

Review

Pollution prevention technologies: A review and classification

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Abstract

Waste minimization practices, reported in the literature for major industries using or generating hazardous materials, were reviewed. Technologies are summarized briefly in this paper. The information was reorganized according to the function served by the material industrially, and the general chemical nature of the material. Ten basic functions were identified, as binding, pigmentation, reactants, reaction inhibition, catalysis, bleaching, mass deposition, mass removal, by-products, and end-products. The resulting perspective of this review is general with respect to industry, and with respect to waste phase, and considers productivity benefits along with prevention of risks associated with pollution. Similarities in waste reduction opportunities are evident between processes where hazardous materials perform similar functions, suggesting general approaches to industrial hazardous waste reduction.

1. Introduction

A review of waste minimization practices reported in the literature, for major industries using or generating hazardous material, is presented in this paper. The information was summarized, and reorganized according to ten beneficial functions served by hazardous materials, and their chemical nature. Industry groups are outlined in Table 1. A ranking of the importance of each technology for preventing wastes associated with each function is presented in Table 2. Infectious and radioactive wastes were not considered. Detailed technical and economic information regarding specific waste minimization technologies can be found in the references.

Many references on waste minimization technologies in specific industries have appeared over the last few years, including a series of guidance manuals

TABLE 1

Industrial hazardous waste generators, grouped by hazardous material function

Binding

Wood and building products

Pigmentation

Coating (e.g., paint, lacquer); furniture, motor vehicles, aircraft, appliances, metal and wood products manufacturing

Textiles

Printing

Metal reactants

Organic chemicals manufacture (biocides, pharmaceuticals, solvents, resins)

Inorganic chemicals

Metal refining

Tanning

Photographic processing

Oxidation-reduction reactants

Pulp and paper

Metal refining

Acid-base reactants

Chemical manufacturing

Reaction inhibition

Chemical manufacturing

Metal finishing

Refining

Building products

Bleaching

Pulp and paper

Textiles

Organic mass deposition

Coating (paint, lacquer, etc.); manufacture of metal, wood, and other products

Printing

Organic chemicals; manufacture of solvents, resins, pesticides, pharmaceuticals

Oxidation-reduction mass deposition

Electrolytic metal plating and stripping; automotive, aircraft, electronics, semiconductors, pickled steel, foundries and other metal manufacturing

Organic mass removal

Cleaning, degreasing, and rinsing; vehicle maintenance, manufacture of aircraft, motor vehicles, metal furniture, tools, appliances, paint, ink, organic and agricultural chemicals, adhesives, petrochemical, plastics, rubber, vegetable oil, textiles, semiconductors, and other products, photographic processing, coating, printing, and other industries

Paint stripping

Dry cleaning

Acid-base mass removal

Metal stripping; automotive, aircraft, electronics, pickled steel, metal furniture, foundries and other metal manufacturing

Metal etching

Metal refining

Organic by-products

Petroleum refining
Automotive and industrial lubrication
Solvent reclamation

Metal by-products

Mining
Metal refining
Waste incineration
Foundries

Oxidation–reduction and acid–base by-products

Metal refining
Petroleum refining
Inorganic chemicals manufacturing
Organic chemicals manufacturing
Power production

End-products

Organic chemicals: manufacture of solvents, resins, pharmaceuticals, biocides
Metal pigment manufacture
Manufacture of inorganic acids, bases

for specific industries developed by the California Department of Health Services [1]. Specific technical information is also available in the 'Compendium on Low- and Non-Waste Technology' (United Nations Economic Commission for Europe [2]), which consists of monographs of specific waste reduction technologies reported by various industries. Theodore and McGuinn [3] give an integrated discussion of theory and technologies. Recent publications include California Department of Health Services [4], which gives an informative overview of technologies for reducing metallic, solvent, and oil wastes, PRC Environmental Management [5], in which waste minimization in the metal finishing industry is discussed, and Munroe et al. [6], in which unit processes being used for industrial waste reduction are considered. Jicha and Remini [7] review waste minimization in the nuclear industry.

2. Binding

Organic binders are used in the manufacture of building materials, including plywood, fiberglass insulation, and composite boards. Binders include phenolic resins and formaldehyde, as well as certain wood preservatives and flame retardants such as creosote, which perform essentially a binding function. Material losses represent hazardous wastes. If substitution is not possible, waste can be reduced by minimizing the number of different hazardous materials purchased and used, and tracking material to maintain accountability.

TABLE 2
Ranking of pollution prevention technologies by industrial hazardous material function^a

Method	Binding	Pigment- ation	Reactants	Reaction inhibition	Catalysis	Bleaches	Mass deposition	Mass removal	By- products	End- products
Substitution	5	3	3	3	1	4	5	5	1	3
Alternate process	1	5	3	1	1	1	5	5	3	2
Loss reduction	5	5	5	5	1	5	5	5	1	4
Process control	3	5	5	3	1	4	5	4	5	5
Reuse	2	3	4	1	3	1	2	4	5	1
Recovery	3	5	5	2	5	5	4	5	5	4
Specialization	2	2	2	2	1	1	3	4	1	4
Tracking	4	1	3	4	1	2	1	4	1	2
Segregation	2	1	2	2	2	1	2	4	2	1
Detoxification	1	2	2	1	2	2	3	1	3	1

^a Legend: 5 = most important, 1 = least important.

Specialization, by dedication of equipment, reduces cleanout waste and allows in-process recycling.

Loss reduction, reuse, and recovery, are suggested as further pollution prevention measures. At wood preserving facilities, installation of drip tracks and spill basins have reduced losses, and cooling water has been recycled for reuse [8]. Volatile phenol-derived emissions from industrial processes employing phenolic resins can be absorbed in aqueous solution of phenol-formaldehyde resin. Resin and contaminants can then be condensed, to recover a resin by-product [9]. Waste aqueous phenolic resin glue can be recovered from plywood washwater by evaporation [10]. Sizing chemicals used in textile manufacture can be recovered by ultrafiltration [11].

3. Pigmentation

Metals are used as pigments in three general applications: paints, employed in the manufacture of furniture, motor vehicles, aircraft, appliances, and other metal and wood products; dyes, used in textiles manufacturing; and inks, employed in printing industries. Typically, solvent carriers may represent more of the toxicity present in wastes. However, metals further complicate disposal problems. Some products, such as toilet and tissue paper, may be preferred in a natural color by consumers, especially if the product contains recovered fiber. In other cases, less hazardous replacements are available. Otherwise, computers can aid in the scheduling of operations [12] so as to minimize equipment clean-out. Paint formulations that minimize material costs and waste may be identified in this way [11]. For example, spreadsheet calculations and small linear programs can be used to determine proportions of paint pigments required to match or make a shade. Performing such calculations may result in reduced waste toxicity and material costs, as well as reducing the frequency of producing off-specification batches requiring disposal. Automated process control may reduce process losses. Dye baths can be reconstituted by adding fresh chemicals, and more efficient dyeing methods are being used [11]. Vacuum drying of hot dyed textiles to reduce wastewater volume is economical for rolled or wrapped material [10].

4. Reactants

In many cases a hazardous material serves as a chemical reactant, incorporated in the end-product in a different, generally non-hazardous, form. Examples include acid and base reactants in chemicals manufacturing, reacting metal electrodes, and photographic processing chemicals.

4.1 Metal reactants

Metallic reactants are used in chemical manufacturing, mineral refining, photographic processing, and tanning. For example, spent electrodes, cells,

and anode muds are generated in the refining of crude mineral ores and petroleum to produce metals, phosphates, and fuels (including gasified coal). Anode muds, contaminated with various metals, are generated in electrolytic refining of copper. Chromium tannin salts are commonly used in tanning, to react with skin proteins in animal hides to produce leather; trivalent chrome wastes are generated. Silver is generated in photofinishing processes.

Pollution prevention measures to be considered, prior to metal recovery, tend to be specific to the application. For example, vegetable and synthetic tannins are available to replace chrome tannins. Specialization, by dedication of tanning baths to particular leather products, allows filtration and direct reuse of the bath [11]. Measures employed to reduce losses of photographic processing chemicals include counter-current film washing, and shutting off rinsewater flow when film is not being processed [11].

Metals are prime candidates for recovery, as discussed for oxidizing and reducing carriers. For example, although tanning baths may be recovered directly, it has been more common to precipitate chrome from the used bath with lime, sodium carbonate, or MgO, dewater by filter press, and redissolve it with sulfuric acid for reuse [10, 11, 13]. Chrome wastes from such processes can be reused as coagulant aids [11]. Treatment sludges can be incinerated for heat and chrome recovery [11]. Anode muds from copper refining may be economically recovered by ion exchange or electrodialysis [9]. Silver is recovered from exhausted photographic fix solutions, film scraps, and waste wash waters by electrolysis; commercially available systems are economical even for small labs [11]. Ion exchange can be used to concentrate the solution initially [13]. Precipitation is another alternative. Following primary silver recovery, iron metal may be added to final silver waste to precipitate low grade silver, as a polishing step. Off-site silver recovery may be economical for small volume photographic processors, such as hospitals, medical labs, and schools.

4.2 Oxidation–reduction reactants

Paper is made by depositing and drying a layer of cellulose fibers from a wood pulp suspension; the pulp is made by dissolution of cellulose-binding lignins with heat and mechanical energy alone, or with the addition of such reactants as sodium sulfide, sodium sulfite, and sodium hydroxide. Chemical pulp tends to be stronger than mechanical pulp. In addition to biochemical oxygen demand, reduced sulfur compounds, bleach, and mercaptans formed in the reactions with lignin [11], are generated. Waste can be reduced through closed loop recycling of process waters [10, 11, 14].

Aluminum metal is refined from alumina in a fused salt electrolytic cell containing calcium fluoride flux [14]. Fluorides can be precipitated with lime, avoiding health effects in plant and livestock populations.

4.3 Acid–base reactants

Acids and bases are common reactants in the manufacture of inorganic chemicals. Ion exchangers can be used as solid acids in place of aqueous acids,

avoiding production of acidic or saline liquid waste streams [15]. Spent sulfuric acid recovery is well established in the industry, especially for plants located close to sulfuric acid manufacturing. Diluted acid can be concentrated in two steps. Contaminated acid can be reused as a raw material in the production of virgin sulfuric acid. The contaminated acid is concentrated to 60 to 70%, added together with elemental sulfur and oxygen to the furnace to be cleaved to SO_2 , and catalytically oxidized (using vanadium pentoxide) to SO_3 for absorption in water [16]. Nitric acid can be recovered to 68% acid by steam distillation [9]. Acids containing emulsified organics can be neutralized, which often breaks the emulsion and allows the organics to be skimmed or decanted [9]. Organics can then be distilled or incinerated. Residual or organics in low concentration can be adsorbed, floated, extracted, or treated biologically. In sodium carbonate production, CO_2 is produced by roasting of carbonate rock, which is reacted with a solution of ammonia and salt. Ammonia emissions are recovered to 99.8% by absorbers; emissions can be collected with vacuum hoods, which also prevents equipment corrosion [17].

Hydrochloric acid used for dissolution of minerals in refining operations. The acid can be recovered by roasting, as in pickling liquor recovery. However, the process is energy intensive and may not be economical [13].

In the production of sulfuric acid, sulfur is burned in air to produce SO_2 , which is oxidized over a heterogeneous catalyst to produce SO_3 for absorption in water. Cooling of the SO_2/O_2 reaction to maintain 425°C increases yields from 66 to 98% [15]. Increasing pressure, and decreasing SO_3 concentration by performing the conversion in two steps and withdrawing SO_3 , increase yields further.

Ammonia is made by high pressure catalytic reaction of hydrogen and nitrogen, which are obtained from air and the conversion of methane. Closed-loop processes to recover process heat from steam, flue, and process gases have greatly reduced flue gas emissions.

5. Reaction inhibition

Various organic, metallic, alkaline, and antioxidant chemicals are used to inhibit corrosion, oxidation, chemical degradation, or biological activity in processing agents and end-products. Examples include cooling water additives in chemical manufacturing and metals and petroleum refining, organic and metallic wood preservatives and flame retardants, and metal plating bath additives. Corrosion and microbiological growth inhibitors, such as chlorine and chromium compounds, are used in cooling water in mineral refining and chemicals manufacturing. Three general types of inhibitors are commonly added to solvents used for cleaning [18]: antioxidants, to suppress oxidation of unsaturated solvents; metal stabilizers, which react with metal contaminants that accelerate solvent degradation; and alkaline organics, which absorb hydrochloric acid produced in the breakdown of chlorinated solvents, thereby

inhibiting solvent breakdown and corrosion of equipment and parts being cleaned. Losses result from not recycling process waters, from changing process waters due to contamination, from leakage and accidents, in rinsing steps, and in process water recovery processes.

In general, substitution of less toxic inhibitors is desirable for long term economic sustainability. It may be possible to reduce losses by recovering additives together with metal plating bath solution, by distillation, adsorption, or membrane processes. If solvents are recovered by distillation, inhibitors have been found to carry through the distillation process in excess of 65% of original concentration [18].

6. Catalysis

Catalysts are used to enhance chemical reaction rates in the refining of petroleum and inorganic minerals, in the manufacture of organic chemicals such as pharmaceuticals and inorganic chemicals, and in food processing. Catalysts are most often metals, inert in the reaction, such as platinum, nickel, zinc, cobalt, vanadium, molybdenum, iron oxides, and chromium, sometimes deposited on alumina. For example, powdered nickel catalyzes hydrogenation of vegetable oil, and nickel, iron–chrome alloys, or copper–zinc alloys catalyze steam and thermal generation of hydrogen from hydrocarbons. Catalyst activity is reduced by permanent or reversible fouling or poisoning with contaminants [19]. Spent catalysts can be a significant source of toxic metallic waste in chemicals manufacturing, although regeneration is practiced widely due to costs of material purchase and disposal.

Spent catalysts can be regenerated by solvent stripping, heat treatment, acid washing, or gaseous oxidation or reduction. Such processes can be implemented separately or in combination [13]. When the catalyst is finally spent, the metal may be recovered as discussed for oxidizing and reducing carriers. Zinc waste from rayon manufacturing has been settled and recovered as the hydroxide, and converted to the sulfate for reuse. Zinc oxide has been recovered from pharmaceuticals manufacturing by filtration, solvent extraction, and precipitation. Spent catalysts that cannot be regenerated on-site may be salable for off-site recovery. Nickel catalysts have a particularly high resale value. Bromley [13] discusses methods for off-site recovery of metals from vanadium, molybdenum, and alumina-based catalysts.

7. Bleaching

Chlorine and oxygen bleaches are used in the manufacture of white paper and textiles. Photographic processing operations use permanganate, ferricyanide, and dichromate bleaches, of which ferricyanide is of concern due to

the potential for decomposition to free cyanide in the presence of sunlight. Chlorine reacts with organics to form trihalomethanes in receiving waters.

Substitution and recovery are demonstrated pollution prevention approaches for processes employing bleach [11]. Consumer awareness is increasing the marketability of non-white paper products. Oxygen bleach may be substituted for chlorine. Process waters can be recycled, and counter-current washing can reduce waste volume. Computerized process control measures often reduce losses, as well. Ferricyanide bleach, and bleach-fix solutions can be recovered using ozone oxidation, electrolysis, or persulfate salts. Both ion exchange [11, 20] and electrodialysis units are available for removal of bromide and recovery of developer solutions.

8. Mass deposition

One of the most common functions of hazardous materials is that of mass deposition. Organic solvents are used as carriers of coatings (such as paint and other finishes), ink, and chemicals; acidic cyanide baths are commonly used as the (oxidizing) carrier for metals in electroplating. Solvents are used as thinners for paints, other coatings, and inks, and as media for reactions and extractions in organic chemicals manufacturing. Losses of volatile carriers are in some measure inherent to their use, as they are often used because of their evaporative characteristics. Carriers do not become part of the finished product, and may not be essential for depositing material. Therefore, alternate methods of applying coating, ink, or chemicals, such as by heat or water, are suggested for preventing pollution. Opportunities are discussed at length in many publications [11, 16, 18, 21–24].

8.1 Organic carriers for coatings

Organic solvents are used as carriers of paint, lacquer, and other coatings, in the manufacture of metal, wood, and other products. The use of solvent based coatings results in production of contaminated thinners, volatile organic carbon (VOC) emissions, and in paint sludge from air exhaust scrubbers.

8.1.1 Substitution and alternate processes

Solvent carriers for coatings can often be eliminated; doing so eliminates most hazardous waste, although various paint pigments contain metals. Often water-borne finishes can be substituted for solvent-based types, where the surface is completely free of oils, and where the increased drying time is acceptable. Powdered coatings are applied without solvents, by electrostatic, fluidized bed, and plasma spray methods [11, 18, 21]. Electrostatic painting equipment applies a charge to the powder as it is sprayed, which is opposite to the charge on the item to be coated. The powder is thus held to the item in a uniform layer, for fusing in an oven. Usually the method is used to coat conducting materials such as metals, although non-conducting materials can

be coated by applying a sensitizer to the surface. The item must be able to withstand 350 °F for 30 minutes, which may weaken aluminum alloys and some other materials. The fluidized bed method involves heating the part and immersing it in a cloud of coating powder, for oven curing [18]. Plasma guns contain an extremely hot ionized gas, through which the powdered coating is passed very briefly on the way to the part to be coated. The powder is melted rather than decomposed, and solidified on the part. High temperatures in the gun make the method useful for applying metal coatings. In particular, such coatings may be applied to heat sensitive substrates, as only the coating is heated. Electrocoating involves dipping parts in a solution of ionized paint for electrolytic deposition similar to electroplating, and is used in the automotive industry [11, 18]. Roll, or coil, coating is the pre-painting by roller of sheet metal prior to fabrication; high solids coatings are used and transfer efficiencies are high [11]. Use of such sheet metal for manufacturing can largely eliminate painting wastes. Ultraviolet and other radiation curable coatings, which polymerize rather than dry, are being developed [21]. Two-component catalyzed coatings have been investigated by the automotive industry, however, non-hazardous coatings have not been found [11, 21].

8.1.2 Loss reduction, automated process control, and segregation

Losses of solvent are often reduced through process variations, automation, and segregation of wastes [11, 18, 21]. Coatings with high (25 to 50%) solids contents are replacing conventional solvent coatings; required equipment and procedural changes include heating the coating for viscosity control [20]. Wet electrostatic painting is similar to dry, where the electrostatic attraction reduces or eliminates overspray. Airless methods employ high pressure rather than air to atomize the paint, reducing VOC emissions and overspray, although a coarser finish may be obtained. Equipment maintenance, maintenance of proper pressure for atomization, and segregation are effective in reducing waste [21].

8.1.3 Recovery

Solvent and finishing wastes can be recovered by several methods. Overspray recovery systems are available, in which overspray is collected by a curtain of water and recovered by decantation for recycling. Resulting process water is reused for washing [11, 21]. Oil and alkaline cleaning solutions have been recovered from wastewater by skimming and ultrafiltration [20]. Solvent can be recovered by settling and ultrafiltration [21]. Vapor emissions are often recovered on-site by carbon adsorption; carbon can be regenerated by steam stripping, and solvent can be recovered by condensation and decanting. Evaporation with or without a vacuum is useful for recovering heat-sensitive solvents [21].

8.1.4 Reuse

As a final alternative to purification, solvent wastes can be used as fuel in industrial boilers [25].

8.2 Organic carriers for ink

Solvents are used as carriers for inks, for printing of paper products and metal food and beverage containers. Four processes for printing paper are common [26]. Letter presses are used for books and applications where high quality is desired, although use is declining. Ink is applied to raised surfaces that are either individually cast letters, or plates made by a photochemical process and etched. Intaglio or gravure processes are typically used for long run magazines and catalogs; the printing area of plates is recessed by etching, and filled with thick ink. Planographic or lithographic processes employ a flat plate in which only the printing area is hydrophobic and receptive to grease (ink), and are used for printing of commercial literature, greeting cards, business forms, etc. Screen printing involves the use of a stencil applied to a screen, through which ink is applied with a squeegee.

Most printing plates are made by photochemical reaction and etching. Ink consists of solvent carrier, resin binder, and pigment. All three are primarily derived from petroleum; the primary pigment is carbon black. Other pigments include lead, mercury, cadmium, cobalt, chromium, and nickel. Principle wastes include chemicals from plate making (metal reactants), solvents and vapors from drying ink and equipment cleaning, and waste pigments.

8.2.1 Recovery

Vapor emissions, traditionally vented to the outside air, can be recovered by carbon adsorption. The method is economical for larger shops and where required legally. Waste ink recovery systems are commercially available and economical, and can produce a higher than virgin-quality ink [11].

8.2.2 Substitution and alternate processes

Flexography is a variation of the letter press process which uses water-borne inks. Water based inks require more energy to dry, and may reduce printing speed. Because water does not redissolve the dried ink film, difficulty may be encountered in resuming printing after brief shut downs. Inks cured by polymerization with ultraviolet radiation have been used successfully as replacements for solvent based inks for printing cans [11]. Economics may favor ultraviolet processes over aqueous processes, capital investment notwithstanding [11].

8.3 Organic carriers for chemicals

Solvents are used for extraction and separation, in the manufacture of solvents, resins, pesticides, pharmaceuticals. Textile waste streams, typically high in biochemical oxygen demand but low in hazardous content, may contain solvents used as carriers for dyeing synthetic fibers, as well. Improved maintenance, tracking of materials, dedication of equipment to particular hazardous materials, and computerized process control [27–30] can reduce carrier wastes.

Bromley [13] discussed solvent recovery in organic chemicals manufacturing processes. Solvents that do not evaporate from reactions can be stripped using

steam and, if necessary, reduced pressure. The solvent can then be dried, if necessary for reuse, with a desiccant or by fractional distillation. Solvents that polymerize or form azeotropes can be incinerated as fuel in boilers [25]. Azeotropes can sometimes be separated using a third solvent, phase separation, and further fractional distillation. Solvent recovery by liquid–liquid extraction is common in pharmaceuticals production [21].

8.4 Oxidation–reduction carriers for metals

Acid, base, and cyanide metal baths are used to electrochemically plate metals. Examples include the manufacture of automotive, aircraft, marine vehicles, and other metal products, plating of copper on plastic in the manufacture of printed circuit boards, and metallization in the manufacture of semiconductor chips. Electrolytic processes are those in which an electric current is applied to reduce dissolved metal ions to metallic form for deposition. Metals are reduced and plated at the cathode, and oxygen may be released at the anode. Electroless processes involve the use of chemical reducing agents, and are used, for example, to plate nickel or copper on non-conductors such as circuit boards. Plating processes are discussed in detail in American Society for Metals [31]. Waste reduction technologies are discussed in several references [5, 11, 16, 18, 20, 31–33].

8.4.1 Substitution and alternate processes

A number of alternative processes are in use, or under development, for reduction of hazardous waste [18]. Non-cyanide baths are sometimes preferred economically, if treatment and other waste-related costs are considered. Acid sulfate, chloride, and fluoroborate baths, for example, are used for plating zinc. Non-cyanide cadmium baths are less well developed, but sometimes preferred for the same reason. Trivalent chromium baths are used in place of hexavalent solutions. Although the baths are more expensive, materials costs may be outweighed by reduced waste treatment costs. Ion vapor deposition of aluminum is a promising alternative to cadmium plating for corrosion protection, developed by McDonnell Douglas Corporation. Aluminum is anodic to steel, thereby providing galvanic protection, and is difficult to plate electrolytically.

8.4.2 Loss reduction and automated process control

Loss reduction measures often result in increased efficiencies and product quality, and decreased waste generation, with little investment of capital and time. Regular maintenance of tanks, valves, pumps, racks, and anodes avoids contamination of baths by leaks, and changing of baths due to failures. Other recommended procedures include installation of level alarms, minimization of water usage during cleanup, removal of anodes from tanks except during plating, and cleaning parts thoroughly prior to plating to prevent contamination of bath [18]. Removing defective parts before plating or stripping reduces waste, as well [20].

Significant savings in chemicals and corresponding reductions in waste have been achieved through process modifications to reduce dragout [18]. Rack designs that promote maximum drainage are effective. Increasing the bath temperature, and adding non-ionic wetting agents, reduce dragout by reducing bath surface tension and viscosity. Countercurrent rinsing in multiple (three to four) tanks can reduce flows by 95%, where space is available. The volume of wastewater is thus reduced, although the mass discharge of contaminants may remain constant. Aeration may be necessary for mixing, due to the reduced flow. Rinsing parts with a spray over the plating tanks is effective for recovering metals, if the bath is hot enough so that evaporation losses offset the added volume. Drip recovery devices, such as drainage pans and drip tanks, can be installed to recover bath solution. Machine motion can be controlled to allow parts to drain before being transferred to the next tank. Concentrations of metals in the baths can sometimes be reduced. Air knives can be used to dislodge plating film, for return to tanks. Computerized robotic electroplating systems have been found economical and effective in reducing waste, for larger operations [11, 18, 20].

8.4.3 Recovery

Evaporation is the most established method for metal recovery from rinse waters. Energy costs may limit applicability to rinse water returned to hot baths, or for (more concentrated) countercurrent rinse water [18].

Membrane separation processes, such as reverse osmosis (RO) and electro dialysis, can be used to concentrate rinse waters of moderate pH (2 to 11) that are not strongly oxidizing (such as chromic acid) [18]. Chemical vulnerability of membranes is the limiting factor, although membrane technology is developing. For example, reverse osmosis has been used successfully to recover plating rinse waters, including nickel, copper, zinc, and cadmium [16]. Energy costs for reverse osmosis are less than for evaporation [11]. Plating metals are recovered together with chemical additives (an advantage), and rinse water is reclaimed, as well. Prior concentration by evaporation may be necessary in some applications, for metal recovery. If metals are recovered, baths may require periodic treatment to remove impurities, because membrane recovery is non-specific. Reverse osmosis has been cost-effective in concentrating nickel rinse water, for reuse in plating. The electro dialysis process involves application of voltage across a cell containing alternating anion and cation-selectively permeable membranes, so that anions and cations are concentrated in alternate cells. More concentrated solutions can be generated by electro dialysis than by reverse osmosis, so that an evaporation step may be avoided. Electro dialysis offers greater selectivity, for impurity removal, as well [16].

Electrolytic deposition for metal recovery is economical particularly for single component systems with relatively high metal concentrations (approximately 1% by weight). High value, pure metal is generated. For low metal concentrations, high surface area electrodes, rotating electrodes, or fluidized bed electrodes can be used [32]. Thus, recovery of copper plating and etching

rinse waters has been economical, and tin, silver, zinc, cadmium, and precious metals have been recovered, as well [16]. Ion exchange, evaporation, or precipitation/cyclonic separation/redissolution have been used, when necessary, for concentrating the solution initially [18, 20].

The process of adding a sacrificial metal, typically iron or aluminum, to a waste to reduce and thereby deposit a second dissolved metal in metallic form, is referred at times as cementation or replacement. Iron has been used to recover copper accordingly, and chrome has been reduced to the trivalent state [13]. Sufficient contact area (or time) is required. The process is inexpensive; however, iron or other sludge is produced and the metal is recovered in a low grade.

Ion exchange is appropriate for recovery of metal from dilute systems, less than about 1,000 mg/l. Ion exchange applicability is also limited by the potential for fouling or attack of the resin. An activated carbon or other type of pre-filter may be required to prevent fouling. Neither desirable chemical additives, or unwanted impurities, are recovered. Units are installed in parallel, to allow regeneration during production. Strong cation exchange resins, and acid regeneration, have been used for metal recovery from pickling acids and plating wastes. Anionic resins have been used for separation of chromate/dichromate [32]. The sequence of strong base, strong acid exchange allows recycling of chromic acid to plating baths [13]. If the ion exchange regenerating solution is not returned to plating tanks, it may be recovered electrolytically [20]. Alternatively, the acidic regenerant can be passed through an acid-selective resin which rejects metals; metal salts pass for collection, and the bed is flushed with water to recover the acid [34]. Activated carbon will adsorb mercury, when treated with 0.05 to 3 normal sodium sulfide alkaline solution and rinsed. Regeneration is by the same sodium sulfide solution, and mercury can be precipitated from the resulting mercury bisulfide solution [17].

Metals can be precipitated with various alkaline reactants [16, 32]. Most metals precipitate at a pH above six or seven, permitting separation from iron which can precipitate below pH 5. Sodium carbonate, sodium hydroxide, and ammonium hydroxide all form soluble neutralization by-products, and are therefore preferable for metal recovery. Metal sulfides and carbonates tend to be less soluble than the hydroxides; at acidic pH (below 7), the sulfides of cadmium, cobalt, copper, chromium, nickel, manganese, zinc, and other metals are much less soluble than the hydroxides. Economics may justify lime precipitation, followed by sulfide or carbonate precipitation to reduce the final metal concentration further. Because metal refining operations such as copper, nickel, and zinc are designed for processing sulfide ores, sulfide precipitation may be economical. Organic precipitants are generally expensive and offer poor regenerability.

Metals can be chemically reduced and precipitated in metallic form. Sodium borohydride has been used to reduce and precipitate metals from neutral and alkaline solutions, for filtration and resale [33]. For example, precious metals have been recovered from photographic and plating solutions, and mercury has

been recovered from wastes in chlor-alkali production. Sodium borohydride may cause explosive reaction in acidic solution. Lead and nickel have been recovered, as well [16].

Hexavalent chrome plating waste is reduced to the trivalent form to reduce toxicity before precipitation. Sulfur dioxide gas, ferrous sulfate, metallic iron, sodium metabisulfite, or sodium trisulfate can be used as reducing agents [11, 16]. Use of the combination of ferrous sulfate, sodium sulfide, and sodium hydroxide has been found to reduce precipitated sludge volume [34].

Cyanide baths are oxidized prior to metal precipitation by alkaline chlorination, using chlorine and sodium hydroxide or sodium hypochlorite, or with peroxides or ozone. A two step process at a pH of 10 for cyanide oxidation, followed by a pH of 8 for oxidation of the resulting cyanate to nitrogen and sodium chloride, may be most efficient [11, 31]. Nitric acid treatment of cyanide electroplating wastes can be used to precipitate metals [32].

Thickeners, preceding filtration, can lower the costs of dewatering precipitated clarifier sludges containing 1 to 2% solids. Flotation methods developed in ore refining applications can be used to removing insoluble metal species, and recent adaptations are being used to remove ions [32]. Flocculated precipitate is floated by injection of microbubbles of air, or by electrolysis of the aqueous solution to produce hydrogen and oxygen bubbles.

For dewatering hydroxide sludges, rotary vacuum filters, plate and frame filter presses, and belt presses can be used [11, 16, 19]. Centrifuges are no longer used extensively, as the resulting sludge contains only 15 to 25% solids. Vacuum filters are common, but produce the least dry cake (20 to 40% solids). Also, conditioning of the sludge with a coagulant or a filter aid is often necessary to maintain cake porosity during filtration, which increases sludge volume. Capital costs are high for belt presses, but they are economical for large operations due to their continuous mode of operation, and for sludges which are difficult to dewater. Belt presses increase sludge solids content to as much as 40%. Operating costs are higher for plate and frame filters as they are batch systems, however, lower capital costs and throughput make them suitable for smaller waste streams. Cakes containing 40 to 50% solids are obtained. To reduce sludge weight and volume, air rather than water can be used to 'blow down', or remove, accumulated material from the filter. Dewatered sludges can be dried if necessary for disposal. The high pH of such precipitated sludges makes them well suited for fixation by cement or lime, for which costs are given by Leung et al. [35].

Metals can be extracted from aqueous systems with organic solvents: 8-hydroxyquinoline for cobalt, molybdenum, copper, iron, nickel, cadmium, zinc, vanadium, manganese, lead, and titanium; dimethyl glyoxime specific for nickel (palladium interferes) [32].

High gradient magnetic separators can separate ferrite coprecipitates or very fine (to one micrometer) ferromagnetics (iron, cobalt, nickel) or paramagnetics (chromium, manganese, molybdenum, titanium, vanadium, tungsten, tantalum, uranium, rare earths, and precious metals) from sludges [32].

Metals can be concentrated by acid or microbiological leaching of sludges, or a combination of the two [36]. Reaction of metal sulfides or oxides with SO_2/SO_3 produces water soluble sulfates, which can be extracted with ammonium carbonate [32].

For operation as a closed loop, zero-discharge system, impurities must be removed as they accumulate. For example, carbonates can be removed from cyanide baths by submerging a chilled surface in the bath, allowing sodium carbonate to precipitate on the surface, and removing the surface, although the process is patented (U.S. Patent No. 4,365,481) by the Department of Defense [16]. Nickel baths are purified by carbon adsorption [18].

8.4.4 Reuse

Recovered metals sometimes have value for use in fertilizer manufacture. Waste acids and bases from foundries [18] or other operations can be combined so as to reduce associated hazards.

9. Mass removal

Mass removal is another common function of hazardous materials, often not essential to the process. Halogenated and non-halogenated organic solvents are used for cleaning organic lubricants, coatings, and soil. Acids are used for etching, stripping, and cleaning metal, and bases are used in aqueous cleaning applications and for paint removal.

9.1 Organic solvents in general

Halogenated and non-halogenated organic solvents are used for cleaning, in vehicle maintenance, painting, paint stripping, printing, dry cleaning, and manufacturing of organic chemicals and printed circuit boards. Pollution prevention measures are considered in detail in several references [5, 11, 16, 18, 21–23, 37].

9.1.1 Substitution

Aqueous substitutes and alternate cleaning processes are available for many applications. Short term costs incurred in modifying production procedures may be greatly offset in the long term by reductions in costs associated with employee health and safety.

9.1.2 Loss reduction

Floating lids and controlled release vents widely reported to significantly reduce losses of volatile solvents from solvent tanks, thereby reducing volatile organic emissions at the same time [20].

9.1.3 Recovery

Solvent recovery is economical, and practiced widely. Generally, economics favor purchase of on-site distillation equipment over commercial off-site

recovery. Costs associated with central processing, including transportation, the risk of spills, and liability associated with improper disposal of still bottoms, tend to outweigh economies of scale. Capital cost for a still is generally about \$5000 plus \$1000 per gal/h of capacity (for example, a 10 gal/h unit would cost about \$15000), with an expected lifetime of 20 years [18]. Large volume solvent users can recycle onsite, making the process a closed loop, with recovery of solvent and oil.

Heavily contaminated solvents may require pretreatment by decanting, filtering, settling, or centrifuging. For recovery, one of the following distillation systems can be used: batch distillation, steam distillation, continuous distillation, batch rectification, or continuous rectification. Commercial systems recover 70 to 95% of solvent input. Utility and maintenance costs average \$0.20/gallon [23]. Most recovery systems are automated, requiring attendance by a moderately skilled operator about 10% of the time during operation [18]. Final dewatering, if necessary, can be done by passing the solvent through a bed of calcium salt or molecular sieve desiccant [11]. Non-halogenated still bottom residuals can be burned as fuel or used as asphalt extender. Still bottoms from paint solvent recovery have been reused for low grade paint [11].

Off-site commercial recycling services may be more economical for small quantity generators, or facilities which generate less than 100 kg per month. Commercial recyclers typically pay 20 to 50% of the cost of virgin solvent, and resell recovered material for 75% of the cost [22]. More economical arrangements can be made as 'toll' or 'toll-back' agreements, where the recycler charges a set fee for recovering the solvent. Certain specialized solvents will be taken back by the manufacturer for reprocessing, for no charge or for a fee. Service stations may rent solvent cleaning equipment with solvent included, to be replaced periodically by the supplier.

9.1.4 Recovery of air emissions

Volatile organic carbon (VOC) air emissions can be reduced by adsorption, absorption, condensation, or incineration. Activated carbon offers adequate surface area together with a non-polar surface charge; regeneration is most often by steam, although hot air, hot nitrogen, and vacuum are also used. Vapors can also be removed by scrubbers with water or organic solutions [21]. If a 'sponge oil' is used for absorption, it can be recovered by removing absorbed vapors in a flash tank [13]. Condensation is only efficient for removal of high concentrations of solvent vapor. Vapor recovery is economical for large volume generators, but is only economical for small operations if VOC emissions control is mandatory.

9.2 Organic cleaning, degreasing, and rinsing solvents

Solvents are used for cleaning, degreasing, and rinsing in vehicle maintenance operations, in the manufacture of aircraft, motor vehicles, metal furniture, tools, appliances, paint, ink, organic and agricultural chemicals, adhesives, petrochemicals, plastics, rubber, vegetable oil, textiles, and other

products, and in photographic processing, coating, printing, dry-cleaning, and other industries. Solvents are used to clean grease and oils from automotive or other parts, to prepare metal surfaces for painting, to clean electronic components, to degrease skins for tanning, and to clean equipment in the production of paint, chemicals, and other products. For example, insecticides and herbicides are produced as solvent emulsions, to be diluted with water in the field. For vehicle maintenance, both cold solvent cleaning equipment and vapor degreasers are common. Vapor degreasers consist of a tank of hot solvent, often halogenated. Parts are suspended in the vapor zone, vapor condenses on the part, and contamination is dissolved. Cleaning rags contaminated with ink, grease, and solvents can be cleaned off-site for reuse, although disposable rags may be more economical.

9.2.1 Substitution

Alkaline cleaning solutions can often be substituted for solvents. Cold cleaning tanks can be lined and fitted with an agitator and oil skimmer for use with alkaline cleaners [21]. High pressure hot water washers are available commercially for vehicle maintenance operations.

9.2.2 Specialization, segregation, and computerized process control

For operations using solvents, segregation practices are critical for lowering recovery or disposal costs. A minimum of different cleaning solvent should be purchased and used. Dedication of equipment to particular products minimizes cleaning requirements, as does conversion from batch to continuous processes. Computers can be used to schedule operations to minimize equipment clean-out [12]. For example, computerized scheduling can be used to maximize batch sizes, minimizing the production and cleaning of small batches of different products.

9.2.3 Loss reduction and recovery

Solid contaminants in cold temperature and vapor degreasers can be collected and removed in an external reservoir with a conical bottom, or filtered. Water contamination can be avoided by drying parts thoroughly, rotating if necessary. In humid climates, vapor degreasers should be operated with covers to avoid contamination with condensed water. Chiller coil leaks are another source of water contamination. Water traps should be used and emptied daily. Addition of fresh additives can extend solvent use. In vapor degreasers, sump temperature should be monitored; steam pressure can be reduced to lower temperatures, reducing additive depletion. Freeboard height may be increased and a second set of condenser coils, or chillers, installed to reduce vapor losses [11]. Liquid equipment cleaning wastes from printing processes are recovered economically, either on-site or by a commercial recycler, and even by small shops [11].

9.3 Organic paint stripping solvents

Solvents are used to remove paint in the refurbishing of vehicles, vehicle parts, and other products, generating a solvent–paint residue. Residue remaining on the product is removed with a pressurized water wash and/or scraping, generating contaminated wash water.

9.3.1 Alternate processes

Blasting with plastic media has been found highly economical in comparison with conventional solvent stripping, for removal of aircraft paint prior to repainting. Blasting is done in an enclosure. Media is removed pneumatically for continuous reuse, and replenished as necessary. Paint and plastic dust comprise the only waste produced. Substantial cost savings have been realized at Department of Defense sites [18, 38]. Several other experimental methods, such as stripping with lasers, dry ice blasting, liquid nitrogen, high-pressure water jets, and molten salt baths, are under development [18, 21].

9.3.2 Substitution and loss reduction

Caustic is used for stripping of ferrous automotive parts, although caustic is corrosive to aluminum. Where small parts are stripped by solvent submersion, the solvent bath can be reused indefinitely by withdrawing paint sludge from the tank bottom periodically [38]. Water-miscible methylene chloride strippers can be diluted to less than 25% methylene chloride without affecting performance, and alternate strippers are effective for removal of enamels [39]. Specialization, segregation, and tracking are essential to loss reduction.

9.4 Solvents for high purity cleaning

Certain manufacturing operations, such as semiconductor manufacturing, require cleaning to exceptionally high levels. Semiconductors, for example, are silicon wafers layered with electronic circuitry that may be only micrometers in thickness. Wafers may be rinsed several times between photolithographic, metallization, etching, and doping steps. Solvents used are commonly freon compounds, and may be changed frequently to maintain purity. In such cases, if solvent use is required, solvents may be recovered for use in less sensitive processes.

9.5 Dry cleaning solvents

Dry cleaning of textiles involves cleaning with solvent, often perchloroethylene or Stoddard solvent (a petroleum distillate). Solvents are continually filtered to remove impurities, and evaporated and condensed to remove oil and grease. Solvent can be removed from filter sludges with heat or air. Newer equipment has become more solvent-efficient. Campbell and Glenn [11] discuss pollution prevention opportunities in detail.

Loss reduction measures, including leak detection and elimination, can reduce solvent costs significantly and inexpensively. Solvent can be stripped, drained, cooked, or vacuum filtered from filter residues or cartridges. Still

bottoms can be heated for solvent recovery, or incinerated for energy recovery [25]. Solvent evaporated during drying of textiles can be recovered economically by carbon adsorption, steam stripping, condensation, and separation, especially by larger industrial cleaners. Vapors can also be recovered by refrigeration and condensation.

9.6 Acids and bases

Metal surfaces can be stripped, cleaned, and prepared (for plating, etching, or coating), and copper and other metals can be etched, with acids, oxidizing acids, and bases. In addition, acids are used to extract metals from crude ores in hydrometallurgical mineral refining [14]. Cleaning and etching processes are used in the manufacture of automotive, aircraft, electronics, pickled steel, metal furniture, and other metal products, and in foundries. Metallic rinse waters, and acids containing metals, are generated. While the metal may be the more toxic constituent, the metal is not generally hazardous in its original form. That is, the use of the acid or base solubilizes the metal, rendering it hazardous. Several references discuss pollution prevention alternatives [5, 11, 16, 18, 20, 31–33]. Pollution prevention technologies discussed for mass deposition may also apply.

9.6.1 Substitution and alternate processes

Alternate metal cleaning agents can reduce hazardous waste generation. Sulfuric acid/peroxide can be used in place of chromic acid dip for metal cleaning [20]. Metals can be cleaned with abrasive blasting media or brushes. Chrome and nickel can be stripped electrolytically from brass, instead of by acidic immersion, avoiding the periodic dumping of spent solution [20]. High-pressure water jets and high velocity aluminum shot (for rust, dirt, and grease removal from automotive parts) can be used in place of alkaline cleaning [20].

9.6.2 Recovery

Hydrochloric acid has largely replaced sulfuric acid for pickling (cleaning and removing surface oxide) of steel, due to the ability to economically recover both the acid and iron oxide in a roaster. The liquor is heated to 500 to 1000 °C, evaporating the water and decomposing FeCl_2 to Fe_2O_3 and HCl gas. The reclaimed iron oxide is salable for the manufacture of fertilizers, pigments, and electromagnetics. HCl is absorbed in water, completing the recovery of the pickling acid [14, 31]. The roasting process is generally economical only for large operations, due to capital and energy costs. Alternatively, scrap iron can be added, for recovery of iron chloride [40].

When sulfuric acid is used for pickling, recovery is most commonly by ferrous sulfate crystallization. Iron sulfate heptahydrate is recovered from low temperature sulfuric acid pickling liquor by precipitation with cooling or by evaporation by heating, with or without vacuum [31]. The recovered ferrous sulfate can be resold for the manufacture of inks, dyes, paints, and fertilizers, or as a coagulant for water and wastewater treatment. Recovery of high

temperature sulfuric pickling liquor and iron is accomplished by adding acid, to lower the temperature and iron solubility, and centrifuging. Recovered iron can be resold for fertilizer manufacture.

Aluminum hydroxide can be precipitated continuously from sodium hydroxide in aluminum etching, by pumping the used etching bath to a crystallization tower and returning the etchant to the process. The hydrated alumina crystals are equivalent to commercial grade, allowing possible resale [33]. Acid ion exchange has been used to recover strong phosphoric acid/nitric acid solution used for cleaning aluminum, with sulfuric acid regeneration to yield aluminum sulfate. Copper sulfate can also be crystallized to recover sulfuric acid/hydrogen peroxide copper cleaning solutions used for printed circuit board manufacture and metal finishing [33].

9.6.3 Detoxification

Waste acids and bases from material removal operations can be combined for neutralization. For example, base used to remove sand from castings has been neutralized with the acid used to chemically mill cast parts in foundries [18].

9.7 Oxidants and reductants

In tanning of leather, raw hides are stripped, salted, fleshed, and soaked in a lime/sodium sulfide bath for unhairing. Unhairing bath solution containing sulfide can be recovered by a hydrodynamic sedimentation process or by ultrafiltration [11]. Alternatively, hides can be sprayed individually with the sulfide solution, allowing sulfide recovery by sodium hydroxide absorption [11].

10. By-products

Industrial hazardous materials that do not function as raw materials, reaction intermediates, processing agents, or end products, may be considered by-products. Losses of materials of value to the process, including raw materials, reaction intermediates, processing agents, and end products, are not considered by-products. Materials generated industrially, and not generally considered to be of value in the process, include stack gases, mine tailings, and recovery residues and sludges. Because most hazardous waste is released to the air, air pollution prevention is expected to become a significant area of research.

Reuse and recovery of unavoidable residues are suggested in preference to detoxification and pre-treatment measures. For example, metals may be recoverable from mineral refining wastes, or such material may be used in the manufacture of building materials. Alternate processing, process control, and waste recovery opportunities are common in chemical manufacturing operations. Maintaining accountability by tracking wastes may be effective in reducing discharges.

10.1 Organic by-products

Organic by-products are associated with refining of crude petroleum [20, 42] and used petroleum products. In addition, used motor oil may be considered to be a by-product, because of chemical degradation, and because contamination may result in classification of the used material as a hazardous substance. In petroleum refining, salt, water, and suspended matter are washed from the crude oil with water, a process referred to as desalting. The oil is then distilled to produce naphtha, middle distillate, and a heavy bottom fraction. Naphtha is reformed catalytically to produce gasoline. Various processes are used to obtain products from the middle fraction. For example, lower molecular weight hydrocarbons are obtained by catalytic cracking. Hydrotreating, or catalytically reacting with hydrogen and heat, removes sulfur and saturates hydrocarbons. In the coking process, heat and pressure are used to convert residuums to coke and cracked hydrocarbons. The process referred to as deasphalting involves removal of asphalt from the bottom fraction to produce lubricating oils. Solvent extraction and other processes are employed to obtain high grade motor oil.

Processes used to upgrade petroleum refining by-products and off-specification material include alkylation, polymerization, reforming, and sweetening by scrubbing or absorption. The use of filter clays for purification can be eliminated through the use of the hydrotreating process [8, 41]. Spent filter clays can be incinerated or regenerated. Hydrocarbon wastes are refeed to catalytic crackers and otherwise upgraded, or incinerated. Sulfuric acid is used to sweeten and rerefine oils, producing acid tar containing sulfonates. Acid tar can be burned to produce SO_2 , however, oxidation to SO_3 for recovery of sulfuric acid has not been successful [13].

Used automotive oil, unless recovered for other than energy, is regulated as a hazardous waste because of metal and organic contamination. Lead (from piston blowby in engines using leaded fuel), chlorinated solvents (from careless disposal of degreasing solvents in used oil storage containers), and various organic additives are common contaminants. Oil waste management is discussed in detail in California Department of Health Services [16, 42] and by Nolan et al. [43]. Loss of lubricants can be minimized by replacing lubricants only as necessary for protection of machinery (based on fouling or actual operating hours), rather than on a routine schedule. Specialization and segregation can allow reuse or recycling. Lubricants can be recovered from aqueous waste streams by various separations processes depending on the application. Oil wastes can be recovered, redistilled, reused, or incinerated.

Commercial solvent recyclers typically generate a hazardous still bottom residue. Still bottom sludges can be reused as flux in the production of asphalt roofing, paving, insulating, and other asphalt-based materials [42]. Bottom residual from halogenated and other solvent distillation recovery operations can be incinerated in cement kilns for energy recovery [25], at temperatures and residence times sufficient for halocarbon destruction. In

dedicated incineration systems, hydrochloric acid can be recovered from flue gas by water absorption, as discussed for organic end products.

10.2 Metal by-products

Mining, refining, foundry, and incineration processes generate metallic by-products. Mining operations disturb natural rock formations, making naturally occurring metals available for dissolution. Thus, hazardous tailings and drainage water become by-products, in the production of non-hazardous metal products from non-hazardous raw material. Refining of metal ores produces slags, dusts, and gangue minerals which may contain toxic metals. Incinerators generate fly ash and bottom ash, which may contain leachable metals.

10.2.1 Reuse

Tailings and other mineral residues containing metals may be useful as aggregate in building materials, such as cinder blocks, bricks, concrete, or asphalt, or as a silica source in the manufacture of cement, mineral wool, or glass [44, 45]. Silicas and sodium silicates can be used as raw material for fiberglass, mineral wool, and bottle glass [46].

10.2.2 Recovery

Metals may be recovered as discussed for oxidation–reduction carriers. Direct reduction is practiced commercially in Japan, where metal oxides and coke breeze (coke particles less than 0.5 inch in diameter) are mixed and formed into balls, preheated on a grate, and heated to 1100 °C in a rotary kiln to reduce the oxides to metallic form [33]. Drainage water from molybdenum mining has been reduced and concentrated by diverting upstream runoff, prior to recovering molybdenum by ion exchange for resale. Heavy metals were removed from the effluent by lime precipitation and flotation by electrolysis, with sodium peroxide added for cyanide destruction [20]. Arsenic has been recovered from gold mine stack scrubbing waste sludge by hot water dissolution, addition of hydrogen peroxide to form the trioxide, vacuum crystallization, centrifugation, and drying [13]. Iron can be used to chemically reduce and recover copper from tailings [9]. Sufficient contact area (or time) is required, and iron sludge is produced. Brinkman and Olson [36] reviewed the recovery of metals from solid wastes and ores by leaching, and by bacteriological accumulation of metals from solution.

Air emissions may contain metal particulates or vapors. Vapors can be adsorbed selectively, or removed with scrubbers, although recovered metals have generally been disposed of. Alternatively, flue gases can be used to neutralize alkaline wastes [9]. Particulates are recovered in baghouses, electrostatic precipitators, and wet scrubbers for refeed to the process or resale to non-ferrous metals smelters. Steel making dust recovered from furnace exhaust can be resold to zinc smelters for zinc recovery. The use of high temperature plasma technology for recovery of zinc and other non-ferrous metals from steel making dust is reviewed by Eriksson et al. [47] and Herlitz and Josephson [48].

Enhanced recovery of zinc chloride from waste zinc slag is possible by filtering the waste sludge produced and concentrating the filtrate [10]. Alternatively, the green balling process consists of collecting dust from baghouses or electrostatic precipitators associated with iron and steel furnaces, wetting and forming the dusts into balls, and refeeding them to the process [33]. Lead dust generated at foundries can be recovered by air filtration, and lead powder can be recovered by collection in water, for return to molding processes [10].

Wastes from some foundry melt-furnaces, or from foundries that pour brass or bronze castings, may contain hazardous levels of lead or cadmium. Wastes include dusts and sludges collected by baghouses and scrubbers, and waste system sand from brass and bronze foundries. Hazardous system sand can be recovered for use in the process [49], and wastes can be detoxified [50].

10.2.3 Detoxification

Tailings and sludges can be detoxified as a final measure by chemical fixation or solidification with organic or inorganic binders [35, 51]. Alternatively, such material can be agglomerated by calcining at 1800 °F.

10.3 Oxidation–reduction by-products

Carbon monoxide in stack gases may be considered a reducing by-product of many production processes, and nitrous oxides may be considered acidic oxidizing by-products. Carbon monoxide can be separated from waste gases by cupraammonium absorption and other methods, for combustion directly in furnaces, for venting and incinerating, or for recycling [22]. Nitric acid is produced by the catalytic oxidation of ammonia in air over platinum. NO_x is a major air emission from the process. NO_x can be reduced catalytically by natural gas at high temperature with heat recovery, or by a newer low temperature catalytic process. For existing plants where NO_x emissions are high, adsorption and recovery of NO_x is appropriate. Zeolite brings the residual NO_x concentration to below 0.001%. Silica gel is an appropriate adsorbent in plants having a source of refrigeration or cooling water.

10.4 Acid–base by-products

Flue and stack emissions containing sulfur, nitrogen, and carbon are a major hazardous by-product of many industries, including mineral refining, petroleum refining, organic and inorganic chemicals manufacturing, and electric power production.

10.4.1 Recovery

Whereas traditional lime precipitation stack scrubber equipment have as a by-product CaSO_4 , (gypsum) for which there is little market, various processes are now available to recover SO_2 , H_2SO_4 , or H_2S from the gases [22]. Technologies for reducing hazardous air emissions are discussed in Hagler,

Bailly and Company [22]. Sulfur dioxide can be scrubbed with sodium sulfite, magnesium sulfite slurry, citrate, or various other absorbents. Smelting of high-sulfur non-ferrous metal ores produces SO_2 , which can be oxidized catalytically with heat and oxygen to SO_3 for absorption in sulfuric acid. Hydrogen sulfide emissions can be separated and concentrated by absorption on a solid or in selective or non-selective amine solvents. The Claus process involves vapor phase catalytic conversion of H_2S and SO_2 to elemental sulfur and water. Because the reaction is equilibrium-controlled, one converter can achieve 70 to 75% sulfur conversion, with a second stage providing 90 to 93% conversion. Tail gases can be returned to the converter or the furnace. Water used for cooling natural gas in carbonization of coke can be filtered with paper filters for recycling [10]. Waste heat from the catalytic conversion of SO_2 to SO_3 in sulfuric acid production can be transferred to a boiling liquid or steam, rather than as hot air to the sulfur burning furnace, to reduce nitrogen and sulfur furnace emissions [17]. Alternatively, acidic flue gases can be used to directly neutralize alkaline wastes [9].

Phosphoric acid is produced primarily by a wet process, whereby phosphate rock is decomposed with sulfuric acid, generating phosphoric acid and contaminated calcium sulfate (gypsum). Fluorine gas, evolved from the rock as a by-product of the wet process, are usually precipitated with lime in scrubbers [10, 17, 42]. A process modification involves the use of a mixture of sulfuric acid and recirculating phosphoric acid, thereby producing more concentrated phosphoric acid and a relatively clean gypsum, suitable for use in building materials [17]. The basic wet process has been found more economical than a dry process, involving oxidation of phosphorus to P_2O_5 by burning, and hydration to H_3PO_4 .

Sodium hydroxide (caustic) and chlorine are produced by the electrolysis of salt [7]. The process evolves hydrogen, as well. In the U.S., the use of diaphragm cells for the electrolysis has largely replaced the use of mercury cells, because of toxic mercury wastes associated with the latter process. Chlorine-containing gases can be recycled to the process, neutralized in alkaline scrubbers, or concentrated for recovery.

Ammonia is made by high pressure catalytic reaction of hydrogen and nitrogen, obtained from air and the conversion of methane [17]. Flue gas emissions are reduced, through the use of closed-loop processes for recovering process heat from steam, flue, and process gases.

In organic chemicals production, hydrochloric acid is an input and output of numerous reactions, and can be recycled accordingly [15]. Chlorine gas can be produced by electrolysis of 20 to 30% HCl , with continuous re-concentration of the acid by adding HCl gas. Alternatively, hydrogen chloride can be oxidized chemically, such as by reacting with oxygen at 170 to 400 °C and 15 atmospheres of pressure in the presence of nitric acid catalyst [33]. Hydrogen chloride gas can be produced by high pressure incineration of C-Cl residues with oxygen, at 85% Cl recovery. Alternatively, chlorine gas can be produced by high temperature (2000 °F) incineration.

11. End-products

Hazardous products include organic and inorganic chemicals, solvents, pharmaceuticals, biocides, and metal pigments. Hazardous end products include acids and bases, biocides, pharmaceuticals, solvents, binders, and industrial reactants. Pollution prevention opportunities differ from those in processes where the same materials are used as processing agents or raw materials. However, production of less hazardous substitutes is the first consideration for long term economic and environmental sustainability. As for other functions, computerized process control, and maintaining accountability for the costs of pollution, are high opportunity alternatives. Edgar and Himmelblau [27] give mathematical programming methods for computer-aided optimization of chemical processes. Specialization, by dedication of equipment, allows in-process recycling and reduces equipment clean out requirements. Kafarov [17] describes in detail low-waste, high-yield methods of producing ammonia, nitric acid, sulfuric acid, phosphoric acid, fertilizers, sodium hydroxide, chlorine, and soda ash. Kafarov suggests, in general, recycling of cooling and other process waters to reduce water pollution. Product losses can be reduced by sealing leaks, covering tanks, and condensing emissions. Recycling of cooling and other process waters, and heat recovery, reduce discharges. Tavlarides [14] discusses waste reduction in the production of phosphoric acid, fertilizer, nitric acid, and explosives. Simmler [15] references methods for waste reduction in chemical production.

11.1 Organic end-products

Organic chemical products include processing agents and raw materials discussed previously, such as solvents and resins, as well as pharmaceuticals and biocides. Pollution from organic chemical plants consists of wastewater and air emissions, with some liquid raw materials or products, residues from absorber-desorber columns, and solid waste also generated. Wastewaters from the production of organics contain products, reactants, intermediates, leakages, overflows, wash waters, wastes from coolers, boilers, etc., and scrubber water. Typically scrubbers are used to remove volatiles from air streams, generating wastewater. Condensation can be used to remove high concentrations of VOCs from air streams. Wastewaters are treated variously by decanting, centrifugation, adsorption, membrane filtration, and biological treatment. Common processes in the pharmaceutical industry include fermentation, natural extraction, and chemical synthesis [52]. Gaseous reactants are washed in alkaline solutions or solvents prior to catalytic conversion to avoid fouling expensive catalysts, generating washwater contaminated with bases, salts, and organics. Hydrogen chloride is generated in chlorination of organics.

Pollution prevention opportunities may differ somewhat, where the hazardous material is an end-product, compared with processes in which the same material is used as a processing agent. However, development of less hazardous

products remains a priority in such cases, considering long term economic and environmental sustainability. Due to the diversity of processes, products, and materials, pollution prevention techniques tend to be site-specific. Mathematical programming for computer-aided process optimization of chemical manufacturing processes are discussed by Edgar and Himmelblau [27] and Kafarov [17]. Air emissions can be reduced by improving procedures so as to avoid improper plant operation, improving plant organization and design, and improving plant maintenance. Gas leaks can be reduced through improved maintenance procedures, and through installation of vacuum hoods. Gases can be stripped with activated carbon or resins, or by solvent absorption. The installation of floating roofs in tanks of volatile solvents to prevent evaporation, and conservation vents which release vapors less freely, has been found to result in substantial savings due to reduction in product losses. Solvents are often recycled on or off-site. Filter cakes from fermentation processes may be reused in animal feed, fertilizers, and compost. Filter cakes possessing hazardous characteristics may be used as raw materials in the production of glass, building materials, mineral wool, or cement [46]. Spent sulfuric acid may be reused in battery manufacture [52]. Kafarov [17] discusses production of dichloroethane, methanol, formaldehyde, styrene, ethylbenzene, vinyl chloride, ethylene oxide, ethylene glycol, cumene, acetic acid, xylenes, phenol, cyclohexane, acetone, acetic anhydride, vinyl acetate, carbon tetrachloride, and plastics and synthetic resins, and the generation, composition, and reduction of waste streams. Noll et al. [9] reviewed applications and limitations of waste management unit processes in chemicals production.

11.2 Loss reduction

11.2.1 Specialization

Methane is synthesized from carbon monoxide and hydrogen at high temperature and low pressure. Exit gases are burned in a boiler furnace. Increasing the time between shutdowns by improving equipment reliability reduces wastewater associated with the flushing of equipment each time.

11.2.2 Alternate processes

Overcash [10] diagrammed a dry neutralization process involving the reuse of wastes from the production of ethylbenzene in the manufacture of styrene. A diagram of a process for reducing waste from the production of chloral, involving dehydration with a solvent in a closed loop rather than with hot sulfuric acid, is presented in the same reference.

11.2.3 Recovery

Many in-process conversion and recycling methods for chlorocompounds have become important, including perchlorination at 600 to 700 °C of chlorinated organic residues to give carbon tetrachloride and perchloroethylene [15]. Vinyl chloride has been produced by pyrolysis of dichloroethane, although new lower-waste methods are under development. Gas leaks can be reduced

through improved maintenance, and gases can be stripped with activated carbon or by solvent absorption. U.S. EPA [33] cites a process for catalytically destroying chlorinated organic by-products of vinyl chloride production while recovering the energy and chlorine value. Production of polyvinyl chloride (PVC) results in emission of vinyl chloride monomer (a colorless, inflammable gas having a half life of two days in sunlight under typical atmospheric conditions), and the polymer. Emissions can be reduced by reducing leakage from all steps of the process. Tail gases can be stripped by carbon adsorption or solvent absorption; residues can be burned or catalytically digested. Improved production processes for PVC are being developed. Acetic anhydride is often produced by catalytically cracking acetic acid to ketene for reaction with additional acetic acid in an absorber; gaseous organics from gas purification and heavy residues from the acetic acid and the absorption tower are usually burned. Phenol can be recovered from aqueous solutions by polymeric adsorption, regenerated with a vaporized organic solvent which can then be distilled for recovery of phenol and solvent [9].

Activated carbon is a hydrophobic adsorbent, making it efficient for removing non-polar organics. Carbon adsorbents, used for removing hazardous impurities such as polycyclic aromatics, amines, nitriles, or mercaptans, can be stripped with steam or nitrogen and, if necessary, regenerated by partial air oxidation [13]. Kafarov [17] describes a new, continuous flow/regenerating activated carbon filter known as Purasiv HR, which uses 25 to 30% of the energy required by a conventional system with regeneration, and recovers chlorinated or other solvents with greater purity. Synthetic resins are more expensive, but offer high adsorption rates and hydraulic flow rates due to their spherical shape and uniform size distribution. Synthetic resins can be regenerated with solvents such as methanol, allowing recovery of solutes by distillation. Soda lime is used to irreversibly chemisorb ethanoic acid, acetonitrile, acrylonitrile, alkyl chloride, and vinyl propyl disulfide [9]. Membrane filtration can remove oils and various other organics from emulsions and wash waters [9].

Heavy residues are obtained from purification and reaction steps, such as absorber and fractionation columns. Organic residues can be incinerated. Liquid hydrocarbon waste from polymer production has been used to quench acetylene at 1000 °C, producing ethylene [15]. Chlorinated hydrocarbon residues are generated from the manufacture of pesticides and other chemicals. Such residues can be detoxified by incineration at high temperatures and residence times. The HCl gas generated during incineration can be absorbed in water to produce 21% acid, which can then be concentrated to 35% by extractive distillation [33]. Alternatively, the residues have been converted to carbon tetrachloride at 600 °C by exhaustive chlorination, and resold [33].

11.3 Metal pigments

Cadmium, lead, and hexavalent chromium pigments are manufactured for use in paints and dyes. Cadmium is usually removed from pigment production wastes by precipitation at pH 11, filtration, pH reduction of the effluent, and

commercial recovery of cadmium from sludge [9]. Metal recovery methods are discussed for oxidation–reduction carriers for metals.

11.4 Acid–base end-products

The production of inorganic acids and bases involves generation of wastes beyond the stack gases discussed previously. Reduction of the product losses, in particular, is an important area of research and development.

11.4.1 Loss reduction and recovery

Hydrogen can be purified for ammonia production using potassium carbonate instead of methods involving water washes, reducing ammonia waste and energy consumption [10]. Ammonium nitrate can be recovered from steam emissions from two sources in ammonium nitrate production; scrubbing with nitric acid recovers ammonium nitrate from steam used to heat nitric acid and ammonia, and a spray trap can recover product from the product evaporator [10]. In the production of hydrochloric acid by incinerating chlorinated residues and absorbing in water, additional absorbers can be used to recover hydrochloric acid from exit gases [10].

12. Conclusions

The view taken in this review and reorganization of the literature is that the functions served by hazardous materials represent benefits; their chemical natures represent health and environmental risks. Ten functions served by hazardous materials in industry were identified as binding, pigmentation, reactants, reaction inhibition, catalysis, bleaching, mass deposition, mass removal, by-products, and end products [53]. The admittedly uneven representation of industrial technologies reflects the developing state of pollution prevention literature, the proprietary nature of many organic and inorganic chemical manufacturing processes, and the non-comprehensive aspect of the review. Explicit recognition of the functions that hazardous materials serve in industry is of value in identifying pollution prevention alternatives that are economically and environmentally sustainable. A benefit–cost analysis can then be conducted to select a cost effective blend of technologies, while maintaining product quality and productivity. Methods of estimating major uncertain costs, such as environmental and health liabilities, and production uncertainties associated with the use of wastes as raw materials, for inclusion in the benefit–cost analysis are under development [54–56].

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References

- 1 California Department of Toxic Substances, various titles, Sacramento, CA, 1987, to present.
- 2 United Nations Economic Commission for Europe, Compendium on Low- and Non-waste Technology. International Chamber of Commerce, International Environmental Bureau, Geneva, Switzerland, no date.
- 3 L. Theodore and Y.C. McGuinn, Pollution Prevention. Van Nostrand Reinhold, New York, 1992, 366 pp.
- 4 California Department of Health Services, Alternative Technologies: for the Minimization of Hazardous Wastes. California Department of Health Services, Toxic Substances Control Program, Alternative Technology Division, Los Angeles, CA, July 1990.
- 5 PRC Environmental Management, Inc., Hazardous Waste Reduction in the Metal Finishing Industry, Noyes Data Corporation, Park Ridge, NJ, 1989.
- 6 G. Munroe, W. Bradley and F. Neuber, In: D. Lintula (Ed.), Profit from Pollution Prevention: 2nd edn. Vol. 1. Pollution Prevention Foundation, Toronto, 1990.
- 7 J. Remini and W. Remini, Current status of Dept. of Energy program for recovery and utilization of nuclear by-products, In: Proc. Symp. on Waste Manage., Vol. 1, 1985, pp. 529–533.
- 8 Jacobs Engineering Group, HTM Division, Hazardous Waste Minimization Potential Workbook. California Department of Health Services, Toxic Substance Control Division, Alternative Technology Section, Sacramento, CA, December 1987.
- 9 K.E. Noll, C.N. Haas, C. Schmidt and P. Kodukula, Recovery, Recycle and Reuse of Industrial Wastes, In: J.W. Patterson (Ed.), Industrial Waste Management Series. Lewis, Chelsea, MI, 1985.
- 10 M.R. Overcash, Techniques for Industrial Pollution Prevention. Lewis, Chelsea, MI, 1986.
- 11 M. Campbell and W. Glenn, Profit from Pollution Prevention. Pollution Probe Foundation, Toronto, 1982.
- 12 K. Bagadia, Microcomputer-Aided Maintenance Management, Marcel Dekker, New York, 1987, 183 pp.
- 13 J. Bromley, Recycling, reclamation and waste reduction through process design, In: A. Porteous (Ed.), Hazardous Waste Management Handbook, Butterworths, London, 1985, pp. 256–280.
- 14 L. Tavlarides, Process Modifications for Industrial Pollution Source Reduction, In: J. Patterson (Ed.), Industrial Waste Management Series, Lewis, Chelsea, MI, 1985.
- 15 W. Simmler, Removal of chemical waste, chemistry for the future: In: H. Grunewald (Ed.), Proc. 29th IUPAC Congress, Cologne, Federal Republic of Germany, June 5–10, Pergamon Press, London, 1984.
- 16 California Department of Health Services, Alternative Technology Recycling and Treatment of Hazardous Wastes; Third Biennial Report. California Department of Health Services, Toxic Substances Control Division, Alternative Technology and Policy Development Section, Sacramento, CA, July 1986.
- 17 V.V. Kafarov, Wasteless Chemical Processing. Mir, Moscow, 1985.
- 18 T. Higgins, Hazardous Waste Minimization Handbook. Lewis, Chelsea, MI, 1989.
- 19 A. Chauvel and G. Lefebvre, Petrochemical Processes: Technical and Economic Characteristics. Gulf Publishing Company, Book Division, Houston, TX, 1989, 405 pp.

- 20 S. Huisingh, L. Martin, H. Hilger and N. Seldman, *Proven Profits from Pollution Prevention: Case Studies in Resource Conservation and Waste Reduction*. Institute for Self-Reliance, 2425 18th St. N.W., Washington, DC, 1986.
- 21 ICF Consulting Associates, Inc. and Jacobs Engineering Group Inc., Versar Inc., *Guide to Solvent Waste Reduction Alternatives; Final Report*. California Department of Health Services, Toxic Substances Control Division, Alternative Technology and Policy Development Section, Sacramento, CA, October 10, 1986.
- 22 Hagler, Bailly and Company, *Industrial Waste Gas Streams: Control Technologies and R & D Programs*. Final Report no. DOE/CE/40646-H1, E1.99:DE86 014760. U.S. Department of Energy, Washington, DC, June 1986.
- 23 D. Hazelwood and B. Burgher, *Solvent Waste Reduction and Recovery, Toxic and Hazardous Wastes*, In: I.J. Kugelman (Ed.), *Proc. 17th Mid-Atlantic Industrial Waste Conf.* Technomic, Lancaster, PA, 1985.
- 24 U.S. Environmental Protection Agency and ICF Consulting Associates, Inc., *Solvent Waste Reduction*. Noyes Data Corporation, Park Ridge, NJ, 1990.
- 25 C. Castaldini, *Disposal of Hazardous Wastes in Industrial Boilers and Furnaces*. Noyes Publications, Park Ridge, NJ, 1986, 429 pp.
- 26 Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 19, Wiley, New York, 1983.
- 27 T.F. Edgar and D.M. Himmelblau, *Optimization of Chemical Processes*. McGraw-Hill, New York, 1988, 652 pp.
- 28 L.P. Hyvarinen, *Mathematical Modeling for Industrial Processes*. Springer-Verlag, Berlin, 1970, 122 pp.
- 29 V.D. Hunt, *Computer-Integrated Manufacturing Handbook*. Chapman and Hall, New York, 1989, 322 pp.
- 30 D. Popovic and V.P. Bhatkar, *Distributed Computer Control for Industrial Automation*. Marcel Dekker, New York, 1990, 703 pp.
- 31 American Society for Metals, *Surface coating, cleaning, finishing, and coating*, In: W. Wood (Ed.), *Metals Handbook 9th edn.*, Vol. 5. American Society for Metals, Metals Park, OH, 1982.
- 32 C. Brooks, *Metal recovery from industrial wastes*, *J. Metals*, 38 (7) (1986) 50–n57.
- 33 U.S. Environmental Protection Agency, *Waste Minimization; Issues and Options Vol. III*, PB87-114377. U.S. Department of Commerce, National Technical Information Service, Springfield, VA, October 1986, pp. C1–L5.
- 34 J.R. Aldrich, *Ferrous and sulfide, a proven technology*, *Proc. 22nd Annual Airline Plating and Metal Finishing Forum*, Seattle, WA, Feb. 10–13, SAE Technical Paper Series no. 860709, SAE, Warrendale, PA, 1986.
- 35 P. Leung, F. Chen-Chen, A. Jackman and R. Powell, *An Evaluation of the Technical and Economic Feasibility and Impact of Four Technologies in Treating California's Hazardous Wastes*. Department of Chemical Engineering, University of California, Davis, CA, 1988.
- 36 F. Brinkman and G. Olson, *Chemical principles underlying bioleaching of metals from ores and solid wastes, and bioaccumulation of metals from solutions*, In: *Proc. Biotechnology and Bioengineering Symposium*. Wiley, New York, 1986.
- 37 Radian Corporation, *Halogenated Solvent Cleaners: Emission Control Technologies and Cost Analyses*. Noyes Data Corporation, Park Ridge, NJ, 1990.
- 38 U.S. Department of Defense, *Observations, site visit, McClellan Air Force Base, Sacramento, CA (citation approval not requested)*, 1991.
- 39 P. Werschulz, *Reduction of total organics in metal finishing wastewater — Alternative paint strippers, toxic and hazardous wastes*, In: G. Boardman (Ed.), *Proc. 18th Mid-Atlantic Ind. Waste Conf.*, Technomic, Lancaster, PA.
- 40 D.R. Poulsen, *Personal communication, Manager, Environmental Services, California Steel Industries, Inc., Fontana, CA, September 27, 1989*.

- 41 Kirk-Othmer, *Encyclopedia of Chemical Technology*, Vol. 17, Wiley, New York, 1983.
- 42 California Department of Health Services, *Guide to Oil Waste Management Alternatives for Used Oil, Oily Wastewater, Oily Sludge, and Other Wastes Resulting from the Use of Oil Products*. California Department of Health Services, Toxic Substances Control Division, Alternative Technology and Policy Development Section, Sacramento, CA, April 1988.
- 43 J.J. Nolan, C. Harris and P.O. Cavanaugh, *Used Oil: Disposal Options, Management Practices and Potential Liability*. Government Institutes, Rockville, MD, 1988.
- 44 J. Clifton, P. Brown and G. Frohnsdorff, *Uses of waste materials and by-products in construction; Final report, Resour. Conserv. Recov.*, 5(2) (1983) 139–160.
- 45 V.S. Ramachandran, *Waste and recycled materials in concrete technology*, In: S.N. Ghosh (Ed.), *Advances in Cement Technology*. Pergamon Press, London, 1983.
- 46 J.D. Englehardt, *Alternatives to Waste Filter Cake Disposal. Research and Development Report (internal, not for general distribution or republication)*. Manville Corporation, Filtration and Minerals Division, Miami, FL, November 1988, 27 pp.
- 47 S. Eriksson, B. Johansson and S. Santen, *Applications of plasma technology to steel plant waste treatment*, In: J. Feinman (Ed.), *Plasma Technology in Metallurgical Processing*. Iron and Steel Society, Warrendale, PA, 1987
- 48 H.G. Herlitz, *Plasma technology: Use of high-temperature plasma shows promise for metal recovery and hazardous destruction*, *Environ. Sci. Technol.*, 20(11) (1986) 1102–1105.
- 49 R.B. Tippin and R.I. Tate, *Metal Reclamation and Detoxification of Brass Foundry Waste Sand*, *Trans. Am. Foundrymen's Soc.*, 97 (1989) 513–520 (Proc. of the 93rd Annual Meeting, May 7–11).
- 50 P.D. Turpin, R.R. Stanforth and T.P. Kunes, *Treatment of EP-Toxic Foundry Waste: Regulatory and Technical Overview*, *Trans. Am. Foundrymen's Soc.*, 98 (1990) (Proc. of the 94th Annual Meeting).
- 51 J.R. Conner, *Chemical Fixation and Solidification of Hazardous Wastes*. Van Nostrand Reinhold, New York, 1990, 784 pp.
- 52 ICF Technology, Inc., *Waste Audit Study: Drug Manufacturing and Processing Industry*. Alternative Technology Section, Toxic Substances Control Division, California Department of Health Services, Sacramento, CA, May 1989.
- 53 J.D. Englehardt, *Identifying Promising Pollution Prevention Technologies*, *J. Environ. Eng.*, (1993) submitted.
- 54 J.D. Englehardt, *Hazardous waste and risk analysis*, In: *Hazardous Waste Minimization and Pollution Prevention Practices*. American Society of Civil Engineers, monograph, 1993, Chap. 3, in press.
- 55 J.D. Englehardt, *Economic analysis*, In: *Hazardous Waste Minimization and Pollution Prevention Practices*. American Society of Civil Engineers, monograph, 1993, Chap. 9, in press.
- 56 J.D. Englehardt and J.R. Lund, *Information theory in risk analysis*, *Environ. Eng.*, 118 (6) (1992) 890–904.