

Predesign for Pollution Prevention and Control

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A plant's intrinsic cleanliness is determined during the predesign stage. This article provides guidance for making critical decisions during preliminary design.

During the past few decades, pollution prevention and control has assumed a prominent role in the chemical engineering profession. Its study has become part of chemical engineering curricula throughout the world, and a new section on waste treatment has been added to "Perry's Chemical Engineers' Handbook."

The major responsibility for an operating plant's cleanliness falls on its operators, final designers, contractors and maintenance personnel, but its inherent cleanliness is defined before construction. Preliminary designers don't have the time or budget to fully scope a waste system and secure permits, but they can radically improve process cleanliness by devising ways to recycle or reuse streams and minimize or eliminate end-of-pipe remedies.

The three types of emissions are fugitive, native and engineered emissions. Fugitive emissions (1) are the difficult-to-find, -control or -capture leaks from pipe joints, storage tank vents, and static or rotating seals. They include leaking gases, dripping lubricants and evaporating solvents. Final designers and contractors are charged with preventing their escape. Operators and maintenance people are responsible for finding and eliminating them. Preliminary designers can do little to prevent fugitive emissions other than to specify materials and equipment that will contain process streams responsibly.

Native emissions are discharges from equipment such as furnaces, cooling towers and other devices that burn fuels or generate a utility stream. Process designers must usually accept whatever emissions are defined by available fuels and prevailing technology.

A predesigner's major concern is engineered emissions — that is, those from process vessels, reactors and separators, where engineering can influence the nature and quantity of effluent streams. The aim of this article is to help budding process analysts reduce or eliminate engineered emissions in projects that they influence.

Principles of pollution prevention and waste minimization (3-6)

Noxious byproducts that leave a process module must be treated by "end-of-pipe" techniques before they can be discharged to the environment. This is costly, both economically and politically. Ideally, the goal of pollution prevention, or P2, is not simply to reduce noxious emissions, but to avoid creating them in the first place. In this regard, safety expert Trevor Kletz's famous adage, "What you don't have, can't leak" can be aptly rephrased and applied to environmental protection: "What you don't emit, can't pollute." This premise leads to the following hierarchy of pollution-prevention/waste-minimization rules (5):

1. Source reduction. Faced with a serious emissions problem, consider alternative processes or different feedstocks that do not create noxious byproducts. If complete elimination of a pollutant is not feasible, modify the process to reduce its quantity.

Many chemical processes employ chloride-containing feedstocks, for instance, where non-halogenated substances might be used instead. The latter can often be converted to natural substances like water and carbon dioxide, whereas chlorides are not easily transformed to a non-polluting form.

Table 1. Predesign for pollution prevention involves four basic steps.

Step	Tools	Experimental and Analytical Resources
1. Identify	1. Well-executed process flow diagram 2. List of pollution-related properties 3. Stream hazard chart (on flowsheet) 4. Permissible emissions chart	Equilibrium calculations Mass balances BOD and other analytical testing Reactor design calculations
2. Eradicate (PP rules 1 and 2: process substitution, source reduction, reuse, recycle)	1. Consider alternative processes 2. Explore conversion efficiency improvements 3. Check internal recycle possibilities 4. Consider marketable disposal of wastes	Equilibrium calculations Mass balances BOD and other analytical testing Reactor design calculations
3. Minimize (PP rule 3: treat)	1. Tables 3 and 4; Figures 1, 2 and 3	Sound chemical engineering analytical and computational skills
4. Isolate (PP rule 4: ultimate disposal)	1. Table 4	Sound chemical engineering judgment, responsible legal advice, and common sense

Table 2. Relevant pollution-related properties of acrylonitrile.

Property	Data	Comments
Formula	C ₃ H ₃ N	Clear, colorless liquid at room temperature with a faintly pungent odor
Molecular Weight	53	
Boiling Point	77.3°C	
Freezing Point	-83.5°C	
Density @ 20°C	806 kg/m ³	
Vapor Pressure @ 20°C	0.115 bar(a)	High vapor pressure at room temperature; air pollution risk
Vapor Density (Air = 1)	1.8	Unlike hydrogen, vapors will not dissipate in air; leaks can produce pockets of high pollution levels
Solubility in Water @ 20°C	6.0–7.5 wt. %	Severe potential for pollution; all wastewater will require careful treatment
Viscosity @ 25°C	3.4 × 10 ⁻⁴ Pa·s	Viscosity is about one-third that of water; anticipate pollution from seal leakage

Hazard Details:

Acute Effects: Acrylonitrile is highly toxic if ingested, moderately toxic when inhaled, extremely irritating and corrosive to skin and eyes, readily absorbed through the skin, carcinogenic and mutagenic. Average allowable 8-h exposure in the U.S. is 2 ppm; 10 ppm maximum for no more than 15 min. Acrylonitrile can burn to produce HCN, a deadly gas. Biodegradable in water, converted to innocuous CO₂, H₂O and N₂.

Coal, abundant and cheap in the U.S., also contains sulfur and ash. Burning coal reasonably requires several expensive end-of-pipe operations. Most of these can be avoided by substituting natural gas that contains only carbon and hydrogen. (This is more easily said than done, since natural gas is usually more expensive or may be unavailable.)

2. Recycle. Look for ways to take an otherwise waste stream and recycle it as a raw material, solvent or wash fluid. Aqueous operations gain when clean water from filtration, cell harvesting, etc. can be recirculated to the feed. Raw material costs, wastewater quantity, and biological oxygen

demand (BOD) are all reduced. This reflects a byproduct of pollution prevention: steps taken to reduce or eliminate waste often save money.

3. Treat. This alternative, when source reduction and recycling are impractical or incomplete, is meant to bring a plant's effluent to near-natural conditions. Examples include incineration, biological oxidation, filtration and various other procedures.

4. Dispose. As a last resort, waste is placed somewhere in permanent isolation.

These four steps are illustrated by the evolution in municipal waste disposal over the past few decades. Unlike the days when garbage was simply dumped in a remote area, people are now encouraged to reduce at the source by buying or consuming in ways that minimize packaging and other wastes. Useful materials like glass, metal, plastic and paper are extracted from waste and recycled to decrease trash volume and reduce the need for virgin raw materials. (Other forms of recycling include composting, trash-to-energy schemes such as burning waste to generate electricity or process steam, and methane recovery from anaerobic decomposition of landfill garbage.) Effluents like flue gases or leachates are treated or neutralized. And residues, reduced in volume, are deposited in secure landfills or other permanent storage sites.

Steps for pollution prevention predesign

With pollution prevention and waste minimization in mind, a pioneer process designer must first identify problem streams and then eradicate, minimize or isolate those streams (Table 1).

1. Identify

Identification begins with a good process flow diagram (PFD). From a hydrocarbon process PFD, for instance, typical potential pollutants such as off-gases, aqueous residues and heavy impurities are easily identified as streams other

Table 3. Stream hazard chart.

Compound	Molecular Weight	Melting Point, °C	Flash Point, °C	Boiling Point, °C	Liquid Density kg/m³	Flammability	Deadly Poison?	Toxin?	Irritating?	Corrosive?
C ₃ H ₆	42					High		Suffocation Hazard	No	No
NH ₃	17					Moderate		Yes	Strongly	Moderately
O ₂	32					Powerful Oxidant			No	Sometimes
N ₂	28					Nonflammable		Suffocation Hazard	No	No
C ₂ H ₃ N	53	-83	0	77	806	High	Yes	Deadly		
HCN	27	-14		26	700		Yes	Deadly		
C ₂ H ₃ N	41	-88	5	82	786	High		Yes		
CO	28					High	Yes	Deadly	No	No
CO ₂	44					Nonflammable		Suffocation Hazard	No	No
H ₂ SO ₄	98					Powerful Oxidant		Yes	Strongly	Strongly
(NH ₄) ₂ SO ₄	132									

Other factors to consider are whether the stream is carcinogenic or causes genetic damage.

than product or byproduct leaving the process at the right margin. From a typical biomanufacturing process, problem streams like vent gases and wastewater would be obvious as they exit the right margin of the PFD.

The next step is to compile pollution-related properties for each substance in all of the problem streams. Table 2 is a compilation of such for acrylonitrile (an example discussed in our previous article on safety (2)). Similar tables for all relevant compounds in a process are used to prepare a stream hazard chart, such as the partially completed example for the acrylonitrile process in Table 3.

By combining information from the PFD and stream hazard charts, one identifies problem streams and defines their pollution intensity. Consider a wastewater stream, for example. Suppose, according to the stream hazard chart, that some contaminants in the effluent are noxious, but that the stream is more than 99% water otherwise. How clean must it be for discharge to the environment? One must not only identify the problem compounds, but also the concentrations above which they impact the environment.

In most jurisdictions, acceptable emissions levels are established by federal and state or provincial governments. Federal pollution-control agencies like U.S. Environmental Protection Agency (EPA) post detailed regulatory standards on their websites. Clearly, the designer must know something about regulations in the region where a prospective

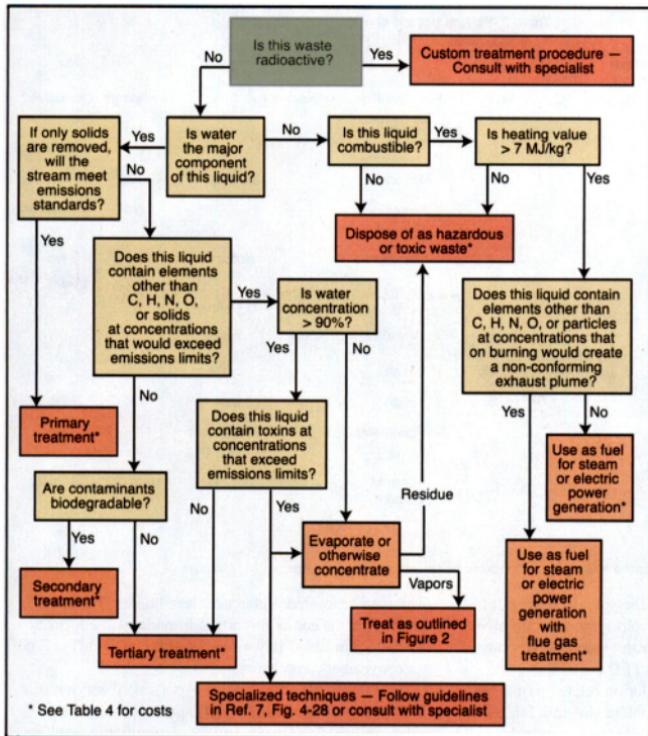
plant is to be located. References listed under "Further Reading" at the end of this article provide such information. (Table 11.3 in Ref. 7 [www.ulrichvasudesign.com/T11.3.pdf] is a convenient compilation.)

Consider wastewater from a hypothetical acrylonitrile (ACN) plant that contains 7,700 ppm contaminants in water. Of this, 7,400 ppm, or 96%, is ammonium sulfate; 100 ppm is mixed organics and 200 ppm is dissolved carbon monoxide and carbon dioxide gases. Based on Table 11.3 in Ref. 7, the stream can be discharged to natural water if organics are reduced to 30 ppm or less BOD, and ammonium sulfate (dissolved solids) is lowered to a concentration of less than 250 ppm (limits prescribed by U.S. drinking water standards).

2. Eradicate

To achieve this, one should, according to the pollution prevention hierarchy and Table 1, first consider ways to eliminate pollutants by: substituting processes or operations; reducing waste at the source; recycling; and reusing.

Acrylonitrile was originally manufactured from hydrogen cyanide and either ethylene oxide or acetylene. Synthesis from ammonia and propylene emerged in the 1960s and, for safety and economic reasons, this route has prevailed. Process substitution is an unlikely option for a mature technology like this. Certain operations



■ Figure 1. Decision tree for selecting among alternatives for waste treatment and disposal of liquids.

within an existing process might be reconsidered, however. More than 90% of the wastewater originates as water fed to the scrubber (see ulrichvasudesign.com/ACN.pdf, pp. 512–515 of Ref. 7). This suggests several routes for source reduction:

1. Recycle some of the wastewater to replace process water.
2. Use a refrigerated heat exchanger to separate streams by condensation and eliminate the scrubber.
3. Replace the scrubber with a distillation column having a refrigerated condenser.

All of these alternatives could eliminate wastewater or reduce its quantity. Process economics for each option can be evaluated by conventional techniques (7, 8). Costs thus obtained can be compared with costs for waste treatment. A method for obtaining the latter is illustrated below.

3. Minimize

As mentioned previously, the hypothetical wastewater will meet standards for discharge to a natural waterway if the sulfate level is reduced to less than 250 ppm and the mixed organics to non-toxic BOD levels below 30 ppm.

The decision tree in Figure 1 can be used to help define treatment protocols for liquids. (Figures 2 and 3, for gases and solids, appear at the end of the article.) For the ACN wastewater stream, the answers to the questions in Figure 1 are: radioactive? no; major water? yes; solids removal only? no; elements other than C, H, N and O? yes; major water? yes; toxins? no. This leads to tertiary waste treatment.

Since detailed design of waste treatment facilities is impractical in a study estimate, a short-cut method to estimate costs is needed. The following simple and quick technique, originally derived to calculate utility costs, can be used to calculate the cost of tertiary treatment for the wastewater stream described above.

Utility and waste treatment costs depend on two coefficients, a capital cost multiplier, a , and an energy multiplier, b (7, 9). These coefficients are listed in Table 4.

The unit cost of treating 1 m³ of wastewater is given by:

$$C_{t,WW} = a(CEPCI) + bC_f \quad (1)$$

where $CEPCI$ is a capital cost index (*Chemical Engineering Plant Cost Index*) that adjusts for inflation and C_f is the prevailing price of fuel in \$/GJ. (Historical values of $CEPCI$ and C_f can be found at ulrichvasudesign.com/CEPCI.pdf and ulrichvasudesign.com/FP.pdf.)

Based on a waste stream flowrate of 0.026 m³/s, coefficient a , from Table 4 for tertiary wastewater treatment, is:

$$a = 0.001 + (2 \times 10^{-4})q^{-0.6} = 0.0028$$

Table 4. Coefficients for calculating waste treatment costs.

and b is 0.1. Using a cost index of 500 and an energy price of \$7/GJ (approximate current values), the unit treatment expense is estimated to be:

$$C_{t,ww} = 0.0028(500) + 0.1(\$7/GJ) \\ = \$2.1/m^3$$

Assuming an operating factor of 0.92, the annual treated volume is 750,000 m³/yr. The annual treatment expense is, therefore, \$1,600,000. This provides a basis on which to compare some of the options identified in Step 2.

This estimate can undoubtedly be improved given more familiarity with the process. The wastewater rate of 0.026 m³/s is small compared to that of standard tertiary treatment systems, which have capacities up to 10 m³/s. If this stream were blended with another one going to a larger treatment plant, its capital share (coefficient a) would be less and unit treatment cost smaller. This suggests searching for another similar effluent to which this waste could be added. For example, if the wastewater above were part of a larger stream flowing at 1 m³/s, the unit treatment cost would be \$1.30/m³ and the annual treatment expense for the original fraction becomes \$980,000, a reduction of more than one-third. For more on economics of wastewater treatment, see Ref. 10.

4. Isolate

To discharge only compounds that exist in nature, such as oxygen, nitrogen, water, carbon dioxide and minerals, is an ideal that is seldom achieved. (In the past, CO₂ was not a problem compound, but with increasing concern about its contribution to the greenhouse effect, projects emitting large amounts of carbon dioxide must deal with it.) When objectionable materials contained in gas or liquid streams cannot be eliminated, the next best alternative is to convert them to a marketable byproduct, even when doing so costs money (see box on next page). Otherwise, wastes are usually converted to solids and stored in special secure terrestrial sites under the control of licensed specialists.

	<i>a</i>	<i>b</i>
Wastewater Treatment, \$/m³*		
Primary	0.0001 + 2 × 10 ⁻⁷ q^{-1}	0.002
Secondary	0.0007 + 2 × 10 ⁻⁶ q^{-1}	0.003
Tertiary	0.003 < q < 10 m ³ /s 0.001 + 2 × 10 ⁻⁴ $q^{-0.6}$	0.1
Membrane Processes, \$/m³†		
Concentration of dissolved solids in feed 20,000–40,000 ppm	0.0015 + 6 × 10 ⁻⁵ $q^{-0.6}$	0.13
5,000–20,000 ppm	0.0015 + 5 × 10 ⁻⁵ $q^{-0.6}$	0.08
Up to 5,000 ppm	0.0015 + 4 × 10 ⁻⁵ $q^{-0.6}$	0.02
Liquid/Solid Waste Disposal, \$/kg ‡		
Conventional solid or liquid wastes	4.0 × 10 ⁻⁴ —	—
Toxic or hazardous solids and liquids	2.5 × 10 ⁻³ —	—
By combustion§	1 < $m \times HHV$ < 1,000 MJ/s	
As supplemental fuel	3.0 × 10 ⁻⁵ (HHV) ^{0.77} $m^{-0.23}$	-5 × 10 ⁻⁴ (HHV)
With flue gas cleaning	5.0 × 10 ⁻⁵ (HHV) ^{0.77} $m^{-0.23}$	-4 × 10 ⁻⁴ (HHV)
Gas Emissions Treatment, \$/Nm³ *		
Endothermic flaring	0.05 < q < 50 Nm ³ /s 1 × 10 ⁻⁶ $q^{-0.23}$	0.004
Thermal or catalytic incineration With flue gas cleaning	1 × 10 ⁻⁵ $q^{-0.23}$ 1.5 × 10 ⁻⁵ $q^{-0.23}$	0.002 0.003
By combustion	1 < $q \times HHV$ < 1,000 MJ/s	
As supplemental fuel	3.0 × 10 ⁻⁵ (HHV) ^{0.77} $q^{-0.23}$	-6 × 10 ⁻⁴ (HHV)
With flue gas cleaning	5.0 × 10 ⁻⁵ (HHV) ^{0.77} $q^{-0.23}$	-5 × 10 ⁻⁴ (HHV)

* q is total water capacity, m³/s. Primary treatment consists of filtration, secondary treatment is filtration plus activated sludge processing, and tertiary treatment is filtration, activated sludge processing and chemical processing.

† q is total water capacity, m³/s. In many cases, the concentrated effluent from a membrane separation unit must be treated by secondary or tertiary methods as well. In these situations, membrane separation is not an ultimate waste treatment method. Its viability depends on the value of the purified stream and on savings available from reducing the volume of concentrated waste requiring subsequent treatment.

‡ Use these numbers advisedly. Waste disposal costs depend on local public attitude and other political factors that are capricious and location sensitive. See Ref. 5, page 25-101 for typical U.S. regional variations.

§ m is the waste's flowrate, kg/s, and HHV is its higher heating value, MJ/kg. Note that b is negative in these cases, because waste burning as a supplementary fuel returns a credit.

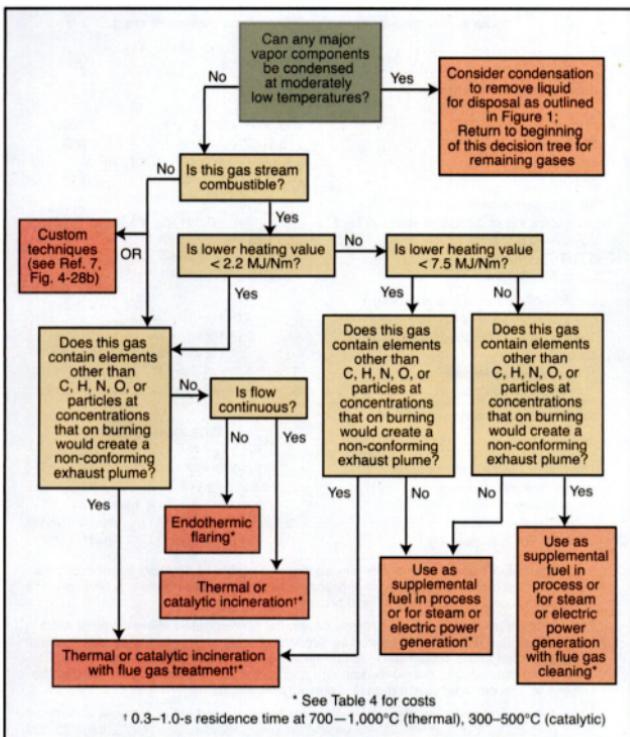
* q is the total treatment system flowrate in normal (273 K, 1 atm) cubic meters per second, Nm³/s and HHV is the lower (or net) heating value in MJ/Nm³. Note that b is negative in these instances, because waste burning as a supplementary fuel returns a credit.

Assume that a heavy liquid organic waste stream from the hypothetical acrylonitrile process is about 25% water and 75% mixed acrylonitrile and acetyl nitrile, and it is flowing at a rate of 4 g/s. Also assume that the answers to the questions in Figure 1 are: radioactive? no; major water content? no; combustible? no. Thus, this stream must be disposed of as a toxic waste.

Based on Table 4 and using the same CEPCI and energy price as before, the unit treatment cost is:

$$C_{t,ww} = a(500) + b(\$7GJ) = \$1.25/kg$$

At 4 g/s, the annual disposal cost is \$150,000/yr.



■ Figure 2. Decision tree for selecting among alternatives for waste treatment and disposal of gases.

Alternatively, one might explore combining this discharge with the larger wastewater stream. This would increase the latter's BOD by 35 ppm with negligible increase in flow.

Air pollution

The above examples demonstrate how liquid effluents might be handled in pioneer design. Similarly, vapor and gas streams, depending on combustibility and toxicity, can be treated by the various alternatives listed in the termini boxes of the decision tree in Figure 2. Costs are estimated using the appropriate coefficients from Table 4. The following example illustrates the disposal of the gaseous vent stream from the hypothetical acrylonitrile process.

Consider a waste gas composed primarily of nitrogen with some water, propylene, acrylonitrile, acetonitrile, ammonia, a trace of cyanide, carbon monoxide and carbon dioxide. Figure 2 poses the question of combustibility. The stream's com-

posite lower heating value (l/hv), calculated from composition and net combustion enthalpies given in Ref. 5 (Table 2-221, page 2-199) is 2.2 MJ/Nm³. The stream flowrate is 3.76 Nm³/s.

According to Figure 2, this gas stream is borderline, a candidate for either incineration or use as a supplemental fuel.

The cost of thermal or catalytic incineration (from Table 4) is:

$$C_{t,ic} = a(500) + b(\$7/GJ) \\ = \$0.018/Nm^3$$

At a flowrate of 3.76 Nm³/s, the annual incineration expense is \$2,000,000.

For supplemental fuel use:

$$C_{t,sf} = [(3.0 \times 10^{-5}) \\ \times (l/hv)^{0.77} q^{-0.23}(500)] \\ + [(-6 \times 10^{-4}) (l/hv) \\ \times (\$7/GJ)] \\ = \$0.011/Nm^3$$

At \$0.011/Nm³, disposal as supplementary fuel costs \$1,200,000/yr.

Because this off-gas stream is so large (a large amount of nitrogen is introduced with reagent air), its disposal is a major expense. In this situation, a predesigner would report both cost figures and most likely recommend energy recovery, but emphasize that special precautions must be observed to handle vent gases safely in the steam plant. Alternatives and their relative safety will be debated by the HAZOP team and others later if and when this project progresses to final design.

Closing thoughts

From an ethical standpoint, pollution prevention is no doubt the best route to follow in preliminary design. Society, through fines or financial incentives, often makes it the most economic path also. When options like deep-well injection or contract removal are most economical, other factors should be considered. A manufacturing cost summary displays short-term economics. With deep-well injection or contract removal, waste sometimes returns to haunt a firm. Federal law often holds a generator legally and finan-

Finding a New Market

Faced with disposal of a byproduct acid, one company found that there was a market for the acid alone, but this material was a concentrated scrubber liquid that contained mineral sludge. The sludge was inert and non-toxic, but its presence made the acid off-spec. Creative marketing people learned that the liquid matched the composition of a popular toilet bowl cleaner, and the sludge improved its performance by increasing viscosity, which resulted in better adherence to the bowl. Thus, the "waste byproduct" was successfully wholesaled to the distributor of the cleaner.

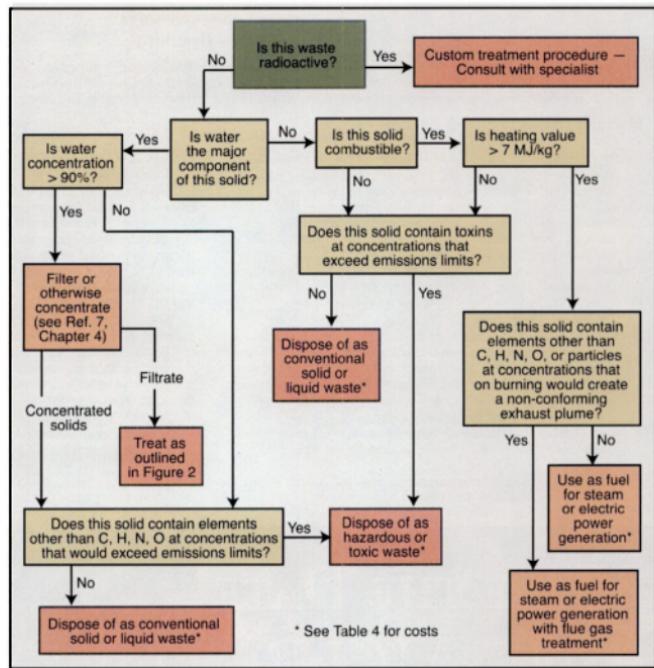
cially responsible even when a contractor has been paid to dispose of the waste.

Public attitude, not easily measured in dollars or euros, can easily sabotage a project through startup delays, regulatory barriers and unexpected legal fees. Public image can also influence sales volume and price, either of which affects the bottom line. Responsible pollution control and prevention in predesign is important to assure that the public's first impression, shaped largely by the design report, is positive.

CEP

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■ Figure 3. Decision tree for selecting among alternatives for waste treatment and disposal of solids.

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Article continues with Further Reading on next page



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Further Reading

Many excellent books and articles have been written on the subject of this article. The literature is wider than it is deep, however. It contains interesting historic, encyclopedic and qualitative information that all chemical engineers can profit from, but that is not required for process design. The following citations have been selected as primary sources of quantitative information for inexperienced process designers.

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