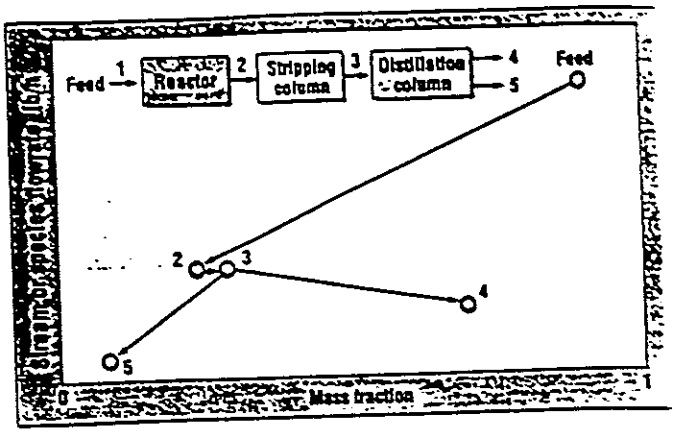

FIGURE 4. As this species-path diagram shows, streams (such as Streams 3 and 4) with a high target-species composition, a high flowrate, or both, are generally the most economical candidates for a mass-exchange operation. Stream 2 is already undergoing such an operation (stripping)

The current version of the WAR Algorithm considers eight health- and environmental-impact categories, k: ozone-depletion potential; global-warming potential; acid-rain potential; photochemical-oxidation or smog-formation potential; human-toxicity potential by ingestion; human-toxicity potential by inhalation or dermal exposure; aquatic-toxicity potential; terrestrial-toxicity potential. The weighting factor, α_k, allows us to assign relative importance to each of the eight categories. A default value of 5 for α_k can be assumed, but it can be adjusted between 0 and 10 to better represent the process and locale.

Values for ψ^s_{jk} can be obtained from a database developed by the authors, or from the database within the ChemCAD IV chemical-process simulator. The Box on p. 118 shows how the WAR Algorithm improved an acrylic-acid process.

Process Integration

The PI methodology considers the intricate relationships among flow streams, unit operations, operating parameters, and performance requirements, and then uses these relationships during process design to determine the ideal order of the unit operations and mass and energy streams; to calculate mass and energy balances for proper equipment sizing; and to optimize an existing process, increasing product flow, or reduce energy use and waste generation.

The Mass-Exchange Network (MEN), at the heart of the Process Integration simulation methodology, reduces the amount of waste generated in a process by concentrating the non-useful byproducts into waste streams, and capturing and recycling products and useful byproducts back to appropriate downstream unit operations. A MEN allows a designer to simulate any process design to determine what unit operations, if any, are needed. The analysis or optimization of a series of MENs can be performed numerically or graphically; the graphical technique is demonstrated below.

Components of MENs

In a mass-exchange network, the waste streams are referred to as *sources* and unit operations, including reactors, distillation columns and treatment units, are referred to as *sinks*. In a given process, various output streams, and any waste- or mass-separating agents, can be either emitted, recycled back to a unit operation (sink), recycled to a processing stream, or sent for post-treatment.

The mass-transfer and separation portions of a MEN typically rely on mass-exchange equipment — including absorbers, strippers, liquid-liquid extraction units, adsorbers, ion exchangers and leaching systems — which separate and concentrate the waste streams. Mass-separating agents (MSA) — including solvents used in liquid-liquid extraction or gas absorption, granulated activated carbon, ion-exchange resins, and gases used in stripping operations — are often added to enhance the recovery of the useful components.

MENs also use stream-management techniques, such as recycling to a sink, stream mixing to achieve a desired flowrate or composition, and stream segregation to avoid mixing of streams that would require further treatment downstream. Temperature, pressure and flowrate can also be adjusted to enhance performance.

Analysis of MENs

The first step in designing an MEN that will simulate a process is to define the problem to be solved — how to increase production rates, reduce pollution emission, reduce utility consumption (such as cooling water) and so on — and to list any associated constraints, such as product specifications, pollutant concentrations or flowrates, and so on. The next step is to define the target components — those chemicals that need to be identified to address the problem statement and constraints. For example, water would be a target component in a system where you are trying to reduce cooling-water consumption; hydrogen would be a target component in a dehydrogenation process where the goal is to trim gas emissions. The graphical tools used in the MEN analysis focus around these components.

The *source-sink diagram* (Figure 3) plots the composition of the target species (shown as mass fraction) against flowrate to identify recycle opportunities. The red circles represent all sources or streams, and describe the relationship between flowrate and the composition

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of the target species in that stream.

The current operating condition of each sink (unit operation) is shown by a blue circle. The values plotted in Figure 3 represent the flowrate through the sink versus the composition of the target species inside that sink. For sinks that have variable concentrations, an average composition is shown. A source-sink diagram can be drawn for each target species.

Each sink has physical constraints that limit the compositions and flowrates within which it can operate. These are shown as box-like boundaries in Figure 3. These constraints limit the feasible operating conditions that may be considered during simulation in a "greener" design alternative. Any source that lies within this box can be recycled back to any sink within the box. While Figure 3 only highlights one sink, such a graphical analysis should be done for each sink.

A source-sink diagram can also be used to identify streams that can be combined and then recycled. For instance, in Figure 3, combining Streams 1 and 2 will increase the flowrate to an appropriate level, and adjust the composition to an acceptable level, allowing the combined stream to be recycled back to the flash unit sink shown within the box.

Similarly, if a source lies to the right of a sink but is still within its flowrate constraints, the stream can be recycled back to that sink — but only after the target-species composition has been reduced to meet the unit's constraints. The composition can be altered by using a stripper, absorber, or other mass-exchange unit.

The distance that a source lies to the right of a sink also provides information as to which units can be used to accomplish the desired degree of separation. A source that lies above a sink must reduce its flowrate before it can be recycled to that sink.

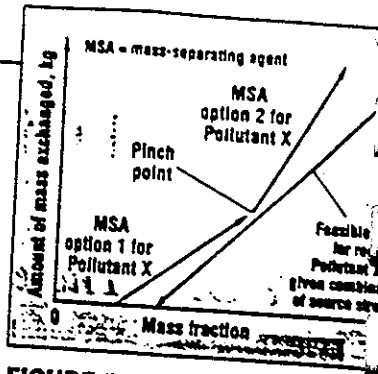

FIGURE 5. In this mass-pinch diag the curves on the left show the abil two different mass-separating age (MSA) in a given mass-exchange u remove Pollutant X from a given was stream or streams. The composite c on the right shows the range of fea for removing Pollutant X from a co tion of streams. The pinch point (whe the two curves are closest) shows th best point at which to apply the MS tions for removing Pollutant X, fro economic and thermodynamic stan

Another graphical tool, the *pa agram* (Figure 4), shows the flo specific component (i.e., a process actant) through a process. Such a d gram is used to determine where a exchange could be used to captu target species and remove them fr the system.

We Made A Long Story

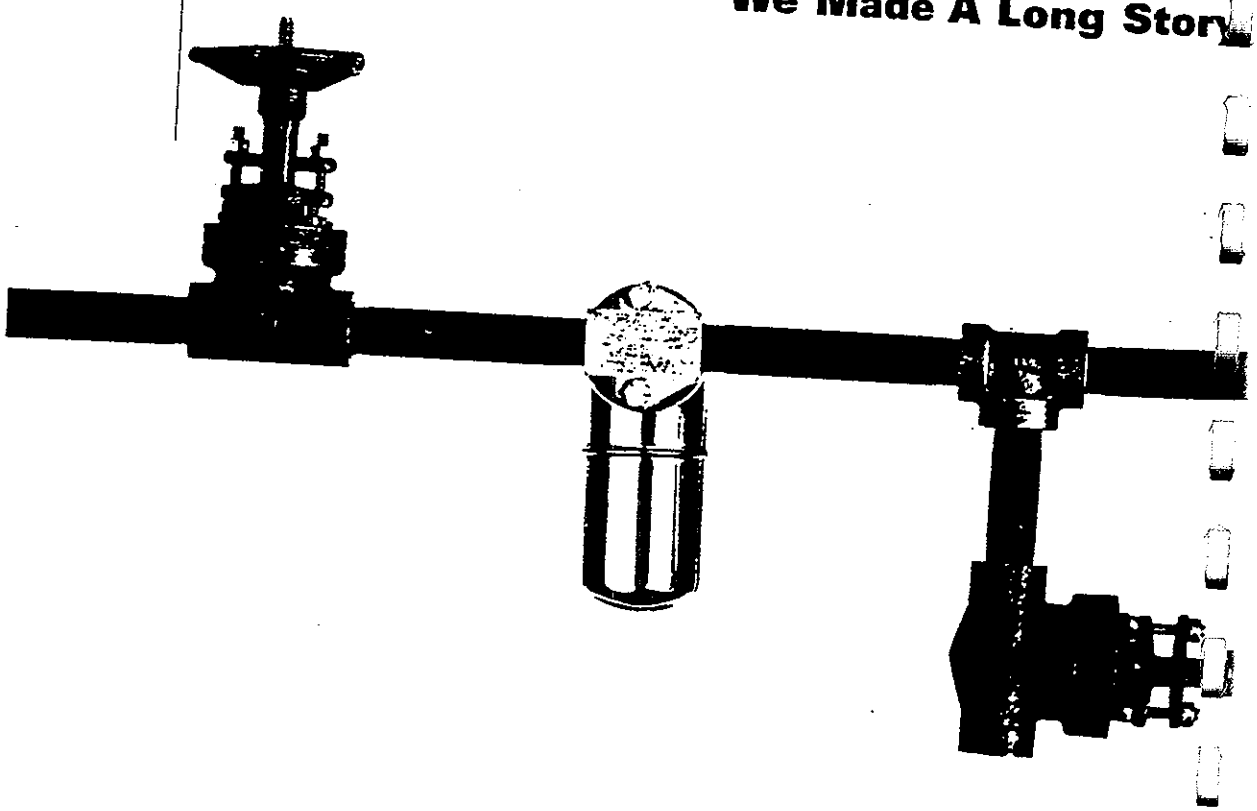

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Figure 4 shows a section of a hypothetical process design, and only shows the streams that contain the target species. The arrows represent the flow. More than one arrow arising from a single source represents the separation of the stream into multiple streams, and implies that the target species is in each. Multiple arrows into a single source means several flows are feeding a mixer or reactor.

In general, streams with higher target-species compositions or higher flowrates — such as Streams 3 and 4 in Figure 4 — are the most-cost-effective candidates for mass exchange or stream-management techniques.

When the goal is to reduce the concentration of a target species (i.e., Pollutant X) from a source (waste) stream or streams using a mass-exchange system, a *mass-pinch diagram* (Figure 5) can be used to evaluate the options. While construction of such a diagram is beyond the scope of this article, a discussion of Figure 5 may be illustrative. In that figure, the curves on the left show the feasibility ranges for two different MSAs (in terms of the amount of Pollutant X each can remove). The curve on the right shows the feasible range over which Pollutant X can be reduced in a given combination of source streams. The pinch point, where the two curves are closest, is the most cost-effective, thermodynamically desirable point at which to apply mass exchange. ■

Edited by Suzanne Shelley

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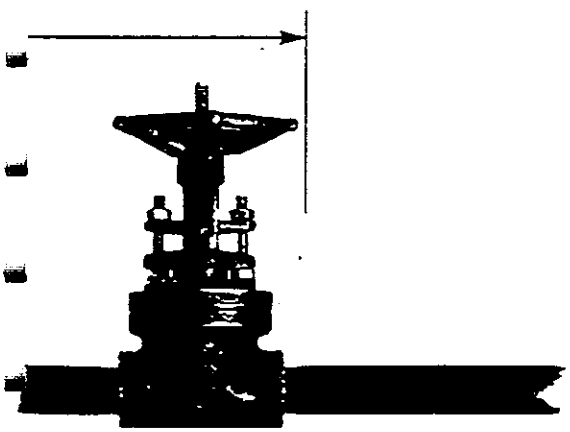

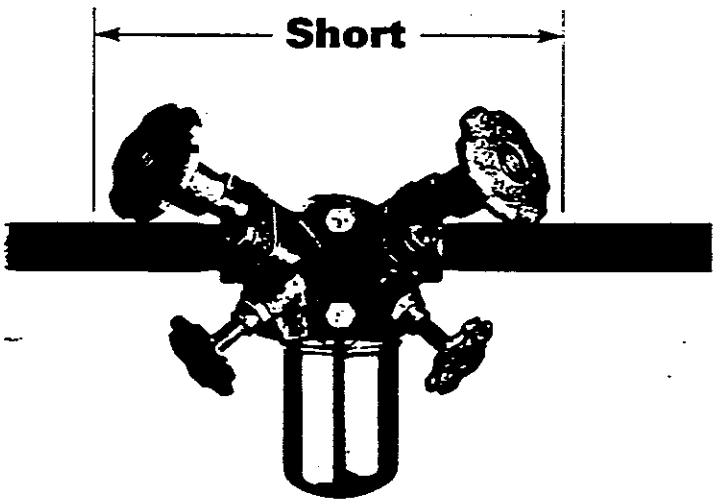

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Pollution Prevention with Chemical Process Simulators: The Generalized Waste Reduction (WAR) Algorithm-Full Version

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Abstract - A general theory for the flow and the generation of potential environmental impact through a chemical process has been developed. The theory defines six potential environmental impact indexes that characterize the generation of potential impact within a process, and the output of potential impact from a process. The indexes are used to quantify pollution reduction and to develop pollution reducing changes to process flow sheets using process simulators. The potential environmental impacts are calculated from stream mass flow rates, stream composition, and a relative potential environmental impact score for each chemical present. The chemical impact scores include a comprehensive set of nine effects ranging from ozone depletion potential to human toxicity and ecotoxicity. The resulting Waste Reduction methodology or WAR Algorithm is illustrated with two case studies using the chemical process simulator Chemcad III (Use does not imply USEPA endorsement or approval of Chemcad III).

INTRODUCTION

There is currently a great deal of interest in the development of methods that can be used to prevent or at least minimize the generation of pollution; and there are numerous efforts underway in this area (Lederman and Weber, 1991; El-Halwagi, *et al.* 1992; Fonyo, *et al.*, 1994; Rossiter, 1995; Manousiouthakis and Allen, 1995; Mallick *et al.*, 1996). This interest stems from the belief that pollution prevention is likely to lead to the creation of technologies that have a much more benign impact on human health and the environment. Because this technology is inherently less polluting, it is likely to be more robust and economical than simply adding pollution control devices to conventional designs. In chemical manufacturing, these pollution prevention methods take the form of an effort to design process plants that generate as little pollution as possible. Since chemical process simulators are widely used in the design and operation of chemical manufacturing plants, the development of a pollution prevention methodology for chemical process simulators is likely to have a significant impact on the pollution generated by the chemical industry. At the National Risk Management Research Laboratory, research efforts are underway to develop a methodology for commercial chemical process simulators. The research effort is called the WAste Reduction or WAR Algorithm after Hilaly and Sikdar (1994) who performed some of the early work in this area.

This paper presents a generalization of the WAR Algorithm, discusses the methodology for evaluating potential environmental impacts, and illustrates the use of the method in the design or modification of chemical processes with two case studies.

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ENVIRONMENTAL IMPACT THEORY

Potential environmental impact is the unrealized effect or impact that the emission of mass and energy would have on the environment on average. It is, therefore, essentially a probability function for the realization of a potential effect. Thus, the potential environmental impacts of chemical manufacturing processes are generally caused by the energy and material that the process takes from or emits to the environment. Potential environmental impact is a conceptual quantity that can not be directly measured, *i.e.*, there are no potential environmental impact meters. However, one can calculate potential environmental impact from related measurable quantities using functional relations between the two. This situation is common in science and engineering. For example, the energy of a fluid can not be directly measured, but it can be calculated from temperature and pressure by the use of heat capacities and equations of state. Exactly how to perform a calculation for potential environmental impacts will be discussed later in this paper.

Conservation Equation

Traditionally, chemical process design has been based on the creative application of mass and energy balances along with thermodynamics, chemical reaction engineering, and engineering economics. Our methodology proposes to add a conservation relation over potential environmental impact to the aforementioned two balance equations. The conservation equation for impacts is based on an accounting of the flow of potential environmental impact in and out of the processes. This flow of impact is related

to the mass and energy flows but it is not equivalent to them. The impact conservation equation is

$$\frac{dI_{syst}}{dt} = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (1)$$

where I_{syst} is the potential environmental impact content inside a process, $\dot{I}_{in}$ is the input rate of impact, $\dot{I}_{out}$ is the output rate of impact, and $\dot{I}_{gen}$ is the rate at which impact is generated in the system by chemical reactions or other means. Note that processes can also consume potential environmental impact so that $\dot{I}_{gen}$ can, in fact, be negative. For steady state processes, the conservation equation reduces to,

$$0 = \dot{I}_{in} - \dot{I}_{out} + \dot{I}_{gen} \qquad (2)$$

which implies that no potential environmental impact accumulates in the system. Also note that Equations (1) and (2) serve as definitions of the function $\dot{I}_{gen}$.

The significance of potential environmental impacts can be better understood by considering the following definitions. If one were to dump into the environment all of the mass and energy flows entering a process, the resulting impact on the environment would equal to I_{in}; if one were to also dump into the environment all of the mass and energy flows exiting a process the resulting impact on the environment would be equal to I_{out}. However, due to chemical transformations and changes in state conditions (temperature and pressure), I_{in} is never exactly equal to I_{out}, and consequently I_{gen} is never exactly equal to zero for steady state processes.

Chemical Processes

Application of either Equation (1) or (2) to chemical manufacturing processes requires an expression that relates the conceptual potential environmental impact to measurable quantities. Potential environmental impacts are caused by energy and material inputs and outputs to or from the environment. But, as a first approach, this treatment is restricted to potential impacts due to material flows while neglecting any impacts due to energy. Effects due to energy flows can be incorporated into the analysis by extending the boundary over which the impact balance is done to include the energy generation process. Effects due to resource depletion are also neglected mainly because there is no effective methodology for measuring them. This is consistent with the focus of this work which is the chemical process plant rather than a global life-cycle type of analysis. The expression relating potential chemical environmental impacts to measurables is

$$\dot{I}_i = \sum_j \dot{I}_j^{(i)} = \sum_j \dot{M}_j^{(i)} \sum_k x_{kj}\psi_j + \cdots \qquad (3)$$

where the sum over j is taken over the streams of input i or output i, the sum over k is taken over all chemicals k, $\dot{I}_i$ is the rate of potential environmental impact either in (i=in) or out of the process (i=out), $\dot{I}_j^{(i)}$ is the rate of potential environmental impact for stream j which may be an input or an output, $\dot{M}_j^{(i)}$ is the mass flow rate of stream j which may again be either an input or an output, x_{kj} is the mass fraction of chemical k in stream j, and ψ_j is the overall potential environmental impact of chemical j.

Note that Equation (3) is a first order approximation that does not include the synergistic effects that can occur when multiple chemicals are present.

Impact Indexes

For steady state processes one can use Equation (2) to define two categories of indexes for the environmental impact of chemical manufacturing. The first category of indexes measures the generation of potential environmental impact within processes, and the second one measures the potential environmental impact emitted by processes. There are various indexes that can be defined within each category. However, only the six indexes, three from each category, that seem most useful for waste reduction will be treated here.

Following Hilaly and Sikdar (1994), all non-products are considered to be pollutants and the potential environmental impact of all products is set to zero, *i.e.*, ψ_j=0 for all products j. These assumptions are consistent with the objective of this paper which is to present a methodology for waste reduction, *i.e.*, the primary concern is reducing the impact and the amount of the non-products. The broader implications of Equation (1), including other impact indexes for which $\psi_j \neq 0$ for products j and further conjectures on the implications for sustainability, will the subject of future publications.

The first index of the first category of indexes (impact generation) is obtained by solving Equation (2) for $\dot{I}_{gen}$ and adding the superscript NP for Non-Products to give,

$$\dot{I}_{gen}^{NP} = \dot{I}_{out}^{NP} - \dot{I}_{in}^{NP} \qquad (4)$$

where $\dot{I}_{out}^{NP}$ and $\dot{I}_{in}^{NP}$ are the potential environmental impacts due to non-products, *i.e.*, pollutants in the outputs and inputs, respectively. Equation (3) is used to give explicit expressions for $\dot{I}_{out}^{NP}$ and $\dot{I}_{in}^{NP}$ where all components, products and non-products, are included in the summation, but where ψ_j=0 for all products j which effectively removes all products from the summation. The index, $\dot{I}_{gen}^{NP}$, measures the total rate at which the process generates potential environmental impact due to non-products (NP). $\dot{I}_{gen}^{NP}$ has units of potential environmental impact generated per time.

The second index, $\hat{I}_{gen}^{NP}$, of the first category is obtained by dividing Equation (4) by the rate at which the process generates products to give a specific impact generation,

$$\hat{I}_{gen}^{NP} = \frac{\dot{I}_{gen}^{NP}}{\sum_p \dot{P}_p} = \frac{\dot{I}_{out}^{NP} - \dot{I}_{in}^{NP}}{\sum_p \dot{P}_p} \qquad (5)$$

where the sum over p is taken over all the products p, and $\dot{P}_p$ is the mass flowrate of product p. $\hat{I}_{gen}^{NP}$ measures the potential impact created by all non-products in manufacturing a unit mass of all the products p. The index, $\hat{I}_{gen}^{NP}$, has units of potential environmental impact per mass of products.

The third index of the first category, $\hat{M}_{gen}^{NP}$, is obtained from Equation (5) by setting the potential environmental impact (ψ_j) of all products to zero and that of all non-products to one. This has the effect of assigning the same potential environmental impact to all non-products. The index, $\hat{M}_{gen}^{NP}$, is a measure of the mass inefficiency of the

process, *i.e.*, it gives the ratio of mass converted to an undesirable form to mass converted to a desirable form. The expression for $\hat{M}_{gen}^{NP}$ is

$$\hat{M}_{gen}^{NP} = \frac{\sum_j \dot{M}_j^{(out)} \sum_k x_{kj}^{NP} - \sum_j \dot{M}_j^{(in)} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}_p} \quad (6)$$

where the summation over $\dot{M}_j^{(out)}$ is taken only over output streams, the summation over $\dot{M}_j^{(in)}$ is taken only over input streams, and the summation over x_{kj}^{NP} is taken only over all non-products k in stream j. The units of $\hat{M}_{gen}^{NP}$ are mass of non-products per mass of products.

The first index of the second category of indexes (impact emission) $\dot{I}_{out}^{NP}$ is simply the total rate of potential environmental impact output due to non-products. $\dot{I}_{out}^{NP}$ is calculated from Equation (3) subject to ψ_j=0 for all products j. The index, $\dot{I}_{out}^{NP}$, is a measure of the rate at which the process emits potential environmental impact, and it has units of potential environmental impact per time.

The second index of the second category, $\hat{I}_{out}^{NP}$, is obtained by dividing the rate of potential environmental impact output due to non-products by the output rate of products to give,

$$\hat{I}_{out}^{NP} = \dot{I}_{out}^{NP} \Big/ \sum_p \dot{P}_p \quad (7)$$

The index, $\hat{I}_{out}^{NP}$, has units of potential environmental impact per mass of products. This expression gives the pollution index Φ of Mallick *et al.* (1996) which measures the potential environmental impact emitted in manufacturing a unit mass of products.

The third index of the second category, $\hat{M}_{out}^{NP}$, is obtained from Equation (7) by setting the potential environmental impact (ψ_j) of all products to zero and that of all non-products to one. The resulting expression is,

$$\hat{M}_{out}^{NP} = \frac{\sum_j \dot{M}_j^{(out)} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}_p} \quad (8)$$

which is related to the pollution index ϕ_n of Hilaly and Sikdar (1994) by,

$$\hat{M}_{out}^{NP} = \sum_n \phi_n \quad (9)$$

where the summation is taken over all products n. $\hat{M}_{out}^{NP}$ measures the amount of non-product or pollutant mass emitted in manufacturing a unit mass of products, and it has units of non-product mass per mass of products. It is also a mass inefficiency measure.

Significance of Impact Indexes

The first category of indexes, *e.g.*, $\dot{I}_{gen}^{NP}$, $\hat{I}_{gen}^{NP}$, and $\hat{M}_{gen}^{NP}$, characterize some aspects of the generation of potential environmental impact within a manufacturing process. They are most useful in addressing questions related to the internal environmental efficiency of the process plant, *i.e.*, the ability of the plant to produce desired products while creating a minimum of new, undesired potential environmental impact. It is important to note that once new potential environmental impact is created, resources such as potentially costly remediation efforts will likely be required to prevent the potential impact from being realized. Obviously, the smaller the values of $\dot{I}_{gen}^{NP}$, $\hat{I}_{gen}^{NP}$, and $\hat{M}_{gen}^{NP}$ the more environmentally efficient the process, and, all others factors such as economics being equal, the more desirable. $\dot{I}_{gen}^{NP}$ would be useful in comparing different designs on an absolute basis, while $\hat{I}_{gen}^{NP}$ and $\hat{M}_{gen}^{NP}$ would be useful in comparing different designs independently of manufacturing plant size.

The second category of indexes, *e.g.*, $\dot{I}_{out}^{NP}$, $\hat{I}_{out}^{NP}$, and $\hat{M}_{out}^{NP}$ characterize some aspects of the emission of potential environmental impact from a manufacturing process. Their principal use is in addressing questions related to the external environmental efficiency of the process plant, *i.e.*, the ability of the plant to produce desired products while inflicting on the environment a minimum of undesired potential environmental impact. It is again obvious that the smaller the values of $\dot{I}_{out}^{NP}$, $\hat{I}_{out}^{NP}$, and $\hat{M}_{out}^{NP}$ the more environmentally efficient the process, and all other factors such as economics being equal, the more desirable it is. Since $\dot{I}_{out}^{NP}$ is a total rate of impact output, it could be useful in deciding whether a given plant is compatible with a particular site. For example, it would be unwise to locate a plant with a high $\dot{I}_{out}^{NP}$ in an ecologically sensitive area. $\dot{I}_{out}^{NP}$ could also be used in matching the size of a plant to the capacity of the surrounding environment to dissipate environmental impact. $\hat{I}_{out}^{NP}$ and $\hat{M}_{out}^{NP}$ are more useful in comparing the potential environmental impact of alternative processes independently of plant size.

CHEMICAL ENVIRONMENTAL IMPACT

Application of the methodology so far developed requires that the potential environmental impacts of chemicals be estimated. Further, it is required that a relative impact number ψ_j be given for each chemical j over a wide range of different chemical environmental impacts. This is, unfortunately, not a trivial matter because chemical impacts are measured on different relative scales that can not be simply added without some form of normalization.

Chemical Impact Expression

To apply the WAR methodology to chemical processes, the following expression for ψ_j has been developed (Mallick *et al.*, 1996),

$$\psi_j = \sum_l \alpha_l \psi_{j,l}^{s} \quad (10)$$

where the sum is taken over categories of potential chemical environmental impacts, e.g., ozone depletion potential, human health, etc. listed below under *Classification of Impacts*. α_l is a relative weighting factor for impact of type l independent of chemical j, and $\psi_{j,l}^{s}$ is the specific potential environmental impact of chemical j for an impact of type l. α_l has units of potential environmental impact per mass.

The relative weighting factor α_l allows Equation (10) to be customized to specific or local conditions. The suggested procedure is to initially set all the α_l's to same value of say one, and to allow users to vary individual α_l's from 0 to 10 according to local needs and policies.

Please note that for a relative comparison, the absolute value is not critical. For example, photochemical oxidation potential would be weighted more heavily than other impacts in an area that suffers from smog. There is an effort underway in our research group to develop more sophisticated methods of determining values for the α_j's. The values for the $\psi^s_{j,l}$ were obtained from the relative rankings or scores for chemicals by normalizing according to,

$$\psi^s_{i,j} = \frac{(Score)_{i,j}}{\langle (Score)_i \rangle_j + 2\sigma_j} \qquad (11)$$

where $(Score)_{i,j}$ is the relative score of chemical i on some arbitrary scale within impact category j, $\langle (Score)_i \rangle_j$ is the arithmetic average of the scores of all chemicals i within impact category j, and σ_j is the standard deviation of all the chemical scores in impact category j. The normalizing factor $\langle (Score)_i \rangle_j + 2\sigma_j$ assures that about 75% of the normalized chemical score numbers $\psi^s_{j,l}$ will be between 0 and 1 irrespective of the statistical distribution of the initial scores as expected from Chebyshev's theorem (Lapin, 1975). If the chemical scores happen to follow a normal distribution, then the normalization range extends to approximately 95% of the scores.

Classification of Impacts

The classification of chemical environmental impacts and the values for the $(Score)_{i,j}$ were adopted from the study of Heijungs *et al.* (1992)* and normalized according to Equation (11) to obtain the $\psi^s_{j,l}$'s. In the calculation of $\langle (Score)_i \rangle_j$ and σ_j, the chemical scores for dioxin, chromium VI, and vinyl chloride were excluded. The reason is that the score numbers for these three chemicals were several orders of magnitude higher that those for all other chemicals, and including them in the normalization process would have made the normalization meaningless. Therefore, the normalized $\psi^s_{j,l}$ for these three chemicals would appear as outliers which they, in fact, are.

Table 1: Normalized Chemical Impact Scores

	H2	MEK	SBA	H2O
$\psi^s_{j,l}$	0	0.42	4.1E-4	0
	N2	Ar	CH4	NH3
$\psi^s_{j,l}$	0	0	7.4E-3	0.93

There are nine different impact categories. These can be subdivided into four environmental physical potential effects (acidification, greenhouse enhancement, ozone depletion, and photochemical oxidant formation), three human toxicity effects (air, water, and soil), and two ecotoxicity effects (aquatic and terrestrial).

The normalized chemical scores used in the two case studies presented in the next sections are given in Table 1 above where H2 is hydrogen, MEK is methyl ethyl ketone, SBA is secondary butyl alcohol, H2O is water, N2 is molecular nitrogen, Ar is argon, CH4 is methane, and NH3 is ammonia. These acronyms will be used throughout the rest of the paper.

* Use by the authors does not imply endorsement or approval by the U.S. Environmental Protection Agency.

CASE STUDY #1: MEK PRODUCTION

To illustrate the use of the generalized WAR Algorithm, a case study from the production of methyl ethyl ketone (MEK) from secondary butyl alcohol (SBA) is presented. The case study was adopted from the Chemcad III (Chemstations, Inc.) chemical process simulator, and all the material and energy balances were performed using Chemcad III. However, any commercial process simulator could have been used. This case study presents a typical chemical engineering process for the production of a commodity chemical that involves several unit processes such as reactors, separators, mixers, dividers, and heat exchangers. It is, therefore, sufficiently complex to illustrate the WAR Algorithm but still treatable within the space of this paper. Essentially, the chemical process consists of a SBA dehydrogenation reactor followed by a MEK purification train and associated equipment.

Base Flowsheet

Figure 1 shows the base process flow diagram for the production of MEK from SBA. SBA is fed to a hydrogen scrubber where the feed SBA scrubs residual MEK from the hydrogen stream. The SBA feed is then pumped up to reaction pressure and heated to reaction temperature with a heat exchanger and a heater. The heated SBA is fed to the reactor where the chemical transformation occurs. The

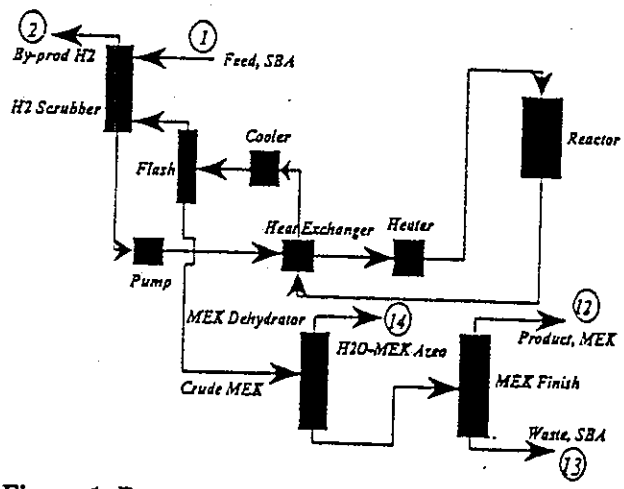

Figure 1. Base process flow diagram for the production of methyl ethyl ketone from secondary butyl alcohol.

Table 2: MEK Production Flow Summary (kg/hr)
Input & Output: Base Process

Stream (State)	# 1 (L)	# 2 (G)	# 12 (L)	# 13 (L)	# 14 (G)
SBA	3362	19	3	2670	1
MEK	0	0	567	13	71
H2O	8	0	0	0	8
H2	0	18	0	0	0

reactor output stream is sent to a heat exchanger where it is partially condensed. The mixture of MEK, hydrogen, and unconverted SBA is cooled further and sent to a separator where the hydrogen is flashed off. The hydrogen is then scrubbed and the liquid phase fed to a MEK purification system. The mass flow rates and the state of the various input and output streams as calculated by Chemcad III are listed in Table 2 above.

Modified Flowsheet

Examination of the base process indicates that waste stream 13 contains large amounts of unreacted SBA and small amounts of MEK. It is, therefore, logical to try to recover the SBA and MEK as the first step in a waste reduction strategy. Consequently, the process flow diagram was modified by the addition of a recycle from

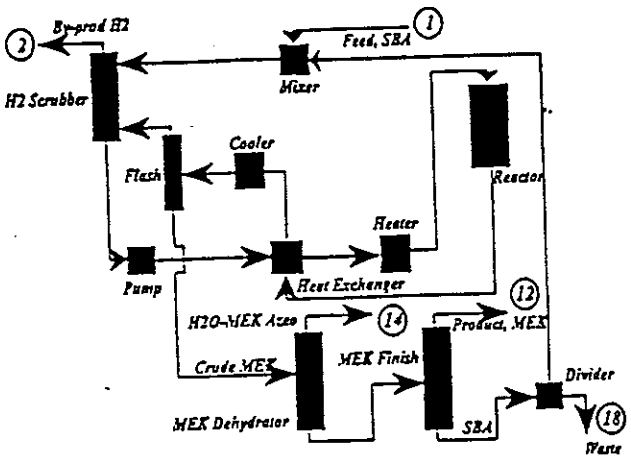

Figure 2. Modified process flow diagram for the production of methyl ethyl ketone from secondary butyl alcohol.

stream 13 to the feed, stream 1. Two cases were studied with this modification, recycling 50% and 100% of stream 13. Recycling 100% of stream 13, *i.e.*, closing off stream 18, is appropriate for this illustration. But, it is clearly not practical because stream 18 is the only liquid waste stream in the modified process and the only means of purging the system of liquid impurities. Without this purge, impurities would build up inside the process causing it to eventually cease to function. Figure 2 above shows the flow diagram for the modified process. The mass flow rates and the state of the various input and output streams for the modified process with 50% recycle are listed in Table 3

Table 3: MEK Production Flow Summary (kg/hr)
Input & Output: Modified Process (50% Recycle)

Stream (State)	# 1 (L)	# 2 (G)	# 12 (L)	# 14 (G)	# 18 (L)
SBA	3362	168	5	1	2124
MEK	0	1	980	64	10
H2O	8	2	0	6	0
H2	0	29	0	0	0

The process modification increased the amount of product by approximately 73% while reducing the amount of waste SBA in stream 18 by about 20%.

It is important to note that an examination of Tables 2, 3, and 4 will indicate that waste was generally reduced, and that environmental impact was probably also reduced. However, the information so far considered is not sufficient to allow a quantitative comparison of the overall waste and environmental impact reduction associated with each of the three cases studied here. For this comparison one must calculate the impact indexes already described. For the modified process with 100% recycle, the mass flow rates and the state of the various input and output streams are listed in Table 4 below. Note that increasing the recycle increased the amount of product by 269% while simultaneously reducing the amount of waste SBA in stream 13 to zero.

Table 4: MEK Production Flow Summary (kg/hr)
Input & Output: Modified Process (100% Recycle)

Stream (State)	# 1 (L)	# 2 (G)	# 12 (L)	# 14 (G)
SBA	3362	1117	11	1
MEK	0	11	2094	59
H2O	8	3	0	5
H2	0	60	0	0

Impact Index Calculations

Six different impact indexes were calculated for the base case and the two modified processes each. The indexes were obtained using Equations (3) to (8), the flow rates from Tables 2, 3, and 4, Equation (10), and the normalized chemical impact scores of Table 1. The relative weighting factors, α_i, were all set to one for these calculations.

The first category indexes, *i.e.*, the impact generation indexes, $\dot{I}^{NP}_{gen}$, $\hat{I}^{NP}_{gen}$, and $\hat{M}^{NP}_{gen}$, are shown on Figure 3 below. It should be noted that $\hat{M}^{NP}_{gen}$ is a negative number since some of the input mass is always converted to product, and the products are not included in the summation of the outputs. The specific indexes, $\hat{I}^{NP}_{gen}$ and $\hat{M}^{NP}_{gen}$, were multiplied by a factor of 100 so that they could be shown on the same scale as the rate index $\dot{I}^{NP}_{gen}$.

The second category indexes, *i.e.*, the impact output indexes $\dot{I}^{NP}_{out}$, $\hat{I}^{NP}_{out}$, and $\hat{M}^{NP}_{out}$, are shown in Figure 4. The specific index $\hat{I}_{out}$ was multiplied by a factor of 1000, and the specific index $\hat{M}^{NP}_{out}$ was multiplied by a factor of 10 so that they could both be shown on the same scale as $\dot{I}^{NP}_{out}$.

The largest source of uncertainty in the calculation of the impact indexes is the environmental impact scores. These measurements are probably accurate to no more than one significant figure or an order of magnitude. It is, therefore, prudent to assume that impact index calculations are also accurate to no more than one significant figure. Two significant figures are used in Figures 3 and 4 in order to help the readers to reproduce the calculations, if necessary.

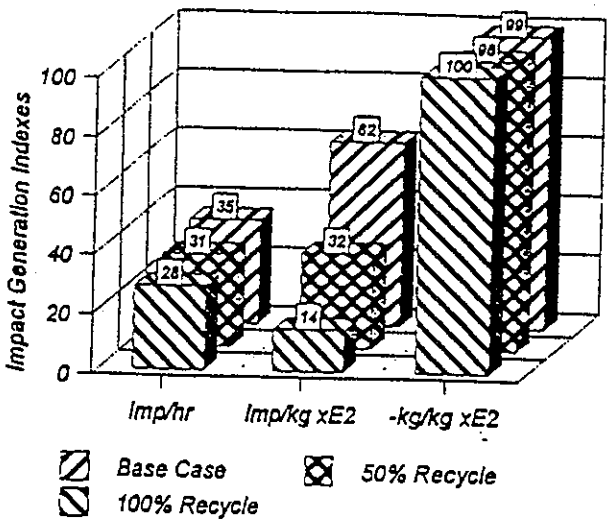

Figure 3. Impact generation indexes for the production of methyl ethyl ketone from secondary butyl alcohol: $\dot{I}_{gen}^{NP}$ in impact units per hour, $\hat{I}_{gen}^{NP}$ in impact units per kilogram of product, and $-\hat{M}_{gen}^{NP}$ in kilograms of pollutants per kilogram of product.

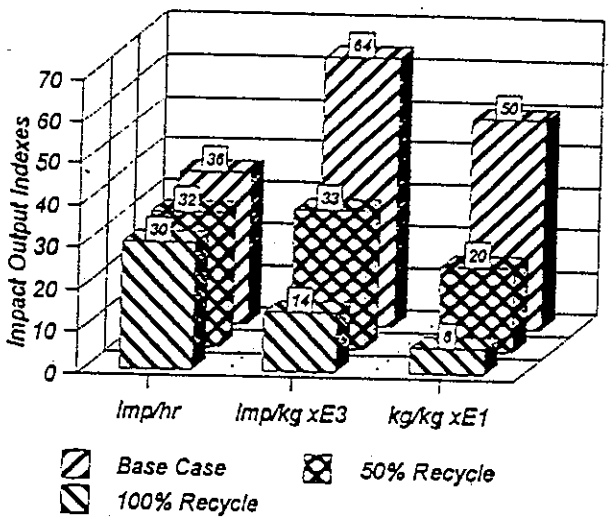

Figure 4. Impact output indexes for the production of methyl ethyl ketone from secondary butyl alcohol: $\dot{I}_{out}^{NP}$ in impact units of pollutants per hour, $\hat{I}_{out}^{NP}$ in impact units of pollutants per kilogram of products, and $\hat{M}_{out}^{NP}$ in kilograms of pollutants per kilogram of products.

DISCUSSION OF CASE STUDY #1

The impact generation indexes of Figure 3 show that: (1) the rate of impact generation by non-products decreases by 13% for 50% recycle and by 20% for 100% recycle, (2) the impact generated by non-products per kilogram of product decreases by 48% for 50% recycle and by 77% for 100% recycle, and (3) the kilograms of non-products generated per kilogram of product remains nearly constant at -100. The most significant index in this case is the impact generated per kilogram of product. The decrease of this index reflects the increase in the productivity of the plant, *i.e.*, the increase in product flow rate.

The impact output indexes of Figure 4 show that: (1) the rate of impact output from non-products decreases by 11% for 50% recycle and by 17% for 100% recycle, (2) the impact output from non-products per kilogram of product decreases by 48% for 50% recycle and by 78% for 100% recycle, and (3) the output of kilograms of non-product per kilogram of product decreases by 60% for 50% recycle and by 88% for 100% recycle. It is worth noting that the output of impact and waste decreased as measured by all the indexes. The most significant index in this case is the impact output per kilogram of product. The decrease in this index is consistent with the decrease in the impact generation per mass of product index discussed in the paragraph above. This decrease is also a reflection of the increased productivity of the plant.

The decreases in the indexes are sufficiently large such that they represent significant reductions in pollution. The consistent decrease in the impact generation per mass of product (48% to 77%) and the impact output per mass of product (48% to 78%), simply means that the modified plant can meet the needs of a much larger market without increasing its generation or its output of potential environmental impact. It also means that a modified plant that is 48% to 77% smaller than the base case can meet the needs of the same market that the base plant was designed for.

CASE STUDY#2: AMMONIA PRODUCTION

To further illustrate the use of the generalized WAR Algorithm, a second case study from the production of ammonia from synthesis gas is presented. The case study was also adopted from the Chemcad III (Chemstations, Inc.) chemical process simulator, and all the material and energy balances were performed using Chemcad III. However, any commercial process simulator could again have been used. Just as Case Study #1, this case study also presents a typical chemical engineering process that involves several unit processes such as reactors, separators, mixers, dividers, and heat exchangers. It is also sufficiently complex to illustrate the WAR algorithm but still treatable within the space of this paper.

Base Flowsheet

Figure 5 shows the base process flow diagram for the process. Essentially, the overall process is based on the reaction of nitrogen and hydrogen to produce ammonia. The mixture of hydrogen and nitrogen is compressed and

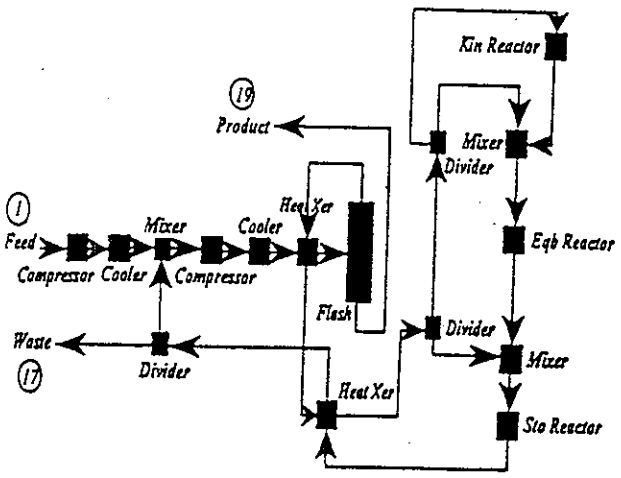

Figure 5. Base process flow diagram for the production of ammonia from synthesis gas.

cooled and feed to a series of three reactors through a flash drum. Several reactors are normally used the to maximize the conversion of feed to products which for this process is difficult to do. This flash drum also serves to separate the ammonia product from the unreacted gases which are feed back into the system. The ammonia is recovered as an anhydrous liquid under modest pressure. The mass flow rates and the state of the input and output streams as calculated by Chemcad III are all listed in Table 5.

Table 5: Ammonia Production Flow Summary (kg/hr)
Input & Output: Base Process (Purge Ratio = 0.1)

Stream (State)	# 1 (G)	#17 (G)	# 19 (L)
N2	33,334	5060	187
Ar	603	428	176
H2	7196	1120	13
CH4	805	700	112
NH3	0	3696	30453

Modified Flowsheet

Examination of the base process indicates that waste stream 17 contains ammonia and some unreacted feed. It is, therefore, logical to try to recover the ammonia and the unreacted feed as an obvious first step in a waste reduction strategy. Consequently, the process flow diagram was modified in two ways. First, the purge ratio was reduced five fold from 0.1 to 0.02, *i.e.*, the flow of stream 17 was reduced five fold. Second, in addition to reducing the purge, a flash drum was added with stream 17 as the feed to recover some of the ammonia.

Table 6: Ammonia Production Flow Summary (kg/hr)
Input & Output: Modified Process (Purge Ratio = 0.02)

Stream (State)	# 1 (G)	#17 (G)	# 19 (L)
N2	33,334	1162	217
Ar	603	199	404
H2	7196	281	16
CH4	805	446	351
NH3	0	856	38001

Figure 5 shows the configuration of the flow diagram for the reduced purge modified process which is identical to that of the base process. The mass flow rates and the state of the input and output streams for the reduced purge modified process are listed in Table 6. The process modification increased the amount of product by approximately 25% while reducing the amount of waste ammonia in stream 17 by about 77%. It is worth noting, however, that there was an small increase in the impurities present in the product stream. This changed from about 2% impurities in the base case to 3% for the reduced purge modified case.

Figure 6 shows the flow diagram for the modified process with reduced purge and addition of a flash drum with stream 17 as the feed. Under this configuration, stream 25 is used to purge impurities from the system. Without this purge, impurities would again build up inside the process, and it would eventually cease to function. Stream 24 which consists of essentially pure ammonia is mixed with stream 19 to form a new product stream, stream 26.

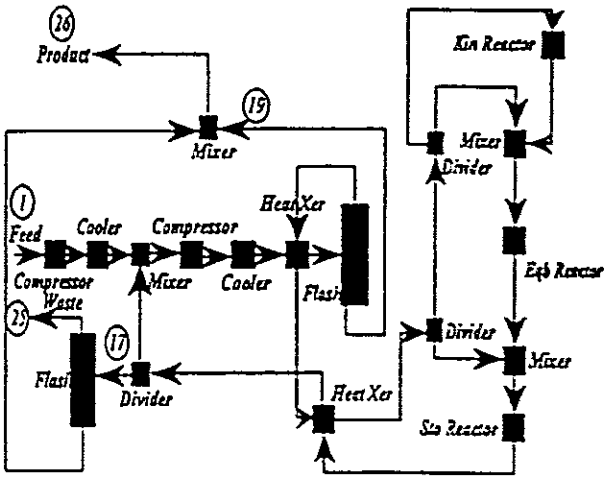

Figure 6. Modified process flow diagram for the production of ammonia from synthesis gas with reduced purge ratio and added flash drum.

The mass flow rates and the state of the various input and output streams are listed in Table 7. Note that adding the flash drum in addition to reducing the purge five fold increased the amount of product by 26% as compared to the base case. This is very close to the 25% increase in product that was obtained by simply reducing the purge. However, the amount of waste ammonia in stream 25 was reduced by 91%, and the amount of total waste in stream 25 was reduced by 78%, both compared to the base case. As compared to the reduced purge process, the addition of the flash drum increased the amount of product by a meager 1%, but it reduced the amount of waste ammonia by 61% and total amount of waste by 18%, both in stream 25. Therefore, the principal effect of adding the flash drum was the reduction of waste.

Table 7: Ammonia Production Flow Summary (kg/hr)
Input & Output: Modified Process
(Purge Ratio = 0.02 & Flash Drum)

Stream (State)	# 1 (G)	#25 (G)	# 26 (L)
N2	33,334	1162	217
Ar	603	199	404
H2	7196	281	16
CH4	805	447	351
NH3	0	335	38,521

An examination of Tables 5, 6, and 7 will again show that waste was generally reduced, that the amount of product made was increased, and that environmental impact of the process was probably also reduced. However, one finds that it is not sufficient to allow a quantitative comparison of the overall waste and environmental impact associated with each of the three cases. In a simple example such this one the task is confusing, but for complex chemical process it can become impossible. For this comparison one must calculate the impact indexes.

Impact Index Calculations

Again, six different impact indexes were calculated for the base and the two modified processes. The indexes were also obtained using Equations (3) to (8), the flow rates from Tables 5, 6, and 7, Equation (10), and the normalized chemical impact scores of Table 1. The relative weighting factors α_i were all set to one for these calculations.

The first category indexes, *i.e.*, the impact generation indexes, $\dot{I}_{gen}^{NP}$, $\hat{I}_{gen}^{NP}$, and $\hat{M}_{gen}^{NP}$, are shown on Figure 7. It should be noted that $\hat{M}_{gen}^{NP}$ is a negative number since some of the input mass is always converted to product, and the products are not included in the summation of the outputs. The specific index, $\hat{I}_{gen}^{NP}$, was multiplied by a factor of 10,000, and the index, $\hat{M}_{gen}^{NP}$, was multiplied by a factor of 1,000 so that they could both be shown on the same scale as the rate index $\dot{I}_{gen}^{NP}$.

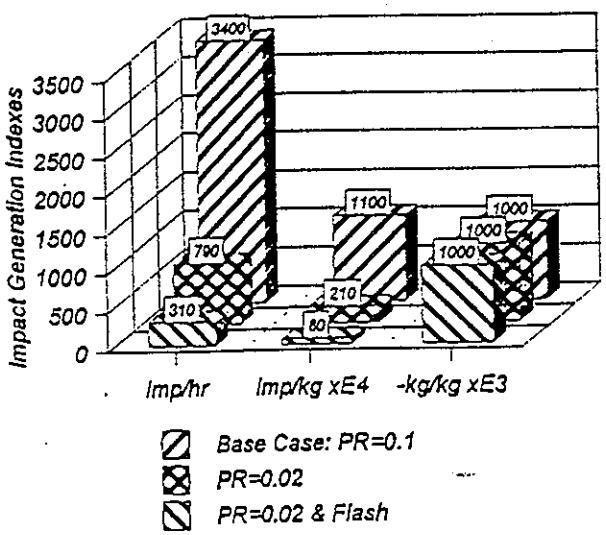

Figure 7. Impact generation indexes for the production of ammonia from synthesis gas: $\dot{I}_{gen}^{NP}$ in impact units per hour, $\hat{I}_{gen}^{NP}$ in impact units per kilogram of product, and $-\hat{M}_{gen}^{NP}$ in kilograms of pollutants per kilogram of product. PR is the purge ratio.

The second category indexes, *i.e.*, the impact output indexes, $\dot{I}_{out}^{NP}$, $\hat{I}_{out}^{NP}$, and $\hat{M}_{out}^{NP}$, are shown in Figure 8. The specific index $\hat{I}_{out}^{NP}$ and the specific index $\hat{M}_{out}^{NP}$ were both multiplied by a factor of 10,000 so that they could be shown on the same scale as $\dot{I}_{out}^{NP}$.

The largest source of uncertainty in the calculation of the impact indexes are again the environmental impact scores. These measurements are probably accurate to no more than one significant figure or an order of magnitude, and it is, therefore, prudent to assume that impact index calculations are also accurate to no more than one significant figure. Two significant figures are presented in Figures 7 and 8 in order to allow readers to reproduce the calculations if necessary.

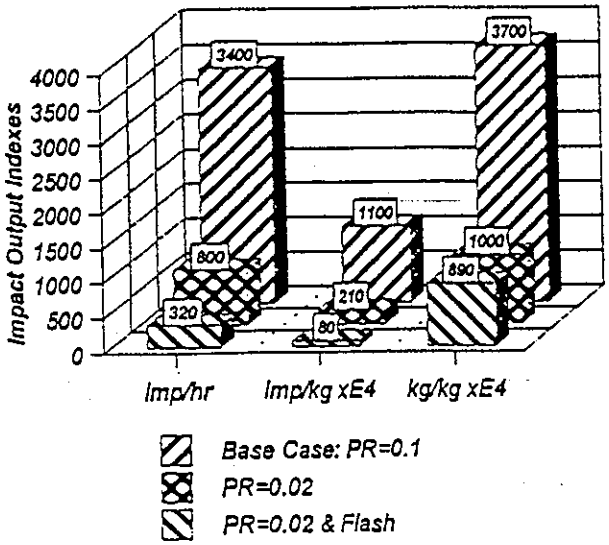

Figure 8. Impact output indexes for the production of ammonia from synthesis gas: $\dot{I}_{out}^{NP}$ in impact units of pollutants per hour, $\hat{I}_{out}^{NP}$ in impact units of pollutants per kilogram of products, and $\hat{M}_{out}^{NP}$ in kilograms of pollutants per kilogram of products. PR is the purge ratio.

DISCUSSION OF CASE STUDY #2

The impact generation indexes of Figure 7 show that: (1) the rate of impact generation by non-products decreases by 77% when the purge ratio is decreased from 0.1 to 0.02 and by 91% when the purge ratio is decreased as above and a flash drum is added to recover waste ammonia, (2) the impact generated by non-products per kilogram of product decreases by 81% when the purge ratio is reduced from 0.1 to 0.05 and by 93% when the purge ratio is decreased as above and a flash drum is added, and (3) the kilograms of non-products generated per kilogram of product remained nearly constant at -1 for all cases. The most significant index in this case is the impact generated per kilogram of product. The decrease of this index reflects primarily the recovery of the waste product and to a smaller extent the increase in the productivity of the plant, *i.e.*, the increase in product flow rate.

The impact output indexes of Figure 8 show that: (1) the rate of impact output from non-products decreases by 76% when the purge ratio is decreased from 0.1 to 0.02 and by 91% when the purge ratio is decreased as above and a flash drum is added to recover waste ammonia, (2) the impact output from non-products per kilogram of product decreases by 81% when the purge ratio is reduced from 0.1 to 0.05 and by 93% when the purge ratio is decreased as above and a flash drum is added, and (3) the output of kilograms of non-product per kilogram of product decreases by 73% when the purge ratio is reduced from 0.1 to 0.05 and by 76% when the purge ratio is decreased as above and a flash drum is added. It is again worth noting that the output of impact and waste decreased as measured by all the indexes. The most significant index

in this case is the impact output per kilogram of product. The decrease in this index was the same as that for the equivalent generation index. This is a reflection of the change in the index being primarily driven by the recovery of waste product rather than increased productivity.

The decreases in the indexes are again sufficiently large that they represent significant reductions in pollution. The consistent decrease in the impact generation per mass of product and impact output per mass of product (81% to 93%) implies that the modified plant can meet the needs of a moderately larger market with much less impact on the environment. The decrease in the rate of impact generation and impact output (76% to 91%) means that the modified process has an environmental impact that is roughly one tenth that of the base plant. Lastly, the decrease in the output of waste mass per mass of product indicates that the modified plant will lose less valuable material in its operation.

FUTURE WORK

In addition to the topics already mentioned, there are two other issues that need to be further mentioned in relation to the WAR Algorithm: Engineering Economics and Computer Aided Process Design. However, both of these are beyond the scope of this paper which is to present the basic generalized waste reduction or WAR Algorithm and to illustrate its use. Engineering Economics and Computer Aided Process Design are the subject of present and future research, and they are included here only for completeness and to aid interested readers applying the method and furthering the work.

Engineering Economics

Whenever a process is modified to reduce waste, there is a consequent change in the economics associated with it. Economic changes are generally due to: (1) the addition or removal of capital equipment, (2) an increase or decrease in energy consumption, (3) a change in the rate of consumption of feed material, and (4) a change in the rate of product generation. When a process is modified, all of the above are frequently affected. There are well established methods for estimating the economics of chemical processes either manually (Peters and Timmerhous, 1968; Richardson Engineering Services, 1997) or with the aid of a computer (ICARUS, 1997; Aspen Technology, 1997).

Modification of a chemical process using the WAR Algorithm needs to be done along with an evaluation of the economic consequences of any proposed process modifications, *i.e.*, one needs to simultaneously compare both the potential environmental impact and the cost of alternate process flowsheets. The reason is that the ultimate objective is always that of developing cost effective reductions in pollution. Unfortunately, there are no consensus criteria for cost effective waste reduction. Although one possibility, consistent with traditional process design procedures, is to require that the sum of the capital and operating costs should not increase with proposed process modifications from the base configuration. This can be expressed as,

$$\left[C_o + C_c\right]_{Base} \geq \left[C_o + C_c\right]_{Modified} \qquad (12)$$

where C_o is the operating cost and C_c is the capital cost that can be estimated by one of the aforementioned methods or some another proprietary method. Equation (12) can then be used jointly with Equations (4) to (8) to evaluate alternative process flowsheets.

Computer Aided Process Design

While it is often possible to devise pollution reducing modifications from an inspection of the process flowsheet, there are many situations where a more systematic approach such as computer aided process design and optimization may be required. This is particularly important with very complex processes that are difficult to analyze by inspection. The WAR Algorithm can be used in computer aided process design and optimization. This can be done by employing the indexes of Equations (4) to (8) as objective functions in a mathematical optimization subject to a cost constraint such as Equation (12). For example, one could minimize the output of potential environmental impact per mass of product given by Equation (7) subject to keeping the total cost from increasing. This can be expressed as,

$$Minimize\ \hat{I}_{out}^{NP} = \hat{I}_{out}^{NP}(\dot{\underline{M}}^{(out)}, \underline{x}_1^{NP}, \underline{x}_2^{NP}, \ldots, \underline{x}_n^{NP}, \dot{\underline{P}}) \quad (13)$$

subject to Equation (12) where $\dot{\underline{M}}^{out}$ is the vector of mass flowrates for all the output streams, $\underline{x}_i^{NP}$ is the vector of mass fractions for non-product component i in all output streams, and $\dot{\underline{P}}$ is the vector of mass flowrates for all products. The optimization could involve the variation of operating variables and modification of the flowsheet configuration both. In this way one can systematically reduce the pollution indexes even in very complex processes. There are several robust algorithms such as simulated annealing (Kirkpatrick *et al.*, 1983; van Laarhoven and Aarts, 1987) that can be successfully used along with mixed integer programing (Grossmann, 1985; Grossmann, 1990) here.

CONCLUSIONS

A general theory and a methodology for incorporating pollution reduction into chemical process design has been presented. The work is still at an early stage of development particularly with respect to its application. However, the fundamental bases along which future work will proceed have been established.

When used in conjunction with chemical process simulators, the WAR Algorithm offers a powerful methodology for evaluating the potential environmental impact of alternative process flow sheets. Although, the WAR Algorithm is intended for use as part of a good faith effort to reduce the environmental foot print of process plants, and it does not obviate the need to make judicious engineering and environmental decisions. For example, there is no completely unambiguous way of setting values for the impact weighting factors or α_i's. The reason is that the α_i's represent the value that society places on particular types of environmental impacts, and this will vary across locations, cultures, and even time. One should point out, however, that engineering design practice has always used human judgement in determining any number of design parameters like safety factors., and,

therefore, this dilemma is not new.

Never the less, there is a need to further improve the methodology for estimating potential environmental impacts and the weighting factors, there is a need to incorporate economics into the analysis, and there is a need to include computer aided process design and optimization. Future work will address these issues. The case studies, however, do illustrate that even in its present state the methodology is a useful process design tool.

ACKNOWLEDGMENTS

The authors wish to acknowledge the support of Chemstations, Inc., Houston, Texas under a Cooperative Research and Development Agreement with the U.S. Environmental Protection Agency. The authors also thank Dr. Douglas Young at the U.S. Environmental Protection Agency for critiquing the manuscript.

LIST OF SYMBOLS

C_c Capital costs associated with a chemical process, monetary

C_o Operating costs associated with a chemical process, monetary

I_{syst} Potential environmental impact content of system, impact

$\dot{I}_{in}$ Potential environmental impact input rate, impact/hour

$\dot{I}_{out}$ Potential environmental impact output rate, impact/hour

$\dot{I}_{gen}$ Potential environmental impact generation rate, impact/hour

$\dot{I}_{in}^{(i)}$ Potential environmental impact flow of stream j input (i=*in*) or output (i=*out*), impact/hour

$\dot{I}_{gen}^{NP}$ Potential environmental impact generation rate by non-products, impact/hour

$\dot{I}_{out}^{NP}$ Potential environmental impact output rate due to non-products, impact/hour

$\dot{I}_{in}^{NP}$ Potential environmental impact input rate due to non-products, impact/hour

$\hat{I}_{gen}^{NP}$ Specific potential environmental impact generation from non-products, impact/ kilogram

$\hat{I}_{out}^{NP}$ Specific output of potential environmental impact due to non-products, impact/kilogram

$\dot{M}_j^{(i)}$ Mass flow rate of stream j, input (i=*in*) or output (i=*out*), kilograms/hour

$\underline{\dot{M}}^{out}$ Vector of mass flowrates for all output streams, kilograms/r hour

$\hat{M}_{gen}^{NP}$ Specific generation of non-product mass, kilograms/kilogram

$\hat{M}_{out}^{NP}$ Specific output of non-product mass, kilograms/kilogram

$\dot{P}_p$ Mass output rate of product p, kilograms/hour

$\underline{\dot{P}}$ Vector of mass flowrates for all products, kilograms/hour

x_{kj} Mass fraction of chemical k in stream j

x_{kj}^{NP} Mass fraction of non-product k in stream j

$\underline{x}_i^{NP}$ Vector of mass fractions for non-product component i in all output streams, kilograms/kilograms

α_l Chemical independent relative weighting factor for impact of type l, impact/kilogram

Φ_n Pollution index, kilograms/kilogram

σ_j Standard deviation of all chemical scores in impact category j, no units

ψ_j Overall potential environmental impact of chemical j, impact/kilogram

$\psi_{j,l}^s$ Specific (s) potential environmental impact of chemical j for impact of type l, impact/kilogram

$(Score)_{i,j}$ Relative potential impact score of chemical i for impact of type j, no unit

$\langle (Score)_{i,j} \rangle_j$ Arithmetic average of the scores for all chemicals i in impact category j, no units

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April 19, 1999

Mr. Douglas M. Young, Ph.D.
Sustainable Technology Division
National Risk Management Research Lab
US Environmental Protection Agency
26 W. Martin Luther King Dr.
Cincinnati, OH 45268

Via Fax: 513-569-7111

Dear Dr. Young:

It has been a pleasure speaking with you about pollution prevention (P2) and the Waste Reduction (WAR) Algorithm. As we discussed, P2 is very near and dear to me; and the WAR Algorithm seems like an excellent tool for comparing P2 options including process and/or chemical changes, and we believe that the WAR Algorithm and its associated database appear to have direct application to the pollution prevention / cleaner production project on which I am working for USAID in the Philippines.

It would be a great benefit to me if you could release to me the part of the database containing information on the Republic of the Philippines Priority Chemicals. These 28 chemicals include the organic compounds: asbestos, benzene, carbon tetrachloride, chlorofluoro-carbons, chloroform, chlorinated ethers, ethylene dibromide, ethylene oxide, halons, hexachlorobenzene, hexachloroethane, mirex, polychlorinated biphenyls, phosgene, pentachlorophenol, polybrominated biphenyls, selenium, tributyltin, vinyl chloride, 1,1,1-trichloroethane, and 1,2-diphenylhydrazine. Also included are arsenic, beryllium, cadmium, chromium, cyanide, lead, and mercury. If any of these chemicals are not in your database, we would be interested to learn how to add new chemicals.

Releasing an electronic copy (Excel format) as soon as possible would be a great benefit to the project, as we are currently in the development stage of the project and would benefit greatly from knowing options available for comparing CP/P2 options.

I look forward to your further input and assistance and can easily be contacted at 703-734-1090 (phone), 703-734-1093 (fax), and mse@erols.com (e-mail). Please ask for Todd Danielson in my absence.

Best Regards,

Dale Rice

cc: T.A. Danielson

CHAPTER 6
ECONOMIC ANALYSIS OF POLLUTION PREVENTION PROJECTS

Although businesses may invest in pollution prevention because it is the right thing to do or because it enhances their public image, the viability of many prevention investments rests on sound economic analyses. In essence, companies will not invest in a pollution prevention project unless that project successfully competes with alternative investments. The purpose of this chapter is to explain the basic elements of an adequate cost accounting system and how to conduct a comprehensive economic assessment of investment options.

A proposed pollution prevention option must compete with alternative investments.

TOTAL COST ASSESSMENT

In recent years industry and the EPA have begun to learn a great deal more about full evaluation of prevention-oriented investments. In the first place, we have learned that business accounting systems do not usually track environmental costs so they can be allocated to the particular production units that created those wastes. Without this sort of information, companies tend to lump environmental costs together in a single overhead account or simply add them to other budget line items where they cannot be disaggregated easily. As a result, companies do not have the ability to identify those parts of their operations that cause the greatest environmental expenditures or the products that are most responsible for waste production. This chapter provides some guidance on how accounting systems can be set up to capture this useful information better.

Standard accounting systems do not track environmental costs well.

It has also become apparent that economic assessments typically used for investment analysis may not be adequate for pollution prevention projects. For example, traditional analysis methods do not adequately address the fact that many pollution prevention measures will benefit a larger number of production areas than do most other kinds of capital investment. Second, they do not usually account for the full range of environmental expenses companies often incur. Third, they usually do not accommodate a sufficiently long time horizon to allow full evaluation of the benefits of many pollution prevention projects. Finally, they provide no mechanism for dealing with the probabilistic nature of pollution prevention benefits, many of which cannot be estimated with a high degree of certainty. This chapter provides guidance on how to overcome these problems as well.

Economic analysis of pollution prevention projects is complex because they:
- *affect multiple areas*
- *have long time horizons*
- *have probabilistic benefits*

highlighting to management both their uncertainty and their importance.

Direct Costs
Capital Expenditures
- *Buildings*
- *Equipment and Installation*
- *Utility Connections*
- *Project Engineering*

Operation and Maintenance Expenses or Revenues
- *Raw Materials*
- *Labor*
- *Waste Disposal*
- *Water and Energy*
- *Value of Recovered Material*

Direct Costs

For most capital investments, the direct cost factors are the only ones considered when project costs are being estimated. For pollution prevention projects, this category may be a net cost, even though a number of the components of the calculation will represent savings. Therefore, confining the cost analysis to direct costs may lead to the incorrect conclusion that pollution prevention is not a sound business investment.

Indirect Costs

Indirect Costs
Administrative Costs
Regulatory Compliance Costs
- *Permitting*
- *Recordkeeping and Reporting*
- *Monitoring*
- *Manifesting*

Insurance
Workman's Compensation
On-Site Waste Management
On-Site Pollution Control Equipment Operation

For pollution prevention projects, unlike more familiar capital investments, indirect costs are likely to represent a significant net savings. Administrative costs, regulatory compliance costs (such as permitting, recordkeeping, reporting, sampling, preparedness, closure/post-closure assurance), insurance costs, and on-site waste management and pollution control equipment operation costs can be significant. They are considered hidden in the sense that they are either allocated to overhead rather than their source (production process or product) or are altogether omitted from the project financial analysis. A necessary first step in including these costs in an economic analysis is to estimate and allocate them to their source. See the section below on Direct Cost Allocation for several ways to accomplish this.

Liability Costs

Liability Costs
Penalties
Fines
Personal Injury
Property Damage
Natural Resources Damage Clean-up Costs
- *Superfund*
- *Corrective Action*

Reduced liability associated with pollution prevention investments may also offer significant net savings to your company. Potential reductions in penalties, fines, cleanup costs, and personal injury and damage claims can make prevention investments more profitable, particularly in the long run.

In many instances, estimating and allocating future liability costs is subject to a high degree of uncertainty. It may, for example, be difficult to estimate liabilities from actions beyond your control, such as an accidental spill by a waste hauler. It may also be difficult to estimate future penalties and fines that might arise from noncompliance with regulatory standards that do not yet exist. Similarly, personal injury and property damage claims that may result from consumer misuse, from disposal of waste later classified as hazardous, or from claims of accidental release of hazardous waste after disposal are difficult to estimate. Allocation of future liabilities to the products or production processes also presents practical difficulties in a cost assessment. Uncertainty, therefore, is a significant aspect of a cost assessment and one that top management may be unaccustomed to or unwilling to accept.

Some firms have nevertheless found alternative ways to address liability costs in project analysis. For example, in the narrative accompanying a profitability calculation, you could include a calculated estimate of liability reduction, cite a penalty or settlement that may be avoided (based on a claim against a similar company using a similar process), or qualitatively indicate without attaching dollar value the reduced liability risk associated with the pollution prevention project. Alternatively, some firms have chosen to loosen the financial performance requirements of their projects to account for liability reductions. For example, the required payback period can be lengthened from three to four years, or the required internal rate of return can be lowered from 15 to 10 percent. (See the U.S. EPA's *Pollution Prevention Benefits Manual, Phase II*, as referenced in Appendix G, for suggestions on formulas that may be useful for incorporating future liabilities into the cost analysis.)

Less-Tangible Benefits

A pollution prevention project may also deliver substantial benefits from an improved product and company image or from improved employee health. These benefits, listed in the cost allocation section of this chapter, remain largely unexamined in environmental investment decisions. Although they are often difficult to measure, they should be incorporated into the assessment whenever feasible. At the very least, they should be highlighted for managers after presenting the more easily quantifiable and allocatable costs.

Less-Tangible Benefits
Increased Sales Due to
- *improved product quality*
- *enhanced company image*
- *consumer trust in green products*

Improved Supplier-Customer Relationship
Reduced Health Maintenance Costs
Increased Productivity Due to Improved Employee Relations
Improved Relationships with Regulators

Consider several examples. When a pollution prevention investment improves product performance to the point that the new product can be differentiated from its competition, market share may increase. Even conservative estimates of this increase can incrementally improve the payback from the pollution prevention investment. Companies similarly recognize that the development and marketing of so-called "green products" appeals to consumers and increasingly appeals to intermediate purchasers who are interested in incorporating "green" inputs into their products. Again, estimates of potential increases in sales can be added to the analysis. At the very least, the improved profitability from adding these less-tangible benefits to the analysis should be presented to management alongside the more easily estimated costs and benefits. Other less tangible benefits may be more difficult to quantify, but should nevertheless be brought to management's attention. For example, reduced health maintenance costs, avoided future regulatory costs, and improved relationships with regulators potentially affect the bottom line of the assessment.

"We wanted to make a major effort to show that industry in the U.S. can simultaneously attack and solve environmental problems while improving both products and profitability."

— John Dudek, value analysis manager at Zytec, as quoted in Perspectives on Minnesota Waste Issues, January-February, 1992.

In time, as the movement toward green products and companies grows, as workers come to expect safer working environments, and as companies move away from simply reacting to regulations and toward anticipating and addressing the environmental impacts of their processes and products, the less tangible

aspects of pollution prevention investments will become more apparent.

EXPANDED TIME HORIZON

Since many of the liability and less-tangible benefits of pollution prevention will occur over a long period of time, it is important that an economic assessment look at a long time frame, not the three to five years typically used for other types of projects. Of course, increasing the time frame increases the uncertainty of the cost factors used in the analysis.

Many of the benefits of pollution prevention accrue over long periods of time.

LONG-TERM FINANCIAL INDICATORS

When making pollution prevention decisions, select long-term financial indicators that account for:

- all cash flows during the project
- the time value of money.

Three commonly used financial indicators meet these criteria: Net Present Value (NPV) of an investment, Internal Rate of Return (IRR), and Profitability Index (PI). Another commonly used indicator, the Payback Period, does not meet the two criteria mentioned above and should not be used.

Discussions on using these and other indicators will be found in economic analysis texts.

Net Present Value, Internal Rate of Return, and Profitability Index are useful financial indicators.

DIRECT ALLOCATION OF COSTS

Few companies allocate environmental costs to the products and processes that produce these costs. Without direct allocation, businesses tend to lump these expenses into a single overhead account or simply add them to other budget line items where they cannot be disaggregated easily. The result is an accounting system that is incapable of (1) identifying the products or processes most responsible for environmental costs, (2) targeting prevention opportunity assessments and prevention investments to the high environmental cost products and processes, and (3) tracking the financial savings of a chosen prevention investment. TCA will help you remedy each of these deficiencies.

Developing a pollution prevention program may well provide the first real understanding of the costs of polluting.

Like much of the TCA method, implementation of direct cost allocation should be flexible and tailored to the specific needs of your company. To help you evaluate the options available to you, the discussion below introduces three ways of thinking about allocating your costs: single pooling, multiple pooling, and service centers. The discussion is meant as general guidance and explains some of the advantages and disadvantages of each approach. Please see other EPA publications (such as those listed in Appen-

Three methods of direct cost allocation:

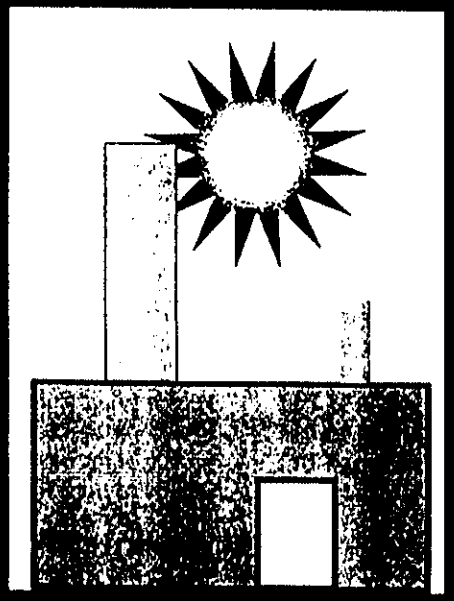
- *single pooling*
- *multiple pooling*
- *service centers*

USEFUL P2 WEBSITES

Web Address	Organization	Description
http://es.epa.gov	US EPA's EnviroSense	Practical Examples of P2; Related Site References
www.epa.gov/opptintr/library/	US EPA	P2 Success Stories
http://enviro.nfesc.navy.mil/p2library	U.S. Department of Defense	Joint Services P2 Library – P2 Technologies and Case Studies
http://epic.er.doe.gov/epic	U.S. Department of Energy	P2 Info Clearinhouse; International P2 Web Sites
http://cpp2.sarnia.com	Canadian Centre for Pollution Prevention	P2 Information; Related Site References
http://clean.rti.org	Research Triangle Institute / US EPA	Solvent Alternatives Guide (SAGE); Searchable Knowledge Base for Surface Cleaning

USEFUL CHEMICAL INFO DATABASE SITES

Web Address	Organization	Description
http://ull.chemistry.uakron.edu	University of Akron	Hazardous Chemical Database (Searchable)
http://hazard.com/msds	NGO	Searchable Material Safety Data Sheet Information



What Are the Industry Sector Notebooks?

This series from the U.S. EPA provides information of general interest regarding industry-specific manufacturing processes and pollution issues associated with specific industrial sectors. The series is unique in taking a holistic, "whole facility" approach to environmental information, instead of separating information related to pollutants of air, water, and land. For each industry the Notebook contains:

- information about size, geographic distribution, products, and economic trends.
- a description of manufacturing processes, including inputs of raw materials and pollution outputs.
- a profile of chemical releases to the environment.
- a summary of federal environmental regulations and compliance history.
- pollution prevention opportunities.
- government and industry initiatives for compliance assurance.
- resource materials and contacts.

The Industry Sector Notebooks are published by the Office of Compliance, U.S. Environmental Protection Agency (EPA), and have been thoroughly reviewed by EPA and outside experts. The Notebooks have all been carefully researched and referenced, and include many tables and figures containing quantitative information relevant to each industry. **Pollutant emission and compliance data from the 1995 Notebooks has been revised in the *Sector Notebook Data Refresh—1997* (see Ordering Information).** The sector Notebooks are one of the few sources of consolidated data about an industry.

Recycled
Printed on paper that contains at least 50% recycled fiber.

What Industries Have Been Captured in Sector Notebooks?

Highlighted titles were newly published in 1997. All others were published in 1995.

Air Transportation
Dry Cleaning
Electronics and Computers
Fabricated Metal Products
Fossil Fuel Electric Power Generation
Ground Transportation
Inorganic Chemicals
Iron and Steel
Lumber and Wood Products
Metal Casting
Metal Mining
Motor Vehicle Assembly
Nonferrous Metals
Non-Fuel, Non-Metal Mining
Organic Chemicals
Petroleum Refining
Pharmaceutical Manufacturing
Plastic Resin & Man-made Fibers
Printing
Pulp and Paper
Rubber and Plastic
Shipbuilding and Repair
Stone, Clay, Glass and Concrete
Textiles
Transportation Equipment Cleaning
Water Transportation
Wood Furniture and Fixtures

Check the Notebook website (www.epa.gov/occa/sector/index.html) for new and future titles.

Industry Sector Notebooks

How Are the Industry Sector Notebooks Used?

This sector-based approach helps readers to:

- build a foundation for developing holistic solutions to environmental problems.
- perform research on an industry and its environmental regulations.
- understand compliance issues.
- develop industry-specific training sessions/ programs.
- develop curricula for environmentally related courses.
- determine probable cause for a lawsuit, citation, or penalty.
- create and improve innovative pollution prevention programs.

Who Should Know About the Industry Sector Notebooks?

- community advocates
- compliance assistance providers
- compliance inspectors (federal, state, and local)
- educators
- engineers
- environmental advocates
- foreign governments
- international agencies
- legal professionals (government and industry)
- librarians
- regulators
- environmental managers
- small business technical assistance providers
- waste facilities managers (water, solid waste)
- members of the public with an interest in an industry

If you have questions about the Industry Sector Notebooks, you may contact:
Sector Notebook Project Coordinator, Office of Compliance (2223A), U.S. EPA, 401 M Street, SW, Washington, DC, 20460. Phone: 202-260-2300, Fax: 202-564-0050.

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1. **Download Notebooks from the Internet, at no charge.** Web versions contain complete text, but they do not always include all graphics or data tables. The Notebooks can be found at **www.epa.gov/oeca/sector/index.html**
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Switch Materials to Prevent Pollution

There are many opportunities in the CPI for replacing hazardous substances with less-hazardous substitutes. This guide can be used to prioritize candidates for replacement and identify potential alternatives.

Adolf W. Gessner,
Consultant

The chemical process industries (CPI) employ many substances that contribute to air and water pollution, hazardous-waste generation, soil contamination, fire and explosion risks, and the exposure of humans, animals, and plants to hazardous and/or toxic materials.

Pollution prevention seeks to reduce or eliminate adverse health, safety, and environmental impacts of manufacturing activities. Material substitution is an approach to pollution prevention that attempts to replace hazardous substances with materials that are less hazardous to humans and less harmful to the environment.

This article examines the replacement of hazardous organic substances that are used in petroleum processing, natural gas sweetening, chemical manufacturing, surface cleaning, and surface coating applications.

WHICH SUBSTANCES ARE HAZARDOUS?

In the U.S., federal and state governmental agencies regulate the use and disposal of many hazardous materials, including:

- substances generating toxic and/or hazardous liquid and solid wastes;
- substances that pose fire or explosion hazards, or that generate ignitable wastes (flash points below 60°C or 140°F);
- reactive substances that may explode or detonate without oxygen supply or ignition source;
- hazardous substances whose use requires annual public disclosure in a Toxic Release Inventory (TRI);
- hazardous air pollutants (HAPs) identified by the Clean Air Act Amendments and by state regulations;
- hazardous substances identified as priority water pollutants (PWPs) by the Clean Water Act;
- volatile organic compounds (VOCs) that are photochemically reactive, forming smog in the atmosphere at ground level;
- substances with low permissible exposure limits (PELs) as defined by regulations of the Occupational Safety and Health Administration (OSHA), or as recommended by the National Institute of Occupational Safety and Health (NIOSH) or the American Conference of Governmental Industrial Hygienists (ACGIH);
- known or suspected carcinogens; and
- substances that tend to deplete the stratospheric ozone layer or that contribute to global warming.

These groups of substances are not mutually exclusive; many materials fall into two or more of these categories. Clearly, many of these substances ought to be considered for replacement.

Flammable, explosive, and reactive substances

The ability of combustible organic chemicals to form ignitable, potentially explosive vapor mixtures with air is characterized by the flash point. The flash point is the lowest temperature at which the vapor pressure of the chemical generates a vapor concentration in air that can be ignited by a low-energy spark.

Substances with flash points below ambient temperature can ignite and explode if they are not properly handled. The Resource Conservation and Recovery Act (RCRA) defines any substance with a flash point below 60°C (140°F) as "ignitable."

To protect against fires and explo-

sions, such substances may sometimes be replaced by substitutes having flash points well above ambient temperature.

However, it often is impractical to replace volatile, low-flash-point substances with less-volatile substitutes. Motor gasoline, diesel fuel, and jet fuel are ignitable, but gasoline, diesel, and jet engines will not operate on high-flash-point substitutes. Many solvents with low flash points are indispensable — wherever rapid solvent evaporation is required, substitution by slowly evaporating, high-flash-point replacements is impractical. In such cases, instead of material substitution, conventional fire protection is used: volatile, ignitable solvents are stored in tightly closed containers to limit the amount of oxygen available for combustion; metal drums are grounded to eliminate static electricity; work areas are ventilated to reduce contaminant concentrations; sprinkler systems are provided; process and storage tanks may be nitrogen-blanketed; explosionproof motors, switches, lighting fixtures, and instruments may be used; and no-smoking rules are strictly enforced.

On the other hand, wherever possible, reactive substances that can explode or detonate without an ignition source or oxygen supply should be replaced by nonreactive substitutes.

Toxic substances

Toxic effects on humans and animals greatly depend on the exposure pathway — inhalation, skin contact, or ingestion — and on the dosage of pollutant received. Vapor inhalation and absorption through the skin by vapor contact are the most common exposure modes. The dosage of toxic substance entering the body is directly related to the concentration of the substance in the air inhaled or in contact with the skin. This concept of toxic exposure is the basis of the health guidelines for industrial chemicals issued by OSHA, NIOSH, and ACGIH.

These guidelines provide a means of distinguishing between highly toxic substances and less toxic or relatively nontoxic ones. OSHA enforces PELs for toxic substances in terms of time-weighted average concentrations in air for a workday of 8 hours. NIOSH publishes recommended exposures limits (RELs), and AGCIH publishes threshold limit values (TLVs); their definitions resemble those of OSHA's PELs, but they are, generally, less permissive. NIOSH RELs typically reflect the most recent toxicological research data.

The lower the PEL, REL, or TLV, the more hazardous a substance is to human health. Pollutant concentrations in air are expressed in parts per million (ppm) by volume, or in mg/m^3. For purposes of this discussion, the line between what is considered highly toxic and what is relatively less toxic is arbitrarily drawn at a NIOSH REL for inhalation and skin absorption of 25 ppm. Substances with RELs of 25 ppm and less are prime candidates for replacement; all others are considered moderately toxic.

Carcinogenic substances

In addition to well-documented carcinogens, NIOSH has identified many potential occupational carcinogens based on an increased incidence of benign or malignant tumors or a shortened latency period between exposure and onset of tumor as a result of inhalation or skin absorption exposure. All carcinogens should be considered for replacement by noncarcinogenic substitutes.

Volatile organic compounds

The list of organic substances considered to be photochemically reactive VOCs (40 CFR, Chapter 1, Section 51.100) is so all-inclusive that the replacement of VOCs by organic non-VOCs is virtually impossible.

However, in many cleaning applications, VOCs have been successfully replaced by aqueous alkaline cleaning formulations. The VOC content of some coating formulations may be reduced. Some solvent-based coatings may be replaced by water-based or powder formulations.

HAPs, PWPs, and TRI-reportable substances

Solvents that fall into these categories deserve consideration for replacement. Also included in this class are important feedstocks used in chemical manufacturing, transportation fuels, and thinners for coating applications; many of these cannot be replaced in the immediate future.

Global warming and ozone depletion

Substances relatively transparent to ultraviolet and visible solar radiation but opaque in the infrared spectral range trap heat by the "greenhouse effect" and contribute to global warming. The principal greenhouse gases in the atmosphere are carbon dioxide, methane, and nitrous oxide.

Volatile substances that rise into the stratosphere and release chlorine help convert stratospheric ozone to oxygen. Ozone depletion permits increased amounts of ultraviolet solar radiation to reach the earth's surface and is linked to human skin cancer and cataracts, and possible damage to plant and marine life.

Among organic solvents, chlorofluorocarbon CFC-113 and methyl chloroform are the principal substances suspected of contributing to the greenhouse effect and to stratospheric ozone depletion. Their manufacture in the U.S. was stopped on Jan. 1, 1996.

POTENTIAL REPLACEMENTS

Solvents may be clasified into several chemical groups: paraffinic (aliphatic and alicyclic) hydrocarbons, monoterpenes, aromatic hydrocarbons, alcohols, ethers, aldehydes, ketones, esters, phenolics, ethylene glycol ethers and their esters, propylene glycol ethers and their esters, chlorinated hydrocarbons, chlorofluorocarbons, fluorinated organic compounds, nitrogen-containing compounds, and sulfur-containing compounds. Some solvents belong to more than one of these categories. Aqueous alkaline cleaning formulations represent an ad-

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ditional class of substances; they may include both organic and inorganic compounds.

Paraffinic hydrocarbons

Straight-chain, branched, and naphthenic (cycloparaffinic) hydrocarbons are relatively nontoxic. However, paraffinic distillate fractions from traditional petroleum processing often contain appreciable concentrations of aromatic hydrocarbons, rendering them potentially toxic, carcinogenic, and classifiable as HAPs and PWPs. The major petroleum processors in the U.S. and their petrochemical affiliates have begun supplying paraffinic hydrocarbon distillate fractions with very low aromatic hydrocarbon content (<0.5%). These are preferred over traditional petroleum distillate fractions, such as straight aliphatic solvents (*e.g.*, Varsol), mineral spirits, kerosene, and Stoddard solvent.

Paraffinic hydrocarbons (many ig-itable, all VOCs) generally are moderately effective solvents for hydrophobic surface soils such as grease, oils, and waxes. Naphthenic hydrocarbons appear to be slightly more effective as solvents than normal- and iso-paraffinic hydrocarbons.

Monoterpenes

Monoterpenes are relatively nontoxic olefinic C10 hydrocarbons derived from natural sources. They include limonene, pinenes, myrcene, and others. Limonene is a very effective solvent for many types of grease, waxes, and organic soldering fluxes. Turpentine, a mixture of α- and β-pinene, is a paint thinner. Monoterpenes are VOCs and are ignitable.

Aromatic hydrocarbons

Aromatic hydrocarbons are important petrochemical feedstocks. They also are excellent solvents for oils, grease, fats, many waxes, tar, and many chemical intermediates and oducts. Aromatic hydrocarbons gen-rally are more versatile as solvents than paraffinic hydrocarbons. However, they are more hazardous.

Benzene is a carcinogen; its NIOSH REL is 0.1 ppm. Obviously, it is a highly toxic substance that should be replaced wherever possible. Toluene, ethylbenzene, the xylene isomers, and cumene, with RELs of 50–100 ppm, are not highly toxic and are not classified as carcinogens. However, they are ignitable, classified as HAPs, PWPs, and VOCs, and subject to TRI reporting. At present, toluene, ethylbenzene, and xylenes are widely used in coating, adhesive, and thinner formulations because of their compatibility with the other components of coating formulations and because of their rapid evaporation rates.

Trimethylbenzene (three isomers), *p*-tert-butyl toluene, biphenyl, terphenyl (three isomers), and polycyclic aromatic hydrocarbons (naphthalene, indene, anthracene, phenanthrene, acridine, chrysine, benzo(a)pyrene, etc.) are toxic and carcinogenic. Aromatic hydrocarbon distillate fractions such as Aromatic 100, 150, and 200 are made up in part of these hydrocarbon constituents. All aromatic hydrocarbons are VOCs and many are ignitable.

The replacement of aromatic hydrocarbon solvents with suitable, less-hazardous aliphatic substitutes clearly would be desirable. Cycloparaffinic hydrocarbons may replace aromatics in some applications.

Alcohols

Methanol, ethanol, *n*-propanol, isopropanol, the isomers of butanol and amyl alcohol, cyclohexanol, diacetone alcohol, and α-terpineol are relatively nontoxic. All except cyclohexanol and terpineol are ignitable, and all are VOCs. Furfuryl alcohol is highly toxic.

Ethers

Light paraffinic ethers such as diethyl ether, diisopropyl ether, and tetrahydrofuran are relatively nontoxic. Among ethers, only methyl tert-butyl ether (MTBE), an octane booster for gasoline, is a HAP; it is not used in cleaning and coating applications. All ethers are VOCs, and all the ethers mentioned here are ignitable. The cyclic ether 1,4-dioxane is highly toxic. (Glycol ethers are discussed below.)

Aldehydes

Furfural is the only aldehyde known to be used on a large scale, as an extractant in lube oil dewaxing. It is highly toxic.

Ketones

Acetone, methylethyl ketone (MEK), methyl isobutyl ketone (MIBK), methyl *n*-propyl and isopropyl ketone, and methyl *n*-amyl and isoamyl ketone are relatively nontoxic, but ignitable; all except acetone are VOCs. MEK and MIBK require TRI reporting. These ketones are popular components of many coating, adhesive, and thinner formulations.

Among ketones, methyl *n*-butyl ketone, ethyl isoamyl ketone, diisobutyl ketone, isophorone, and cyclohexanone are highly toxic.

Esters

Methyl formate and acetate, ethyl, *n*-propyl, all butyl and amyl acetates, ethyl-3-ethoxypropionate (EEP), branched C6 to C10 paraffinic acetates, ethylene and propylene carbonate, and dibasic esters (dimethyl succinate, glutarate, and adipate) all are relatively nontoxic. All these esters are VOCs. The lower esters from methyl formate to amyl acetate are ignitable. These esters are widely used as solvents in chemical manufacturing, surface cleaning, and surface coating. Gamma-butyrolactone, a cyclic C4 ester, is highly toxic. (Glycol ether esters are discussed below.)

Phenolics

Phenol, the cresol isomers, and the dihydroxybenzenes (catechol, resorcinol, and hydroquinone) are all highly toxic. Traditional cleaning formulations and resin solvents containing phenolics have largely been replaced. However, the displacement of phenolics from many specialty uses is expected to be impractical.

Ethylene glycol ethers and their esters

The alkyl ethers of ethylene glycol (Cellosolves) and their acetate esters have been widely used in cleaning formulations because of their remarkable cleaning effectiveness. Diethylene glycol ethers (Carbitols) and their acetate esters, and triethylene glycol ethers and their acetates, also are popular and versatile solvents.

Research on health risks associated with human and animal exposure to glycol ethers and their acetates revealed many adverse effects. Thus, the risk assessments of ethylene glycol ethers and their acetate esters were radically revised. The NIOSH RELs for ethylene glycol monomethyl ether (methyl Cellosolve) and its acetate ester were lowered from 25 to 0.1 ppm; those of ethylene glycol monoethyl ether (Cellosolve) and its acetate ester were dropped from 100 to 0.5 ppm; and those of ethylene glycol *n*-butyl ether (butyl Cellosolve) and its acetate ester were lowered from 50 to 5 ppm. All ethylene glycol, diethylene glycol, and triethylene glycol ethers now require TRI reporting and are listed HAPs and PWPs.

Nevertheless, ethylene glycol ethers and their acetate esters are still widely used in industrial and household cleaners. It is expected that in many applications, chemically similar but less-toxic propylene glycol ethers and their esters will displace the ethylene glycol ethers and their acetate esters.

Propylene glycol ethers and their esters

As a result of the toxicity findings for ethylene-glycol-based ethers and their acetates, several manufacturers have developed low-toxicity propylene-glycol-based alternatives: propylene glycol methyl ether (PM) and its acetate ester (PMA), propylene glycol ethyl ester (PE) and its acetate ester (PEA), propylene glycol *n*-butyl ether (PnB) and its acetate ester (PnBA), dipropylene glycol methyl ether (DPM), tripropylene glycol methyl ether (TPM), and several others.

In some applications, the propylene glycol-based substances are "drop-in" replacements for their ethylene glycol-based analogs; in some applications, there are said to be significant performance differences between ethylene and propylene glycol ethers.

The propylene glycol-based ethers and their acetate esters are not considered to be HAPs and PWPs. The more volatile among them are ignitable (PM, PMA, PE, PEA, PnB), and all are VOCs.

Chlorinated hydrocarbons

Chlorinated hydrocarbons, being relatively inert chemically, are useful solvents for carrying out many organic synthesis reactions. Having high specific gravities and being almost immiscible with water, they are usually easy to separate from aqueous phases by gravity. Being virtually nonignitable, they pose no fire or explosion hazards. The most important chlorinated hydrocarbons used in organic chemicals manufacturing are methylene chloride, chloroform, carbon tetrachloride, ethylene dichloride, methyl chloroform, trichloroethylene, and perchloroethylene, and several chlorobenzenes.

These chlorinated hydrocarbons are also useful in cleaning and degreasing. They dissolve a great variety of surface contaminants, including oils, grease, fats, tars, many resins, and rosin solder fluxes, and they evaporate quickly.

Methylene chloride is the only truly effective, fast-acting paint stripper known at this time. It is relatively nontoxic (OSHA PEL = 500 ppm). Chloroform, carbon tetrachloride, ethylene dichloride, and the dichlorobenzenes are highly toxic. Methyl chloroform, an excellent multipurpose solvent for cleaning and for vapor degreasing of metal parts, is relatively nontoxic (OSHA PEL = 350 ppm). Trichloroethylene and perchloroethylene are moderately toxic (OSHA PEL = 100 ppm for both). The polychlorinated biphenyls (PCBs) are highly toxic.

All these chlorinated hydrocarbons are classified as HAPs, PWPs, and hazardous wastes under RCRA. All require reporting in the TRI. Furthermore, NIOSH classifies them as potential occupational carcinogens. Methyl chloroform, in addition, is believed to contribute to stratospheric ozone depletion and global warming. Chlorinated hydrocarbons, clearly, are high-priority candidates for replacement by nonchlorinated substitutes. Many applications involving chlorinated hydrocarbons have already been eliminated.

Methylene chloride will continue to be used for paint stripping as long as there is no replacement available that is as effective. Trichloroethylene and perchloroethylene will continue to be used in applications where they offer substantial technical and safety advantages over all solvent alternatives, with provisions to minimize their discharge into the environment and to protect personnel from inhalation and skin exposure.

Chlorofluorocarbons

Among chlorofluorocarbons, CFC-113 ($CFCl_2$-CF_2Cl) is the principal substance of interest as a solvent for conducting chemical syntheses and for cleaning applications. CFC-113 is almost nontoxic (NIOSH REL = 1,000 ppm), nonflammable, and chemically very stable. It lends itself to immersion cleaning and vapor degreasing. Other, more-volatile CFCs, because they are nonflammable and nontoxic, are excellent refrigerants and propellants for aerosol spraying. All CFCs contribute to stratospheric ozone depletion and their use has been severely restricted.

Fluorinated organics

Chlorine-free fluorocarbon solvents are in use or under development. Lacking chlorine, they do not destroy stratospheric ozone. However, their possible role as greenhouse gases is unclear at this time. They are nonflammable, chemically stable, and their toxicity is generally low. A fluorinated ether is used for electronic circuit board cleaning. Several perfluorocarbons (*e.g.*, perfluorohexane, C_6F_{14}) are under consideration as protective vapor barriers for immersion degreasing with hot hydrocarbons or aliphatic esters in retrofitted vapor degreasing tanks

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Light fluorocarbons, such as 1,1-difluoroethane, are used as propellants for aerosol spray cans.

Nitrogen-containing organics

Acetonitrile, N,N-dimethyl formamide, N,N-dimethyl acetamide, nitrobenzene, nitromethane, pyridine, and morpholine are highly toxic. Nitrobenzene and nitromethane are potential explosives because they are chemically reactive with a variety of common substances. These compounds, where possible, should be replaced.

Pure monoethanolamine and diethanolamine are highly toxic. In natural gas processing and surface cleaning applications, however, they are ordinarily dissolved in water and largely converted to quaternary ammonium cations. As such, they pose a low inhalation risk at room temperature. However, when heated, they may generate toxic vapor compositions.

N-methyl pyrrolidone, a C4 cyclic lam, is a versatile solvent with applications in natural gas sweetening, aromatic hydrocarbon extraction, surface cleaning, and paint stripping. However, it is harmful to the human reproductive system.

Sulfur-containing organics

Sulfolane (tetramethylene sulfone) and dimethyl sulfoxide (DMSO) are nontoxic. Carbon disulfide is highly toxic and, where possible, should be replaced.

Aqueous alkaline cleaning formulations

Aqueous alkaline formulations may contain amines (ethanolamines, monoisopropanolamine) to achieve alkalinity. As noted earlier, ethanolamines have low RELs (3 ppm) and are potentially toxic; however, they do not ordinarily pose an inhalation risk when dissolved in water.

Other substances that impart alkalinity to aqueous cleaning formulations he sodium or potassium salts of k acids, such as fatty acids (soaps), ethylene diamine tetraacetic acid (EDTA), carbonic acid, phosphoric acid, silicic acid, hydroxyacetic acid, and gluconic acid. The strongest sources of alkalinity are sodium and potassium hydroxide. No inhalation hazards are associated with these substances as long as no aerosols or mists are formed. However, eye and skin contact are highly hazardous.

Optionally, surfactants may be added to such cleaning formulations to improve the wetting of surfaces. Glycol ethers and ethanolamines may also be added. When used for cleaning at elevated temperatures, formulations containing ethylene glycol ethers and ethanolamines may generate toxic vapor concentrations of these substances, calling for exhaust ventilation.

An important consideration in the use of aqueous alkaline cleaning formulations is their possible attack on certain metals, most importantly aluminum and aluminum alloys. At a pH below about 13, and in the presence of silicates, aluminum generally is not attacked. At pH levels above about 13.5, aluminum is vigorously attacked and converted to aluminate anion with the evolution of hydrogen. This destroys the surface being treated and creates a fire or explosion hazard. Highly alkaline aqueous cleaners have also been reported to attack cadmium and chromium-plated steel surfaces and lead alloys, generating heavy-metal contaminated wastes.

MATERIAL SUBSTITUTION

Petroleum processing and natural gas sweetening

In petroleum processing, several solvent candidates are generally available for such extractions as aromatic hydrocarbon recovery (*e.g.*, Sulfolane, N-methyl pyrrolidone, N,N-dimethylformamide), deasphalting (*e.g.*, propane, *n*-butane), and dewaxing (*e.g.*, MIBK, furfural).

In natural gas sweetening, similarly, there is a variety of absorbents to choose from (*e.g.*, methanol, N-methyl pyrrolidone, N-methyl diethanolamine, polyethylene glycol dimethyl ether, aqueous mono- and diethanolamine, and aqueous hot potassium carbonate).

In these processes, the solvent's selectivity for the substances to be absorbed or extracted is the primary selection criterion. Toxic exposure, where potentially present, is generally avoided by appropriate engineering controls, not by material substitution.

Chemical manufacturing

Organic solvents are widely used as diluents in which organic syntheses are carried out, and as means of recovery and purification of intermediates and products by crystallization. Unless special provisions are made, solvents escape into the environment from process and storage tank vents, centrifuges, filters, dryers, vacuum pump discharges, pump and compressor shaft seals, agitator seals, and leaking flanges, pipe fittings, and valves. Solvents dissolved in water are discharged into sewers, entering the atmosphere through sewer catchbasins and manholes, aerated lagoons, and in other ways.

Changing from one solvent to another in a chemical manufacturing process, generally, is a daunting task. Critical factors are the solubilities of intermediates and products in various solvents at different temperatures, the volatilities and specific gravities of the solvents, possible chemical interactions of the solvent with the synthesis feedstocks and products, and many other process-specific issues. Finding a perfect nonhazardous substitute that meets all chemical and physical requirements of a manufacturing process sometimes seems like an impossible task.

Early success stories report the replacement of benzene by cyclohexane and by toluene in the manufacture of specialty chemicals intermediates. The replacement of carbon tetrachloride and ethylene dichloride by methyl chloroform was a another early sucess. Now, owing to methyl chloroform's phase-out, other substitutes must be found.

Surface cleaning applications

Cleaning applications are defined in terms of the surfaces being cleaned, the surface soils or coatings that are being

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removed, and the degree of cleanliness required. The choice of cleaning formulation depends on the chemical nature of the soils or coatings being removed and on the compatibility of the cleaning formulation with the surface.

Ideally, cleaning processes selectively clean the substrate surface without attack on the substrate itself by corrosion, plasticization, embrittlement, and shrinkage by plasticizer extraction, and without removal of paints or varnish finishes that are to be preserved. Also, the cleaning formulation should not release hazardous air pollutants, generate flammable, explosive vapor mixtures with air, or generate hazardous liquid wastes.

Nontoxic, nonhazardous drop-in replacements are rare. Substitutes ordinarily require changes in equipment, processes, work rules, and work habits.

Surface blasting with blasting media ranging from highly abrasive (sand, steel shot, glass beads) to mildly abrasive (walnut shells, dry ice granules) represents an alternative to material substitution in surface cleaning.

Replacement of halogenated degreasing solvents (methyl chloroform, perchloroethylene, CFC-113) by aliphatic hydrocarbons sometimes is successful. The addition of a monoterpene and a propylene glycol ether sometimes enhances solvent power.

Surface coating applications

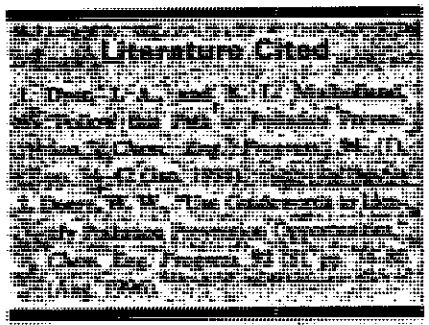
Surface coating processes include the application of primers, paints, enamels, lacquers, adhesives, or varnishes to surfaces that have been suitably cleaned. Organic solvents, as they evaporate during drying or curing, may create fire and explosion hazards and expose workers to high solvent vapor concentrations. Adequate exhaust ventilation, use of explosionproof equipment, and strict enforcement of no-smoking rules are effective remedies. Air pollutants in the exhaust air may be destroyed by incineration or captured by adsorption on activated carbon.

In both surface cleaning and coating applications, the selection of solvent substitutes may be aided by consideration of solubility parameters. These are factors related to the internal energy of vaporization per unit volume of solvent, and they include components for molecular dispersion, dipole interaction, and hydrogen bonding. Substances having similar solubility parameters tend to be miscible in each other, whereas those with vastly different solubility parameters tend to be immiscible. Solubility parameters are useful in predicting interactions between solvents, polymers, and resins; they may be useful as well in predicting solvents' cleaning and degreasing power.

Important steps in pollution prevention

There is no "cookbook" approach to pollution prevention programs, and much has been published on the subject (such as *(1, 2)*). However, the following steps should be undertaken:

- a study of the physics and the chemistry of the problem under consideration;
- a study of the toxicity of the chemical substances present and their disposal pathways from the process into the environment;
- an evaluation of human exposure to toxic substances;
- an evaluation of fire, explosion, or detonation hazards, if applicable;
- sampling and analysis of air, wastewater, other liquid wastes, and solid wastes, as applicable;
- a review of case histories of similar pollution prevention efforts, found in print or electronically, to stimulate ideas;
- identification of potential replacement substances, and evaluation in the laboratory under simulated field conditions; and
- field testing of replacement substances that appeared promising in the laboratory evaluation. CEP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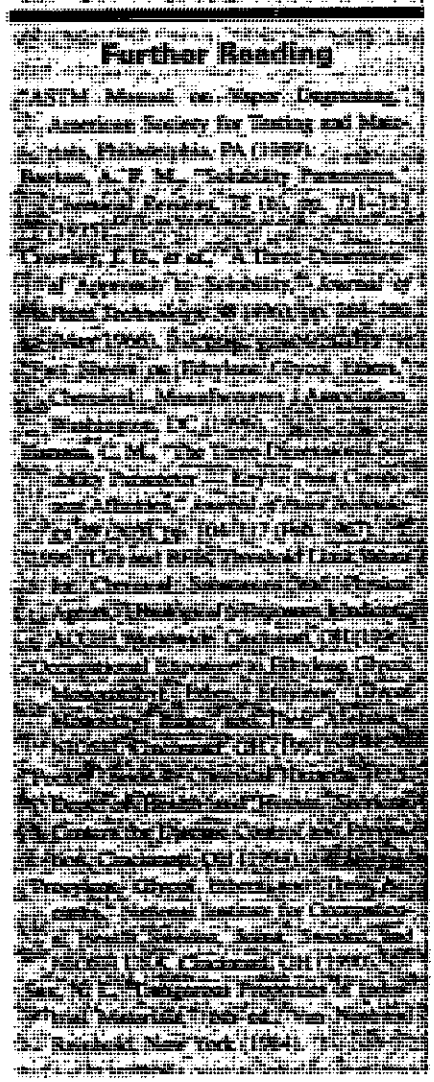
Further Reading

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Prevent Pollution in Batch Processes

These strategies can reduce waste generation by improving reactor charging, operation, discharging, and cleaning practices.

James A. Dyer,
Kenneth L. Mulholland, and
Robert A. Keller,
E. I. du Pont de Nemours and Co.

available on-line www.aiche.org

Batch processes are a preferred operating method for manufacturing small volumes of high-value products, such as many pharmaceuticals, agricultural materials, and specialty chemicals.

Unfortunately, batch operations are also associated with the generation of unacceptably high amounts of waste per unit of product. In the past, many businesses could "afford" this wastefulness, because the high value of the final product often overshadowed the cost of treating the waste and because some of the compounds in the waste streams were previously unregulated.

However, in recent years, two things have changed.

First, businesses are becoming aware of the *true cost* of waste production, which is always greater than the cost for disposal or treatment. The true cost of waste production includes the monetary value of lost product, the cost of solvent purchases, the fees for permitting and monitoring emissions, and the increased exposure to safety and environmental risks.

Second, with increased regulation of emissions to air, water, and land, many plant sites can no longer handle in existing control equipment the often concentrated, toxic waste streams (especially wastewater streams) emanating from batch processes. As a result, facilities relying on batch processes are now facing significant new capital investment to pretreat concentrated wastewater before it can be sent to a biological treatment plant, to expand biological wastewater treatment capacity, to install state-of-the-art hazardous-waste incinerators for liquid wastes, and to provide point source treatment of air emissions.

The true cost of waste generation then, provides an incentive for batch operations to identify and implement pollution-prevention solutions.

This article outlines techniques and technologies that engineers can use to reduce waste generation at the source in batch operations. It covers: strategies for reactor charging, operation, discharging, and cleaning; modeling batch processes; and batch vs. continuous operation. It also discusses three examples: replacing an organic solvent with an aqueous solvent for cleaning; reducing methylene chloride emissions by sealing atmospheric mix tanks; and converting a process from batch to continuous operation.

The nature and sources of emissions

A batch operation is by definition a discontinuous process. Process variables such as temperature, pressure, and concentration vary throughout the batch cycle.

Likewise, waste emissions associated with these cycles are seldom considered constant *(1)*. For example, a batch reaction step may generate a nitrogen purge stream whose volatile organic compound (VOC) concentration varies with time, as shown in Figure 1. The emission rate peaks in the fir

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hour, then decreases with time as the reaction nears completion.

Such time-dependent behavior makes it difficult to effectively specify a continuous gas-abatement system. To meet permit limits, the abatement equipment must be sized to treat the maximum achievable waste flow and concentration. For some emissions, this maximum may last only a few minutes. It is easy to see how uneconomical the "end-of-pipe" approach can be to a business. For this reason, source reduction of these emissions by pollution-prevention strategies can reduce the dependence on such costly control technologies.

Every stage of a batch cycle has some amount of waste emissions associated with it. Noncondensibles (such as nitrogen and air) escape the process during reactor charging and discharging, carrying with them high concentrations of VOCs. Reactor operation may generate unwanted byproducts that contribute to product losses. Most noticeable are the large amounts of cleaning wastes generated during vessel cleaning between batch cycles and product campaigns. The pollution-prevention strategies discussed in the following sections can substantially reduce emissions for all steps of batch operations.

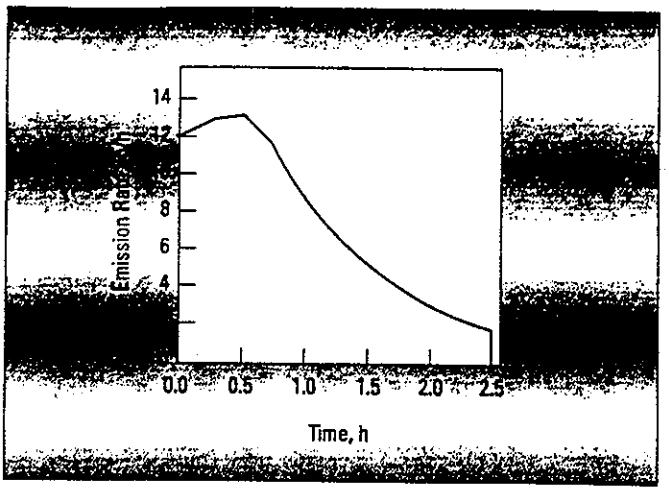
Pollution-prevention strategies

Most waste generation in batch operations occurs in the reactors. For this reason, the pollution-prevention technologies and practices described here focus on the batch reactor. Four key reactor process steps are discussed — charging, operation, discharging, and cleaning.

Reactor charging

Solvent vapor losses during raw material addition occur for two primary reasons — leaks from the process equipment, and vapor displacement as the reactor is filled with liquids or solids. To circumvent these two problems, consider the following pollution-prevention strategies:

■ *Figure 1. VOC concentration profile for a batch reaction nitrogen purge stream.*

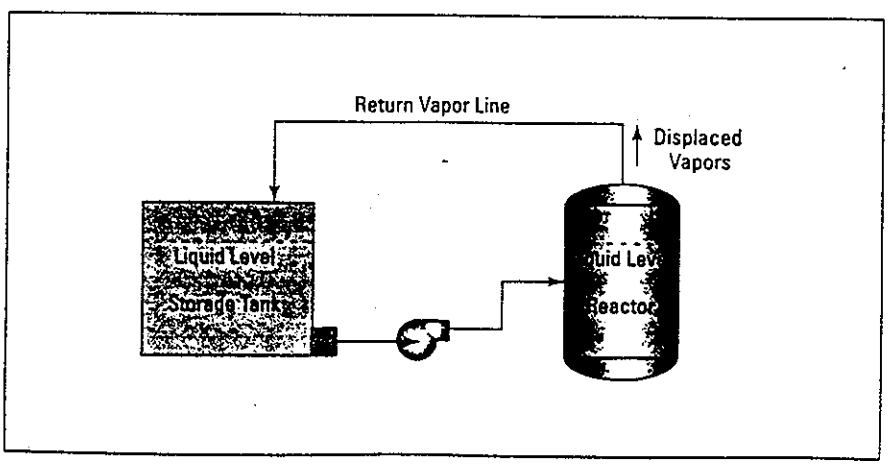


• *Gravity-feed solvents into the reactor vessel* instead of using a centrifugal, positive displacement, or diaphragm pump to reduce the pressure buildup associated with pumping *(2)*. This can often be achieved in new designs by elevating raw material feed tanks above the reactor instead of beside it to take advantage of gravity.

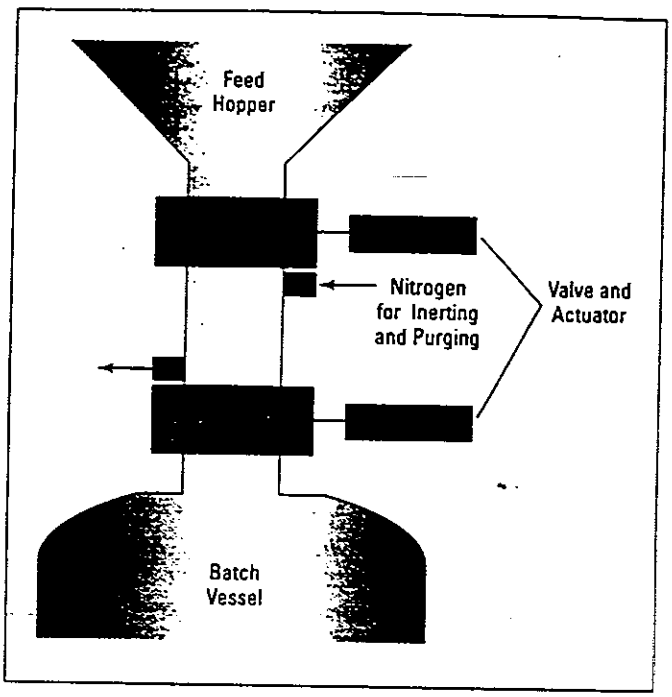
• *Install closed-loop vapor recycling systems for pumping operations (3)*. As shown in Figure 2, this involves piping the displaced vapor from the reactor (as it fills) back to the vessel containing the feed material, *e.g.*, a solvent storage tank. Be careful of materials compatibility, however.

• *Charge solids before liquid solvents* to minimize solvent displacement from reactors *(4)*. A more general strategy is to reconsider the sequence of raw materials addition to minimize unwanted off-gassing due to vapor displacement and/or chemical reactions.

• *Charge solids using lock hoppers* instead of rotary valves or manual dumping through open lids. Lock hoppers isolate the reactor from the open atmosphere so that organic vapor emissions are minimized. (Rotary valves, on the other hand, often allow vapors to escape as they rotate from the reactor vapor space back to the solids feed bin.) Lock hoppers are typically used when solids must be added to a reactor containing a volatile solvent



■ *Figure 2. Closed-loop vapor recycling system for pumping operations.*



■ *Figure 3. Lock hopper arrangement for charging solids to an inerted batch reactor.*

that is at an elevated temperature and/or pressure. In addition, they can be designed to eliminate air infiltration into a reactor for cases where oxygen and moisture would create an unsafe or undesirable condition. Figure 3 illustrates a typical lock hopper arrangement where two sliding gate valves isolate the solids feed bin (open to the atmosphere) from an inerted reactor operating at elevated temperature and pressure.

• *Consider cut-in hoppers for manually charging bags of solids* to a reactor *(5)*. Rather than dumping bags of solid raw material through an open lid (which can lead to significant dusting and solvent vapor losses), cut-in hoppers "cut open" the bags inside a closed feed hopper to contain any dust that is generated.

• *Eliminate manual addition of dry solids* by introducing solids in slurry form *(3)* or using dense-phase conveying. Consider using a raw material or intermediate already in the process to serve as the carrier fluid for the slurry, rather than introducing a new chemical to the process. Dense-phase conveying uses less conveying gas to move the solids, thereby reducing the amount of solvent evaporated from the reactor as the conveying gas is vented.

• *Vent displaced vapors through a refrigerated vent condenser* to recover and recycle condensable solvents *(6)*.

Table 1. Composition of a flammable solvent mixture for cleaning parts.

Component	Liquid Composition, wt. %	Vapor Composition, vol. % or mol. %
Acetone	10%	44%
Methyl Ethyl Ketone	30%	43%
Toluene	30%	10%
Xylene	30%	3%

• *Consider solvents with a lower vapor pressure* to minimize evaporation and facilitate recovery by condensation. Be careful with liquid solvent mixtures where a small weight percentage of a volatile solvent can account for the majority of the vapor emissions. For example, the composition of a flammable solvent mixture used for cleaning parts is shown in Table 1. Even though the liquid mixture contains only 10% acetone by weight, the saturated vapor phase is more than 40% acetone at 26°C and 1 atm total pressure. Removing or reducing the weight fraction of acetone in the solvent mixture would cut vapor emissions significantly.

Reactor operation

The strategies in this section focus on the inert blanketing, sampling, sealing, control, sequencing, and heating of batch reactors. A more exhaustive discussion of reactor design and operation for both continuous and batch chemical reactors can be found in *(7)*.

• *Reduce vapor losses by enclosing open air tanks (3)*. Use lids with gaskets that seal tightly if manual access is a necessity. Otherwise, consider a closed reactor with a permanent top and closed raw-material addition systems as described above.

• *Reduce vapor losses by improving seals on agitators and lids (1)*. In some cases, the agitator can be replaced with a jet mixing system, which consists of a jet nozzle submerged in the reactor fluid, a pump, and a liquid recirculation loop *(8)*.

• *Sequence the addition of reactants and reagents* to optimize yields and lower emissions. Consider, for example, a process in which a base, such as sodium hydroxide, is added at the end of a batch reaction cycle to neutralize the reaction mass before feeding the next process vessel; the pH in the reactor is allowed to vary with reaction progress.

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Adding the sodium hydroxide throughout the reaction sequence to maintain a constant pH may improve yield and minimize byproduct formation.

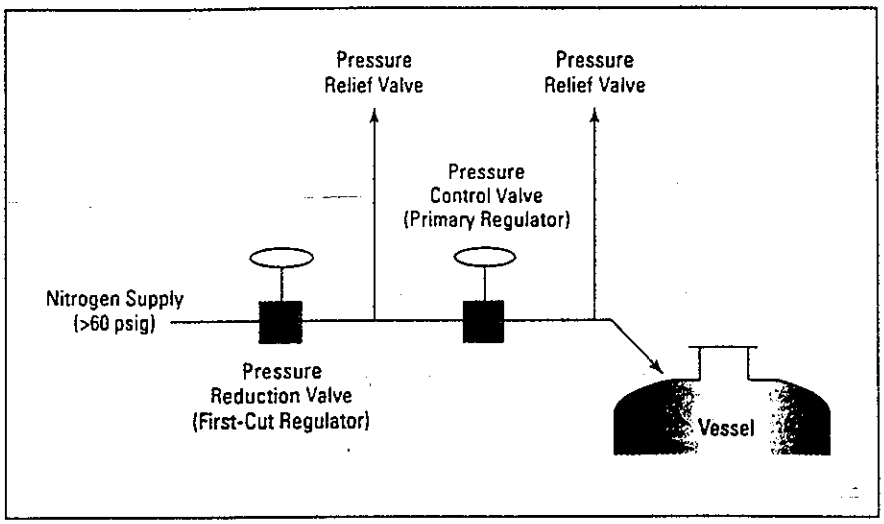
• *Control nitrogen purge rates with automatic flow control devices* instead of manual throttling valves *(1)*. Too often, the manual valves are found wide open, wasting nitrogen and dramatically increasing VOC losses.

• *Better yet, use a nitrogen pad system* (*i.e.*, pressure control of nitrogen in the reactor vessel headspace) instead of a purge based on flow control *(4)*. Figure 4 shows a typical piping diagram for a nitrogen pad system where the nitrogen supply pressure is greater than 60 psig. Dual-pressure regulators are employed to improve low-pressure control in the reactor headspace.

• *Optimize existing reactor design based on reaction kinetics, mixing characteristics, and other parameters* to reduce byproduct formation *(3)*. Further details on this aspect of reactor design and operation can be found in *(7)*.

• *Collect and recycle excess reactants and solvents* used in the reaction *(9)*. Consider adding or upgrading solvent purification equipment to allow recycle.

• *Use a minimum number of intermediate-stage process samples* to determine the reaction endpoint *(4)*. Also, strongly consider automatic, in-line sampling *(6)*, rather than manual sampling from vessel openings, to minimize vapor emissions from openings and the amount of sampling waste. Evaluate the impact of the time lag associated with manual samples analyzed in the site laboratory on reactor yield and waste generation. In many instances, the additional turnaround time required for laboratory analyses leads to excess waste production. For example, in a process for making an agricultural intermediate, manual sampling for a batch, caustic scrubbing system for "%NaOH" led to unnecessary safety margins in the operating procedures for purging the spent caustic scrubbing solution. Because of the long turnaround time from the laboratory, the spent scrubbing solution contained 3–5% unused NaOH. A viable alternative to this approach is to use an in-line pH meter to regulate caustic addition to minimize the amount of NaOH being wasted.



■ *Figure 4. Typical piping diagram for a nitrogen-padded reactor.*

• *Use statistical process control techniques* to regulate the reaction instead of relying on intermediate sampling *(6)*.

• *Eliminate excessive reactor boil-up* by replacing direct steam jacket heating with an external, recirculating, heating loop consisting of a pump and noncontact heat exchanger *(4)*. This may also prevent unwanted tar formation in reactions where a hot vessel wall leads to product degradation.

• *Eliminate fugitive emissions from pressure relief valves* by using an upstream rupture disk in series with the relief valve *(4)*.

Reactor discharging

• *Replace nitrogen blowcasing with a pump.* The pressurized nitrogen used to push the reaction mass from the reactor must be vented downstream. This nitrogen will leave saturated with solvent and, possibly, valuable product and reactants as well.

• *Design and install discharge lines on an incline* to take advantage of gravity flow to the downstream equipment. Avoiding a pump lowers investment and operating costs as well as fugitive emissions from leaks.

• *Reduce the reactor batch temperature before discharge* to lower the vapor pressure of VOCs, which can include solvents and, in some cases, reactants and products *(1)*.

Reactor cleaning

• *Optimize the product manufacturing sequence and product campaigns* to minimize washing operations. This may mean structuring product campaigns to manufacture clear or light-colored products before heavily pigmented products, or products with loose quality specifications before those with tight specifications. Within a single product campaign, it may mean better understanding the chemistry that leads to equipment fouling, and then changing the reaction sequence to minimize tar formation, equipment scaling, polymer buildup, and so on.

• *Maximize production runs* to decrease the frequency of washes *(6)*. Check with customers to see if

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product specifications can be loosened. If some customers can accept higher levels of impurities, fill their orders later in the product campaign, if possible.

• *Minimize the number of solvent rinses* used to clean reactors by understanding the level of acceptable contamination *(4)*. In some cases it may be possible to use off-spec product instead of clean solvent to flush the reactors.

• *Increase the smoothness of vessel internals* to reduce the quantity of cleaning solvent used *(3)*. Consider using nonstick nonporous linings, eliminating baffles, and minimizing other difficult-to-access points where material can accumulate and harden.

• *Use high-pressure rotary nozzles* to reduce the quantity of cleaning solvent used *(2)*.

• *Position drain valves at the lowest point on the reactor vessel* to improve removal of residual solvent and product before drying or the next product campaign.

• *Clean the insides of pipes with plastic or foam "pipe pigs" (2)*.

• *Replace volatile chlorinated solvents with lower-volatility, nonchlorinated solvents.*

• *Replace solvent-based cleaning with aqueous-based cleaning* that uses detergents or other surfactants, if necessary, to increase the cleaning effectiveness. Also, understand how pH affects cleaning.

• *Collect the final wash rinse for reuse as first-pass rinse during the next cleaning cycle (6)*. Lower-quality solvent or water from elsewhere in the plant may be suitable for use as the first rinse.

Modeling batch processes

Changes in standard operating conditions can affect the amount of waste generated by a batch process. However, few plants can accept the risks associated with making experimental batch runs. Recent developments in computer modeling software allow changes in batch operations to be analyzed to a greater extent than ever before.

Most of the major companies that sell process flowsheet simulation software have already developed and/or are greatly expanding their capability to simulate batch unit operations and overall batch processes. The features of several of these programs are outlined in Ref. 8. For information on a variety of such packages, see the *CEP Software Directory* at http://www.aiche.org/cep/softdir/softwareindex.htm.

Batch vs. continuous operation

For some processes, the conversion from batch to continuous operation is an effective way to reduce waste generation, as well as to increase total throughput *(3)*.

Cleaning waste is most significantly reduced by switching to a continuous process. Continuous process operations are rarely interrupted for cleaning, because the equipment is dedicated to the production of one or only a few products. Therefore, switching to a continuous process may mean practically eliminating cleaning waste.

In addition, solvent recovery in a continuous process is feasible, because it becomes more economical to install dedicated distillation equipment to handle the necessary chemical separations. Recovered solvent can then be reused in the process, instead of being incinerated or disposed of as a hazardous waste.

Examples

The following three case studies illustrate successful pollution prevention in batch operations.

Replacing an organic solvent with an aqueous solvent for cleaning. The small lots manufacturing area (SLM) at a facility was converted to aqueous cleaning in order to reduce solvent waste generation. SLM is an agricultural product manufacturing area using batch organic synthesis involving reaction vessels in series. Past operations involved several rinses with various organic solvents to clean the vessels between product campaigns. The spent organic wastes were not recycled, but were discarded off-site as a hazardous waste.

To reduce the production of organic solvent wastes, SLM replaced a number of organic solvent flushes with detergent flushes and water rinses. Solvent usage per cleaning cycle was reduced by 6,000 gallons — a 60% reduction over organic solvent cleaning. Moreover, the resulting aqueous waste can be processed in the site's wastewater treatment facility. (To allow this, it was important to select a biodegradable detergent and to ensure that the additional organic and hydraulic load on the biotreatment basin could be handled.)

Significant benefits other than the environmental benefits were realized as well. The business saved $168,000/yr in solvent waste disposal and $70,000/yr in solvent raw material costs. Cleaning effectiveness, measured by the amount of material carrying over into the next product, was increased tenfold. The increase in production capability resulting from the reduction in cleaning time is estimated to save as much as $750,000/yr.

Reducing methylene chloride emissions by sealing atmospheric tanks. Methylene chloride was used as a coating and cleaning solvent in the manufacture of several graphic arts and electronic photopolymer films. In the late 1980s, the site released more than 3 million lb/yr of chlorinated solvents into the air.

The coating solution preparation areas accounted for the majority of the air emissions. Coating solutions were prepared batchwise in agitated vessels using a blend of polymers, monomers, photoinitiators, pigments, and solvents. These atmospheric mix tanks were not well sealed, resulting in large fugitive and point-source emissions of methylene chloride.

To enclose the batch vessels as much as possible, the mix tanks were fitted with bolted, gasketed lids. The vessels were also designed with pressure/vacuum conservation vents to allow the vapor pressure to rise to 3 psig before the tanks breathed.

By sealing up the process, the site reduced air emissions by 40% and saved $426,000/yr in methylene chloride costs.

Converting from batch to continuous operation. The manufacturer of an herbicide intermediate was unable to meet demand when operating its batch process at full capacity. To overcome the production shortfall, it purchased the intermediate from a competitor at a price higher than its cost of manufacturing.

Duplication of the existing batch process seemed the conservative approach to increasing production. However, the business team saw an opportunity to meet the expansion objectives with minimal investment by changing from batch to continuous reaction technology. The team persevered through many intensive technology and project reviews, and concluded that the continuous process appeared inherently safer and technically viable. Within eleven months from concept to startup, the business team achieved a 240% increase in production capacity over the original batch process. In addition, the methanol emissions per pound of product from the continuous process were 29% less than those of the batch technology. CEP

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This article is excerpted from a new book published by AIChE, "Pollution Prevention: Methodology, Technologies, and Practices," by Kenneth L. Mulholland and James A. Dyer. Information about the book and how to order it is available on the AIChE Web site at http://www.aiche.org/publication/pollutionprevention.htm, or from the AIChE*Express* Call Center at 1-800-242-4363 (U.S.) or 1-212-591-8100.

Prevent Pollution in Equipment and Parts Cleaning Operations

These techniques can avoid the need to clean equipment or, where cleaning is required, replace or reduce the use of organic solvents.

Kenneth L. Mulholland and James A. Dyer,
E. I. du Pont de Nemours and Co.

available on-line www.aiche.org

Cleaning equipment and parts is an important preparatory step in many industrial processes. Cleaning removes dirt, oil, wax, oxides, residual products, monomers, and other contaminants that may adversely affect the final product quality or the operating efficiency of the equipment or part. Two general types of materials are removed: "soft" films, such as dirt, oil, and grease, and "hard" films, such as hardened polymeric films, scale, and paints. Until recently, solvent strippers such as methylene chloride were frequently used to remove both types of films from the surfaces being cleaned.

A chief concern for facilities with batch manufacturing operations that use multipurpose equipment is cross-contamination of product (in addition to environmental concerns, such as air emissions and hazardous waste disposal). This article discusses pollution-prevention engineering practices and technologies that help to avoid the need to clean equipment, and, where cleaning is necessary, the approaches that are available to replace or reduce the use of organic solvents.

The nature of emission sources

Cleaning, degreasing, and coating-removal technologies generally involve the application of an organic solvent (or solvents) to the material being removed. During the process, air emissions are often generated from the use of the solvent. And, after the cleaning process, other waste streams — solvent and metal-containing wastewater and sludges — remain that require disposal. The wastewater streams and sludges often contain materials that classify them as a RCRA hazardous waste *(1, 2)*.

The Pollution-Prevention Continuum

The Pollution-Prevention Continuum in Figure 1 shows the relative merits of options that are available to eliminate or reduce the frequency of equipment cleaning or to minimize the waste generated during the cleaning process. The decision of how far to move toward a zero waste and emissions design will depend on a number of factors, including corporate and business environmental goals, economics, technical feasibility, and applicable regulations.

More than 95% pollution prevention

In the design of a new facility, equipment should be designed without low spots, ledges, or other crevices that will collect material that later becomes difficult to remove. Properly designed vessels will contain sloping interior bottoms and piping arrangements with valved low points or valves that drain back into the main vessels.

Existing process equipment can be retrofitted with drain valves installed at strategic low points. If the low points are too low for standard tanks and pumps, then design a special portable collection vessel to collect and transport the material to a tank *(3)*. (This is discussed further in one of the examples below.)

In addition, equipment can be dedicated to a single product line. This eliminates the need to wash the inside of the equipment between production campaigns.

Alternatively, flush contaminated equipment with the salable product or a process intermediate, then recycle the flush back to the process, where it can be purified in existing separations equipment.

A continuous process inherently generates less waste, because there is no need to shut down, drain, and clean the equipment.

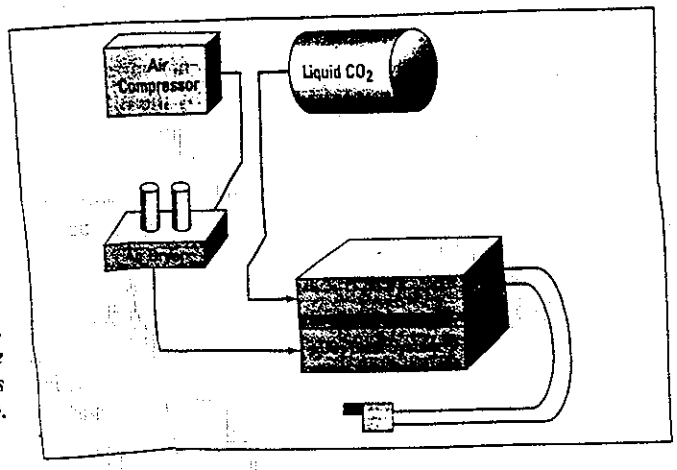
More than 90% pollution prevention

Loosening specifications for finished product allows for higher levels of impurities in the final product or cross-contamination of products. This reduces or eliminates the need for solvent washes between product campaigns. Many times, specifications for products manufactured in the same equipment are different, and one set of specifications may be more stringent than another. Through careful planning and inventory control, product changeovers can be made from products with tighter specifications to products with looser specifications.

Application of an antistick coating, such as polytetrafluoroethylene (PTFE; *e.g.*, Teflon) or silicone, to the interior walls of processing equipment could enable easy drainage and removal of leftover residue.

Degree of Pollution Prevention	Technology or Practice
> 95%	Minimize the need for cleaning Drain completely Dedicate to a single product Flush with process material Continuous vs. batch process
> 90%	Loosen finished product specifications Modify surfaces to eliminate cleaning
> 75%	Carbon dioxide or cryogenic blasting Burning or heat volatilization Mechanical removal
> 50%	High- and medium-pressure water washing Blasting with plastic beads, sodium bicarbonate, wheat starch Water with detergent or ultrasonics Clean with pipe "pigs"
> 10%	Flush with solvent from another process Decrease number of flushes Reuse last flush from previous campaign
< 10%	Solvent substitution (see Chapter 12 in *(10)*)

■ *Figure 1. The Pollution Prevention Continuum for equipment cleaning (above).*



■ *Figure 2. Carbon dioxide blasting systems (right).*

More than 75% pollution prevention

Carbon dioxide blasting systems (Figure 2) consist of a refrigerated liquid CO_2 supply and equipment for converting the liquid CO_2 to solid pellets. The solid pellets remove coatings by a combination of impact, embrittlement, thermal contraction, and gas expansion. Because the CO_2 pellets sublime, a wastewater or liquid waste is not produced, and a dry coating residue is collected *(1)*.

Liquid nitrogen cryogenic stripping uses liquid nitrogen to cool the surface and to help propel the plastic bead blasting media. The liquid nitrogen embrittles and shrinks the coating, and the high-velocity, nonabrasive pellets crack, debond, and break away the coating *(1)*.

The removal of coatings using heat that is generated by flames, lase, or flashlamps results in the vaporition of the coated materials. The nonvotile portions of the coating, such as mls, form particulate ash that is rerved and collected by a vacuum air rerval system *(1)*.

Where feasible, manual cleag using scrapers or spatulas might ɢinate the need for any subsequent vent wash.

More than 50% pollution prevention

High-pressure water wash. High-pressure water washing, called water-jet stripping, uses the pact energy of the water to ren coatings. The water is collected, filtered, and then recycled. The coating thickness and hardness dictate whether a high-pressure (15,000 to 30,000 psig) or medium-pressure (3,000 to 15,000 psig) water-jet is required.

A typical high-pressure water wash system for a process vessel is illustrated in Figure 3. The high-pressure water lance is attached to a carriage, which is in turn attached to the bottom of the vessel. A chain drive moves the lance up and down the carriage as needed. A swivel joint at the base of the lance permits free rotation. The nozzle at the tip of the spinning lance has two apertures that emit cone-shaped sprays of water at 10,000 psi with a combined flow rate of 16 gal/min. Operation of

that only one-tenth of the product crude wash material was really needed to effect cleaning. Second, a dedicated pipeline for each crude was installed, thus eliminating the need to flush the line between campaigns. Third, an extended and improved drainage procedure was developed for a large packed-bed distillation column. Finally, the product specifications were relaxed, so that fewer washes were required to maintain product specifications.

Capital investment for these process changes was $700,000; the project had a positive net present value of more than $3 million, and realized a 78% reduction in waste generation *(3)*.

Using high-pressure washing. At one chemical plant, cleaning kettles required 800 h of labor and 110 t of solvent annually. The cleaning process sometimes involved employees entering the kettles to scrape the walls — a process that took each employee 3 h. Changing to a high-pressure rotating spray head reduced the amount of solvent needed, thereby reducing the time required for cleaning. In addition, employee safety was improved by eliminating the need for employees to enter the vessels. The change required a capital investment of $69,000; it resulted in an annual savings of $61,500.

At another manufacturing site, several types of polymer were made in an agitated vessel that had to be cleaned periodically to maintain product quality. The vessel was cleaned by washing with a flammable solvent. To eliminate the use of the solvent, a special high-pressure water-jet was installed to clean the vessel. The water-jet had a capital investment of $125,000; the project had a net present value of more than $2.5 million and a 98% reduction in waste generation.

In the production of polyvinyl chloride (PVC), polymer buildup on reactor surfaces, agitators, brackets, and other parts required cleaning after every batch. The manual cleaning operation was replaced by a high-pressure water-jet. To minimize the need for water-jet cleaning, a proprietary additive was used to suppress the formation of polymer buildup on the walls. After each batch, a low-pressure water rinse removed sufficient material to prevent contamination of the next batch. Only after 500 batches was a high-pressure water-jet wash required *(9)*.

Flushing equipment with waste solvent. In the manufacture of a cast type product, methylene chloride was used as the process flush and cleaning solvent for 24 years. Two significant changes were made to the cleaning procedure. First, methylene chloride was replaced with a dibasic ester waste stream from another process. Second, the waste load was further reduced by modifying the flushing procedure. Methylene chloride emissions were reduced by 97%, and a proposed $1.5 million project to control methylene chloride emissions to the air was avoided. CEP

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Table 1. Pollution Prevention Through Good Operating Practices

Good Operating Practice	Program Ingredients
Waste Segregation	Prevent mixing of hazardous wastes with nonhazardous wastes
	Store materials in compatible groups
	Segregate different solvents
	Isolate liquid wastes from solid wastes
Preventive Maintenance Programs	Maintain equipment history cards on equipment location, characteristics, and maintenance
	Maintain a master preventive maintenance (PM) schedule
	Keep vendor maintenance manuals handy
	Maintain a manual or computerized repair history file
Training/Awareness-Building Programs	Provide training for
	- Operation of the equipment to minimize energy use and material waste
	- Proper materials handling to reduce waste and spills
	- Emphasize importance of pollution prevention by explaining the economic and environmental ramifications of hazardous waste generation and disposal
	- Detecting and minimizing material loss to air, land, or water
	- Emergency procedures to minimize lost materials during accidents
Effective Supervision	Closer supervision may improve production efficiency and reduce inadvertent waste generation
	Centralize waste management. Appoint a safety/waste management officer for each department. Educate staff on the benefits of pollution prevention. Establish pollution prevention goals. Perform pollution prevention assessments.
Employee Participation	"Quality circles" (free forums between employees and supervisors) can identify ways to reduce waste
	Solicit and reward employee suggestions for waste reduction ideas

Table 1. (Continued)

Good Operating Practice	Program Ingredients
Production Scheduling/Planning	Maximize batch size to reduce clean out waste
	Dedicate equipment to a single product
	Alter batch sequencing to minimize cleaning frequency (light-to-dark batch sequence, for example)
Cost accounting/ Allocation	Charge direct and indirect costs of all air, land, and water discharges to specific processes or products
	Allocate waste treatment and disposal costs to the operations that generate the waste
	Allocate utility costs to specific processes or products

Table 2. Checklist for All Industries

Waste Origin/Type	Pollution Prevention and Recycling Methods
Material Receiving/ Packaging materials, off-spec materials, damaged container, inadvertent spills, transfer hose emptying	Use "Just-in-Time" ordering system. Establish a centralized purchasing program. Select quantity and package type to minimize packing waste. Order reagent chemicals in exact amounts. Encourage chemical suppliers to become responsible partners (e.g., accept outdated supplies). Establish an inventory control program to trace chemical from cradle to grave. Rotate chemical stock. Develop a running inventory of unused chemicals for other departments' use. Inspect material before accepting a shipment. Review material procurement specifications. Validate shelf-life expiration dates. Test effectiveness of outdated material. Eliminate shelf-life requirements for stable compounds. Conduct frequent inventory checks. Use computer-assisted plant inventory system. Conduct periodic materials tracking. Properly label all containers. Set up staffed control points to dispense chemicals and collect wastes. Buy pure feeds. Find less critical uses for off-spec material (that would otherwise be disposed). Change to reusable shipping containers. Switch to less hazardous raw material. Use rinsable/recyclable drums.
Raw Material and Product Storage/ Tank bottoms; off-spec and excess materials; spill residues; leaking pumps, valves, tanks, and pipes; damaged containers; empty containers	Establish Spill Prevention, Control, and Countermeasures (SPCC) plans. Use properly designed tanks and vessels only for their intended purposes. Install overflow alarms for all tanks and vessels. Maintain physical integrity of all tanks and vessels. Set up written procedures for all loading/unloading and transfer operations. Install secondary containment areas. Instruct operators to not bypass interlocks, alarms, or significantly alter setpoints without authorization. Isolate equipment or process lines that leak or are not in service. Use sealless pumps.

Table 2. (Continued)

Waste Origin/Type	Pollution Prevention and Recycling Methods
Raw Material and Product Storage/ (Continued)	Use bellows-seal valves. Document all spillage. Perform overall materials balances and estimate the quantity and dollar value of all losses. Use floating-roof tanks for VOC control. Use conservation vents on fixed roof tanks. Use vapor recovery systems. Store containers in such a way as to allow for visual inspection for corrosion and leaks. Stack containers in a way to minimize the chance of tipping, puncturing, or breaking. Prevent concrete "sweating" by raising the drum off storage pads. Maintain Material Safety Data Sheets to ensure correct handling of spills. Provide adequate lighting in the storage area. Maintain a clean, even surface in transportation areas. Keep aisles clear of obstruction. Maintain distance between incompatible chemicals. Maintain distance between different types of chemicals to prevent cross-contamination. Avoid stacking containers against process equipment. Follow manufacturers' suggestions on the storage and handling of all raw materials. Use proper insulation of electric circuitry and inspect regularly for corrosion and potential sparking. Use large containers for bulk storage whenever possible. Use containers with height-to-diameter ratio equal to one to minimize wetted area. Empty drums and containers thoroughly before cleaning or disposal. Reuse scrap paper for note pads; recycle paper.
Laboratories/ Reagents, off-spec chemicals, samples, empty sample and chemical containers	Use micro or semi-micro analytical techniques. Increase use of instrumentation. Reduce or eliminate the use of highly toxic chemicals in laboratory experiments. Reuse/recycle spent solvents. Recover metal from catalyst.

Table 3. Checklist for the Printing Industry

Waste Origin/Type	Pollution Prevention and Recycling Method
Image Processing/Empty containers, used film packages, outdated material	Recycle empty containers. Recycle spoiled photographic film.
Image Processing/ Photographic chemicals, silver	Use silver-free films, such as vesicular, diazo, or electrostatic types.. Use water-developed litho plates. Extend bath life. Use squeegees to reduce carryover. Employ countercurrent washing. Recover silver and recycle chemicals.
Plate Making/Damaged plates, developed film, outdated materials	Use electronic imaging, laser plate making.
Plate Making/ Acids, alkali, solvents, plate coatings (may contain dyes, photopolymers, binders, resins, pigment, organic acids), developers (may contain isopropanol, gum arabic, lacquers, caustics), and rinse water	Electronic imaging/laser print making. Recover silver and recycle chemicals. Use floating lids on bleach and developer tanks. Use countercurrent washing sequence. Use squeegees to reduce carryover. Substitute iron-EDTA for ferrocyanide. Use washless processing systems. Use better operating practices. Remove heavy metals from wastewater.
Finishing/Damaged products, scrap	Reduce paper use and recycle waste paper.
Printing/ Lubricating oils, waste ink, cleanup solvent (halogenated and nonhalogenated), rags	Prepare only the quantity of ink needed for a press run. Recycle waste ink and solvent. Schedule runs to reduce color change over. Use automatic cleaning equipment. Use automatic ink leveler. Use alternative solvents. Use water-based ink. Use UV-curable ink. Install web break detectors. Use automatic web splicers. Store ink properly. Standardize ink sequence. Recycle waste ink.

Table 4. Checklist for the Fabricated Metal Industry

Waste Origin/Type	Pollution Prevention and Recycling Methods
Machining Wastes/ Metalworking Fluid	Use of high-quality metalworking fluid. Use demineralized water makeup. Perform regularly scheduled sump and machine cleaning. Perform regularly scheduled gasket, wiper, and seal maintenance. Filter, pasteurize, and treat metalworking fluid for reuse. Assigning fluid control responsibility to one person. Standardize oil types used on machining equipment. Improve equipment scheduling/establish dedicated lines. Reuse or recycle cutting, cooling, and lubricating oils. Substitute insoluble borates for soluble borate lubricants.
Machining Wastes/ Metal wastes, dust, and sludge	Segregate and reuse scrap metal.
Parts Cleaning/ Solvents	Install lids/silhouettes on tanks. Increase freeboard space on tanks. Install freeboard chillers on tanks. Remove sludge from solvent tanks frequently. Extend solvent life by precleaning parts by wiping, using air blowers, or predipping in cold mineral spirits dip. Reclaim/recover solvent on- or off-site. Substitute less hazardous solvent degreasers (e.g., petroleum solvents instead of chlorinated solvents) or alkali washes where possible. Distribute parts on rack to allow good cleaning and minimize solvent holup. Slow speed of parts removal from vapor zone. Rotate parts to allow condensed solvent drop-off.
Parts Cleaning/ Aqueous Cleaners	Remove sludge frequently. Use dry cleaning and stripping methods. Use oil separation and filtration to recycle solution.
Parts Cleaning/ Abrasives	Use of greaseless or water-based binders. Use an automatic liquid spray system for application of abrasive onto wheel. Ensure sufficient water use during cleaning by using water level control. Use synthetic abrasives.
Parts Cleaning/ Rinsewater	Improve rack and barrel system design. Use spray, fog, or chemical rinses. Use deionized water makeup to increase solution life.

Table 4. (Continued)

Waste Origin/Type	Pollution Prevention and Recycling Methods
Surface Treatment and Plating/ Process Solutions	Use material or process substitution e.g., trivalent chromium. Use low solvent paint for coating. Use mechanical cladding and coating. Use cleaning baths as pH adjusters. Recover metals from process solutions.
Surface Treatment and Plating/ Rinsewater	Reduction in drag-out of process chemicals: Reduce speed of withdrawal Lower plating bath concentrations Reuse rinsewater Use surfactants to improve drainage Increase solution temperature to reduce viscosity Position workpiece to minimize solution holdup System design considerations: Rinsetank design Multiple rinsing tanks Conductivity measurement to control rinse water flow Fog nozzles and sprays Automatic flow controls Rinse bath agitation Counter current rinse.

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Table 5. Checklist for the Metal Casting Industry

Waste Origin/Type	Pollution Prevention and Recycling Methods
Baghouse Dust and Scrubber Waste/ Dust contaminated with lead, zinc, and cadmium	Identify the source of contaminants, e.g., coatings on scrap, and work with suppliers to find raw materials that reduce the contaminant input. Install induction furnaces to reduce dust production. Recycle dust to original process or to another process. Recover contaminants with pyrometallurgical treatment, rotary kiln, hydrogen reduction, or other processes. Recycle to cement manufacturer.
Production of Ductile Iron/ Hazardous slag	Reduce the amount of sulfur in the feedstock. Use calcium oxide or calcium fluoride to replace calcium carbide as the desulfurization agent. Improve process control. Recycle calcium carbide slag.
Casting/ Spent casting sand	Material substitution, e.g., olivine sand is more difficult to detoxify than silica sand. Separate sand and shot blast dust. Improve metal recovery from sand. Recover sand and mix old and new sand for mold making. Recover sand by washing, air scrubbing, or thermal treatment. Reuse sand for construction if possible.

Table 6. Checklist for the Printed Circuit Board Industry

Waste Origin/Type	Pollution Prevention and Recycling Methods
PC Board Manufacture/ General	Product substitution: Surface mount technology Injection molded substrate and additive plating
Cleaning and Surface Preparation/ Solvents	Materials substitution: Use abrasives Use nonchelated cleaners Increase efficiency of process: Extend bath life, improve rinse efficiency, countercurrent cleaning Recycle/reuse: Recycle/reuse cleaners and rinses
Pattern Printing and Masking/ Acid fumes/organic vapors; vinyl polymers spent resist removal solution; spent acid solution; waste rinse water	Reduce hazardous nature of process: Aqueous processable resist Screen printing versus photolithography Dry photoresist removal Recycle/reuse: Recycle/reuse photoresist stripper
Electroplating and Electroless Plating/ Plating solutions and rinse wastes	Eliminate process: Mechanical board production Materials substitution: Noncyanide baths Noncyanide stress relievers Extend bath life; reduce drag-in: Proper rack design/maintenance, better precleaning/rinsing, use of demineralized water as makeup, proper storage methods Extend bath life; reduce drag-out: Minimize bath chemical concentration, increase bath temperature, use wetting agents, proper positioning on rack, slow withdrawal and sample drainage, computerized/automated systems, recover drag-out, use airstreams or fog to rinse plating solution into the tank, collect drips with drain boards. Extend bath life; maintain bath solution quality: Monitor solution activity Control temperature Mechanical agitation Continuous filtration/carbon treatment Impurity removal Improve rinse efficiency: Closed-circuit rinses Spray rinses Fog nozzles

Table 6. (Continued)

Waste Origin/Type	Pollution Prevention and Recycling Methods
Electroplating and Electroless Plating/ (Continued)	Improve rinse efficiency (continued): Increased agitation Countercurrent rinsing Proper equipment design/operation Deionized water use. Turn off rinsewater when not in use. Recovery/reuse: Segregate streams Recover metal values.
Etching/ Etching solutions and rinse wastes	Eliminate process: Differential plating Use dry plasma etching. Materials substitution: Nonchelated etchants Nonchrome etchants. Increased efficiency: Use thinner copper cladding Pattern vs. panel plating Additive vs. subtractive method. Reuse/recycle: Reuse/recycle etchants.

Table 7. Checklist for the Coating Industry

Waste Origin/Type	Pollution Prevention and Recycling Methods
Coating Overspray/ Coating material that fails to reach the object being coated	Maintain 50% overlap between spray pattern. Maintain 6- to 8-inch distance between spray gun and the workpiece. Maintain a gun speed of about 250 feet/minute. Hold gun perpendicular to the surface. Trigger gun at the beginning and end of each pass. Properly train operators. Use robots for spraying. Avoid excessive air pressure for coating atomization. Recycle overspray. Use electrostatic spray systems. Use turbine disk or bell or air-assisted airless spray guns in place of air-spray guns. Install on-site paint mixers to control material usage. Inspect parts before coating.
Stripping Wastes/ Coating removal from parts before applying a new coat	Avoid adding excess stripper. Use spent stripper as rough prestrip on next item. Use abrasive media paint stripping. Use plastic media bead-blasting paint stripping. Use cryogenic paint stripping. Use thermal paint stripping. Use wheat starch media blasting paint stripping. Use laser or flashlamp paint stripping.
Solvent Emissions/ Evaporative losses from process equipment and coated parts	Keep solvent soak tanks away from heat sources. Use high-solids coating formulations. Use powder coatings. Use water-based coating formulations. Use UV cured coating formulations.
Equipment Cleanup Wastes/ Process equipment cleaning with solvents	Use light-to-dark batch sequencing. Produce large batches of similarly coated objects instead of small batches of differently coated items. Isolate solvent-based paint spray booths from water-based paint spray booths. Reuse cleaning solution/solvent. Standardize solvent usage. Clean coating equipment after each use.
Source Reduction	Reexamine the need for coating, as well as available alternatives. Use longer lasting plastic coatings instead of paint.

Recovery, Reuse, and Recycle of Water in Semiconductor Wafer Fabrication Facilities

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This paper summarizes the benefits and risks associated with water re-use and recycling in the semiconductor industry. The specific items that will be covered in this paper are: characterization of the spent rinse-water types, the composition range of key impurities, different recycling strategies, and water conservation methods. Discussion will include the development of new purification methods for the removal of organic impurities, and the development of a computer model for simulating the effects of recycle.

INTRODUCTION

The semiconductor industry has recently experienced rapid growth at an unprecedented rate. This expansion is causing concern in some communities due to the large quantities of water presently required for semiconductor wafer manufacturing. Along with this expansion cones the construction and installation of new wafer fabrication facilities (FABS). Each new facility willuse 1 to 3 million gallons per day. The water use in some locations approaches several milions of gallons per day. The only cost effective long-term solution is the proper segregation and collection of waste rinse waters and the implementation of a true recycling strategy.

TABLE 1. Benefits Associated With Recycling Water

1. Improved feed water quality, final UPW quality
2. Improved reliability of UPW facility, Less downtime:
   - Reduced frequency of RO membrane cleaning processes.
   - Reduced frequency of ion exchange regenerations.
   - Reduced frequency of filter backwashes/rinses.
   - Improved efficiencies in UPW treatment processing.
3. Reduced chemical usage for ion exchange regenerations.
4. Signified cost savings:
   - Less feed water and wastewater discharge costs.
   - Less regeneration chemical cost.
   - Less industrial waste treatment cost.
5. Improved RO reject quality for other reclamation purposes.
6. Less demand on the municipal water supply and waste water treatment systems.

TABLE 2. Risks Associated With water Recycling

1. The introduction of impurity spikes into the system.
2. The buildup of recalcitrant compounds.
3. Inadequacy of the present purification methods in removing process generated compounds.
4. Risk of new chemical interactions caused by recycle.
5. Contamination due to biofouling.

Recycling of water that was previously purified to an ultrapure level and then used to rinse off ultrapure chemicals from clean wafers, provides many advantages, including an improvement in final water quality. This alone

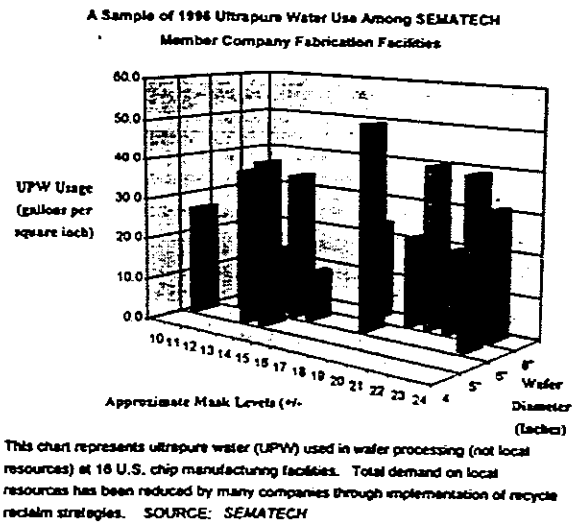

FIGURE 1. Ultrapure water use in semiconductor wafer processing.

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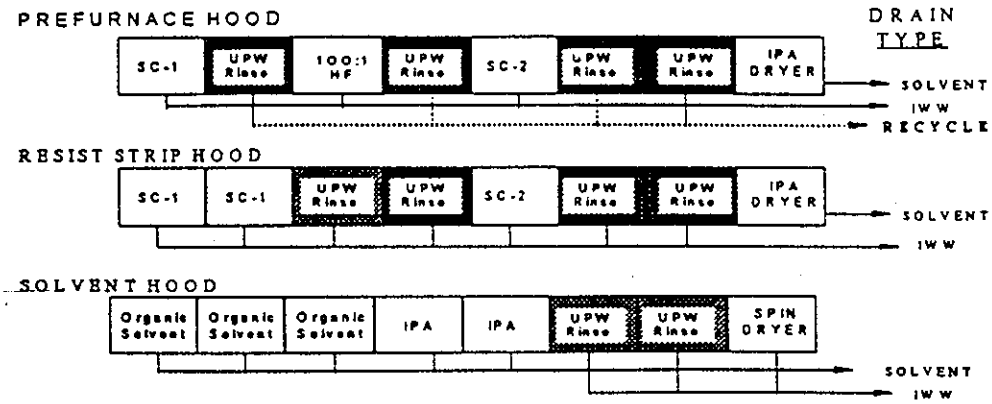

FIGURE 2. Typical process tool setup.

justifies the efforts associated with the implementation of a recycle strategy. It is not necessary to justify the effort based only on water conservation principles. There are many benefits to be realized, both in cost and in processing, associated with recycling once purified water, back through the purification process again. Much of the spent rinsewater generated in the semiconductor processes, is still of superior quality compared to most municipal feedwater supplies, This spent rinsewater can be used as a feed water source, replacing a portion of the municipal feedwater supply, to be reprocessed in the ultrapure deionized water (UPW) facility. The benefits to this are multi-fold, and include the items listed in Table I.

There are also risks, however, associated with recycling spent process rinsewater back into a UPW facility, to be used once again in the wafer fabrication process. These risks include the items listed in Table 2.

DISCUSSION OF WATER CONSERVATION STRATEGIES

Figure 1 shows the wide range of water usage rate reported by semiconductor manufacturing plants. This chart is the result of a survey performed by Sematech and the data obtained from its member companies. The amount of Ultra Pure Water (UPW) used per wafer produced varies from site to site, from company to company, and with wafer size. Each wafer fabrication facility typically uses 1-3 MGPD (million gallons per day). Some company sites have 3-4 fabs per site, resulting in large quantities of UPW use per site which can easily exceed 10 MGPD. This data is not the amount of municipal water demand, but the amount of UPW. The actual demand on municipal water supply is approximately 25% greater than the quantity of UPW, due to losses in the water purification process. The demands can be quite significant on the municipal water supply and have been a problem for some communities, especially those located in arid regions. Most of this UPW is used for wafer rinsing purposes. Figure 2 indicates some typical semiconductor process tool setups and a general indication of the various types of wastewater generated (DeGenova and Williams [2]).

Typically, ultrapure rinse water is contaminated with residual chemicals carried in with the process flow. The ultrapure rinse that typically follows acid/base treatments usually can be readily recycled; the contaminants are removed from the water using standard separation techniques. Hence, these streams are considered easily recyclable. One must only segregate the rinse water drains away from the industrial waste drain to collect the water for recycle purposes. Due to the nature of the semiconductor chemical process steps, however, some of th. rinse water becomes contaminated with compounds that are not read removed with standard separation techniques. Although they foll acid/base chemistries, the actual product itself may carry contaminant into this rinse water. The rinse water, from the resist strip hoods, m

TABLE 3. Rinse Water Reduction

- Spray rinsing vs. Overflow, Quick Dump
- Rinse Tank Geometry Improvements
- Hot UPW vs. Cold UPW
- Megasonic Rinsing
- Idle Flow Rate Reduction
- Analystical Monitoring of Rinse Water
- Computer Modeling; Convective/Diffusive

not be readily recyclable. The rinse that typically follows organic che ical baths may also become contaminated with compounds not readil removable and recyclable. The segregation of these waste streams i important to achieve a reliable recycle system.

The contaminants in the spent rinsewater generating most of concern in the industry today are organic solvents. The method o

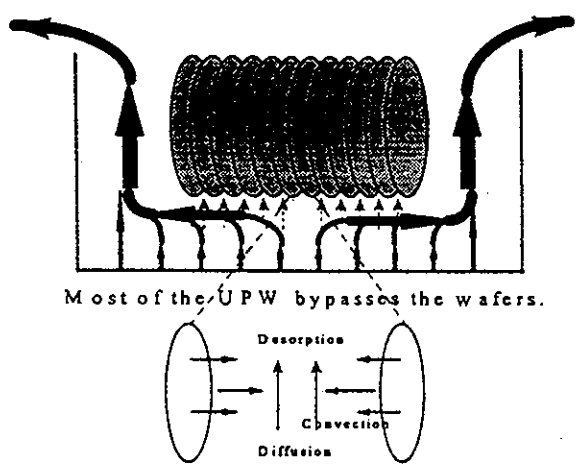

FIGURE 3. Typical overflow rinsing

TABLE 4. Water Reclamation/Reuse

- RO Reject: C/T, Air Scrubbers, Irrigation
- Ultrafilter Reject: UPW System Rinsing
- Analytical Instrument Discharge: Various Use
- Spent Rinse Water: C/T Makeup

choice for the removal of these organic compounds is oxidation. Filtration and adsorption present a risk of biofouling. The concept of photocatalytic oxidation reactors, as applied to recycle systems, has been developed at the University of Arizona in Tucson (Chen and Shadman; Shadman and Governal [1]). The photocatalyzed oxidation of process-generated impurities like surfactants, organic solvents, and trace chlorinated hydrocarbons in ultrapure water is promising.

Process simulation is another important tool in the design and analysis of recycle systems. Work is presently underway at the University of Arizona (Shadman [5]) in developing a process simulator for this application. This simulation consists of a solution to the governing equations for transport and removal of impurities. The equations for the simulator modules representing reactions and transport of impurities are combined

TABLE 5. Water Recycling

- Spent Rinse Water: Recycled to UPW System:
- Feed Water Storage Tank
- Semi-Pure Storage Tank
- Ultrapure Water Storage Tank

to determine the processes that take place in a typical ultrapure water treatment facility. In solving these equations, one can obtain the dynamics of contaminant distribution in the primary supply and the polishing loop as well as the final concentrations at the point of use.

The primary strategy to conserve UPW is by reducing the water used for water rinsing. Some of the techniques, indicated in Table 3, are quite simple but can make significant impacts to the overall water consumption. Spray type rinsing has been shown to use much less water than typical overflow type. However, spray rinsing generally adds dissolved oxygen and possibly other contaminants.

Hot water is generally more effective than cold water in cleaning wafers. In some cases, the rinse water temperature can be elevated to

TABLE 6. Typical Water Quality Comparison

Water Quality Parameter	Units	Typical Municipal Water Supply	Typical Ultrapure Water Product	Segregated (50%) Spent Rinse Water
Resistivity	M Ohms-cm	0.004	>18	0.8
pH	units	8	6	5-7
TOC	ppb	3500	<10	20
Ammonium	ppb	300	<1	300
Calcium	ppb	22000	<1	68
Magnesium	ppb	4000	<1	26
Potassium	ppb	4500	<1	25
Silica	ppb	4780	<10	338
Sodium	ppb	29000	<1	237
Chloride	ppb	15000	<1	100
Fluoride	ppb	740	<1	100
Sulfate	ppb	42000	<1	500

accomplish a better rinse, reducing the quantity of rinse water required. However, hot ultrapure rinse water has also been shown to cause defects after certain process steps. Megasonic rinsing is another method of improving the rinse process. By adding megasonic action, one can improve the rinsing process in some cases, thereby reducing the required quantity of rinse water. Until recently, rinse tanks were typically designed with large volumes . It was originally thought that large water volumes would provide a cleaner rinse. Nonetheless, Figure 3 shows this is not necessarily the case. As the wafers are typically loaded into wafer carriers, or boats, and are tightly spaced relative to one another, the path of least resistance for the water flow is actually around the wafer boat, rather than in between the wafer product spacing. It has been shown that nearly 80% of the rinse water actually bypasses the product (Rosato et al. [4]). A smaller rinse tank actually provides for a better rinse process with this arrangement. New semiconductor process tools are being designed with smaller rinse tanks and with directional flow patterns forcing the water in between the wafer spaces, producing faster, better rinsing. Less process time for rinsing is required and better process control is achieved.

In addition, reducing flow rates during idle periods can also make significant differences in water reduction. However, low flow rates can lead to bacterial growth, which could be devastating to the UPW system and to the production line. Studies are underway to evaluate sensors for

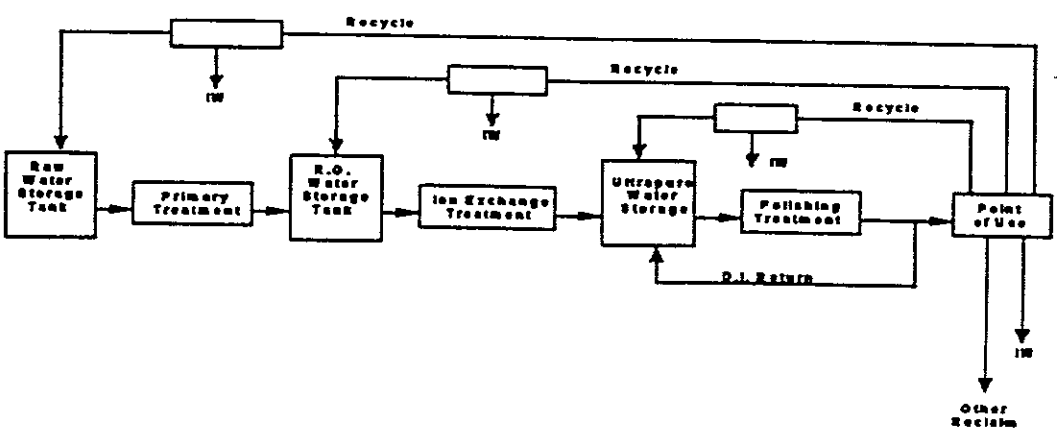

FIGURE 4. Water recycling strategies.

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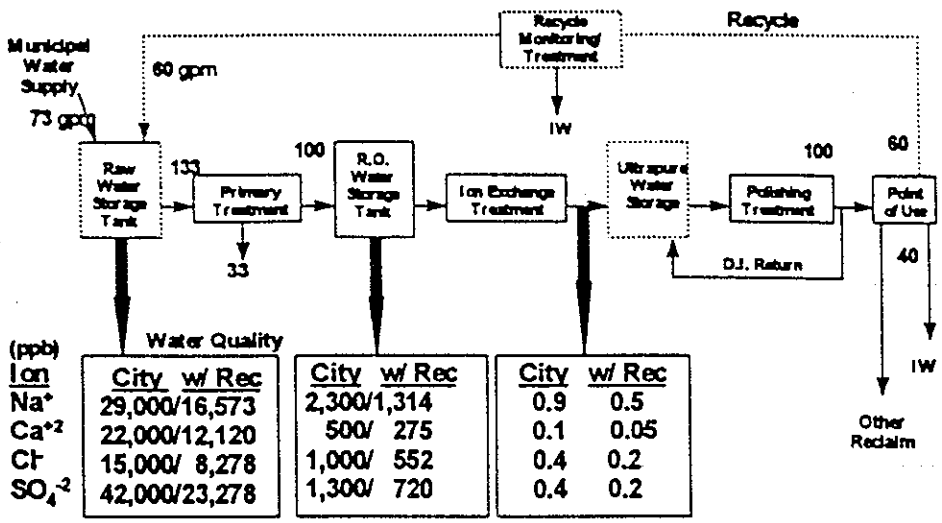

FIGURE 5. Typical UPW system with recycle. Recycle effects on water quality levels.

monitoring the quality of water in each rinse tank to determine when adequate rinsing is achieved. Some studies have focused on the development of rinse models using both diflusion and convection equations to help optimize the rinsing process (Helms [3]). These models include the processes that occur in between the tight wafer spacing, including the desorption of the removal of chemicals from the wafer surface and the difflision of the chemicals through the boundary layer into the bulk fluid where impurities are carried away by convection.

A second water reduction strategy currently underway is in the re-use of water in other areas such as in the cooling towers, air scrubbers, and non process applications. The reject water from the reverse osmosis process is a good candidate for this type of re-use. Some of the more common applications of water re-use are listed in Table 4. Spent rinse water can also be used for some of these re-use applications. However, due to its relatively pure nature, this water is quite aggressive and will attack most materials. Additional treatment may be necessary prior to re-use of this water, such as in raising the alkalinity to decrease the corrosion characteristics.

Another water use optimization and reduction strategy is in recycling of the spent rinse water back into the UPW treatment system. Because of the relatively high purity level of the rinse water, one can consider recycling this water back into the UPW process at various points within the process. It can be combined with the feed water at the treatment process input, thereby reducing the demand for this feed source. It can also be combined at other points in the UPW system, such as with reverse osmosis purified water, in a semi-pure state. Or, one can consider recycling this spent rinse water back into the UPW process at an ultrapure state, such as in the ultrapure water storage tank where it will be re-polished prior to use. Table 5 lists these options, which are also illustrated in Figure 4, which indicates a typical UPW tearment process, with primary treatment, ion exchange or secondary treatment, and a final polishing treatment step with holding tanks. The spent rinse water can be brought back to any of these holding tanks. Naturally, the highest benefit would be gained by bringing the recycle back to the UPW tank prior to polishing. However, this option also carries the highest risk.

Table 6 indicates some typical water purity levels at different s of processing. Shown here are a typical municipal supply water pu typical Ultrapure Water quality, and what one would expect from lecting approximately 50% of the spent rinse water, specifically s gated according to recycle readiness.

Table 6 indicates that the spent rinse water is still in a semi state, and is of better quality than water supplied by the municip It seems quite logical that replacing the municipal city feed water ply with this spent nnse water in a recycle mode would have bene consequences. However, due to the risks associated with recy these spent rinse waters back into the process flow, the consequen which could be devastating to manufacturing, a much more de effort is required. If the final UPW product becomes contaminat any time, the manufacturing facility must srop production, riskir work in progress. It may take significant time to bring the UPW ty back to the required specifications, thereby causing downtim extra costs and risks. The task at hand is to eliminate any risk assoc with water recycling.

The benefits of recycling, listed in Table I, can be quite substa With a better quality of feed water at the source, the unit process the ultrapure water facility operate with improved efficiency. D the improved processing, there is less required maintenance and d time, resulting in a more reliable, and safer facility. A reducti chemical usage can also be realized, as less membrane cleaning an ion exchange regeneration are required. There is also a reduction i amount of industrial wasrewater requiring treatment. In fact, w better quality feed source, reject from a reverse osmosis system improves in quality, rendering this water much more amenabl other reclamation purposes. Figure 5 illustrates a schematic of a ty UPW system with recycle back to the primary feed water storage Indicated here, are quality levels through various points in the U facility, with and without the recycle of water. The estimated v quality with recycle, based on quality levels listed in Table 6, fe the final polishing loop is of superior quality.

The risks, listed in Table 2, include bringing new and unk process contaminants to the UPW system. Compounds not pro

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removed could build up in the system. The product yield could then be negatively impacted. There is very little data available on the removal of organic compounds typically used in wafer processing. Any of these compounds in the UPW product at the point of use could be devastating. Hence, the proper segregation of the spent rinse water is imperative in order to keep these compounds out of the recycle loop, at least until data is available for the removal of these compounds with existing technology, and/or until newer and more effective technologies can be developed.

In addition to the process simulation, improved metrology and sensing techniques are required to minimize the recycling risk. Of utmost importance is on-line instrumentation with fast response that can be used to monitor recycle water quality. The fast response is necessary so that quick decisions can be made on whether to direct the recycle water back into the UPW process, or to divert the flow away from the UPW process. This action must be fast enough to avoid any quality upsets. Special valve switching arrangements can be installed, based on the monitoring devices, in order to minimize the risk or system upsets. Eventually, there will be a need to integrate the metrology and the simulator for both predictive and control purposes.

SUMARY AND CONCLUSION

A water recycling strategy focused on the segregation and re-use of semi-pure rinsewaters will provide for a cost effective system. Many benefits can be also be realized in the area of final UPW product quality, safety, waste chemical reduction, energy reduction, and improved process reliability.

There is a definite need for process simulation and more advanced metrology and control techniques. The risks associated with recycling can be minimized and managed properly.

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World Bank Publication Abstract

Title:	Pollution Prevention and Abatement Handbook 1998: Toward Cleaner Production
Author(s):	World Bank
Date:	4/1/99
Series:	
Country:	
Region:	
Subject Categories:	Environment / Environmental Management
Status:	In print

550 pages / 8 x 10 / (ISBN 0-8213-3638-X) / Stock no. 13638 / $125.00 / Price code S125

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____	Manufacturer of Electrical Rotating Devices	EPA/600/S-94/018
____	Manufacturer of Parts for Truck Engines	EPA/600/S-94/019
____	Bourbon Distillery	EPA/600/S-95/002
____	Manufacturer of Paper Rolls, Ink Rolls, Ink Ribbons, and Magnetic and Thermal Transfer Ribbon	EPA/600/S-95/003
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____	Manufacturer of Gear Cases for Outboard Motors	EPA/600/S-96/027
____	Manufacturer of Electrical Load Centers	EPA/600/S-96/028
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