

INDUSTRIAL PROCESSES
REFERENCE MANUAL

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CHAPTER 1
FURNITURE FINISHING

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CHAPTER 1

FURNITURE FINISHING

1.1 INDUSTRY DESCRIPTION

Furniture manufacturing facilities vary in size based on the type of furniture manufactured, the range of materials employed in the manufacturing processes, the number of manufacturing and coating lines, and the amount of assembly required. While there are many manufacturing operations, this discussion deals with finishing operations related only to metal and wood operations. This distinction has been drawn because the predominant number of emission points from the industry come from manufacturing (finishing) operations of metal and wood.

The coatings applied at a manufacturing facility vary with personal preference, type of furniture, application technique, pretreatment, and end use. Most of the coatings applied to metal furniture are enamels, with the most common consisting of alkyds, epoxies, and acrylics containing various mixtures of ketones, aromatic, aliphatic, terpene, ester, ether and alcohol solvents. Other metal furniture facilities use lacquer, metallic coatings, and powder coatings. The majority of wood furniture manufacturing facilities use traditional nitrocellulose coatings with high solvent contents. Typical solvents used in wood furniture finishes are alcohols, aliphatics, aromatics, esters, glycol ethers, and ketones. Some wood manufacturing facilities use waterborne or radiation-curable coatings.

Metal furniture is manufactured for both indoor and outdoor use, and may be divided into two general categories: business and institutional, and household. Business and institutional furniture is manufactured for use in hospitals, schools, athletic stadiums, restaurants, laboratories and other types of institutions, and government and private offices. Household metal furniture is manufactured primarily for home and general office use. Items often considered to be metal furniture include tables, chairs, waste baskets, beds, desks, lockers, benches, shelving, file cabinets, lamps, and room partitions and other fixtures.

Wood furniture is generally categorized as high, medium, or low end with the quality of the furniture correlating closely with the number of finishing operations performed on the piece. A low end piece might undergo from six to 12 finishing operations, while a high end piece could require up to 30 finishing steps. Much of the low end furniture is constructed of medium density fiberboard (MDF) with some plastic and natural wood components. Low end furniture is often painted rather than finished. Manufacturers of low end furniture will frequently use high-speed production techniques to apply a coating of plastics, laminated vinyl overlays, and lower quality veneers. High end furniture manufacturers construct their products of solid wood and wood veneers with the wood grain showing through the finish. These manufacturers finish their products with more topcoats and intermediate handcraft steps than medium and low end furniture manufacturers. The number of finishing steps involved in the manufacture of high end furniture makes it a very labor intensive industry. Medium end furniture combines the techniques used in both low and high end facilities. The finishing practices for exposed wood surfaces are similar for all household wood furniture, including television and other cabinets. Exhibit 1-1 illustrates a typical spray coating line in a wood furniture facility.

Furniture, regardless of type, is finished in essentially the same manner. Both metal and wood furniture parts may be finished while they are unassembled, partially assembled, or completely assembled. Furniture may also be finished either manually or by automatic methods.

1.2 PROCESS DESCRIPTION

A schematic of the steps in metal furniture finishing is found in Exhibit 1-2. With the exception of the cleaning and pretreatment step, this is the same process used in finishing wood furniture which is illustrated in Exhibit 1-1. The arrows rising from the individual steps indicate emissions of volatile organic materials.

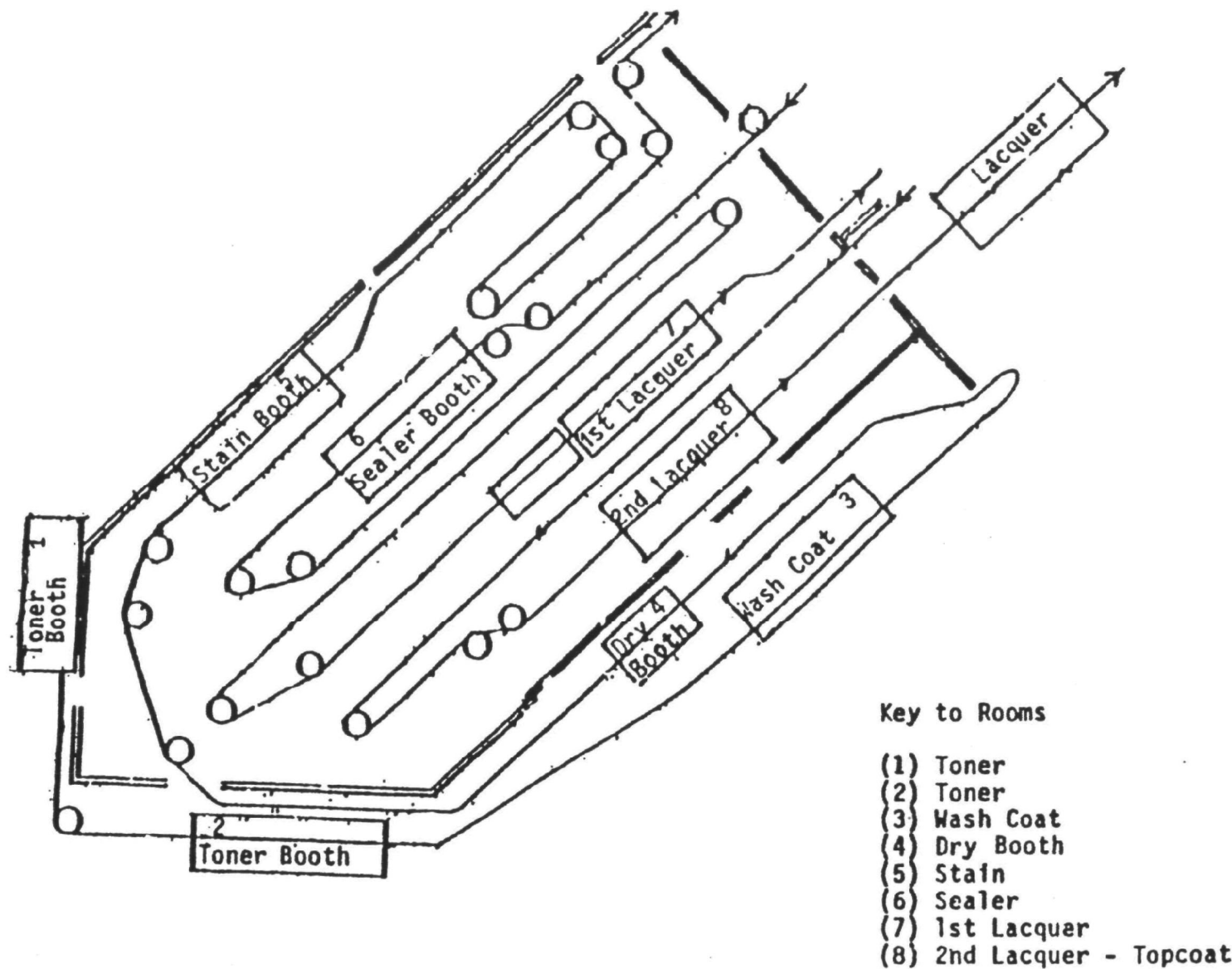


Exhibit 1-1. Schematic Drawing of a Typical Spray Coating Line.³

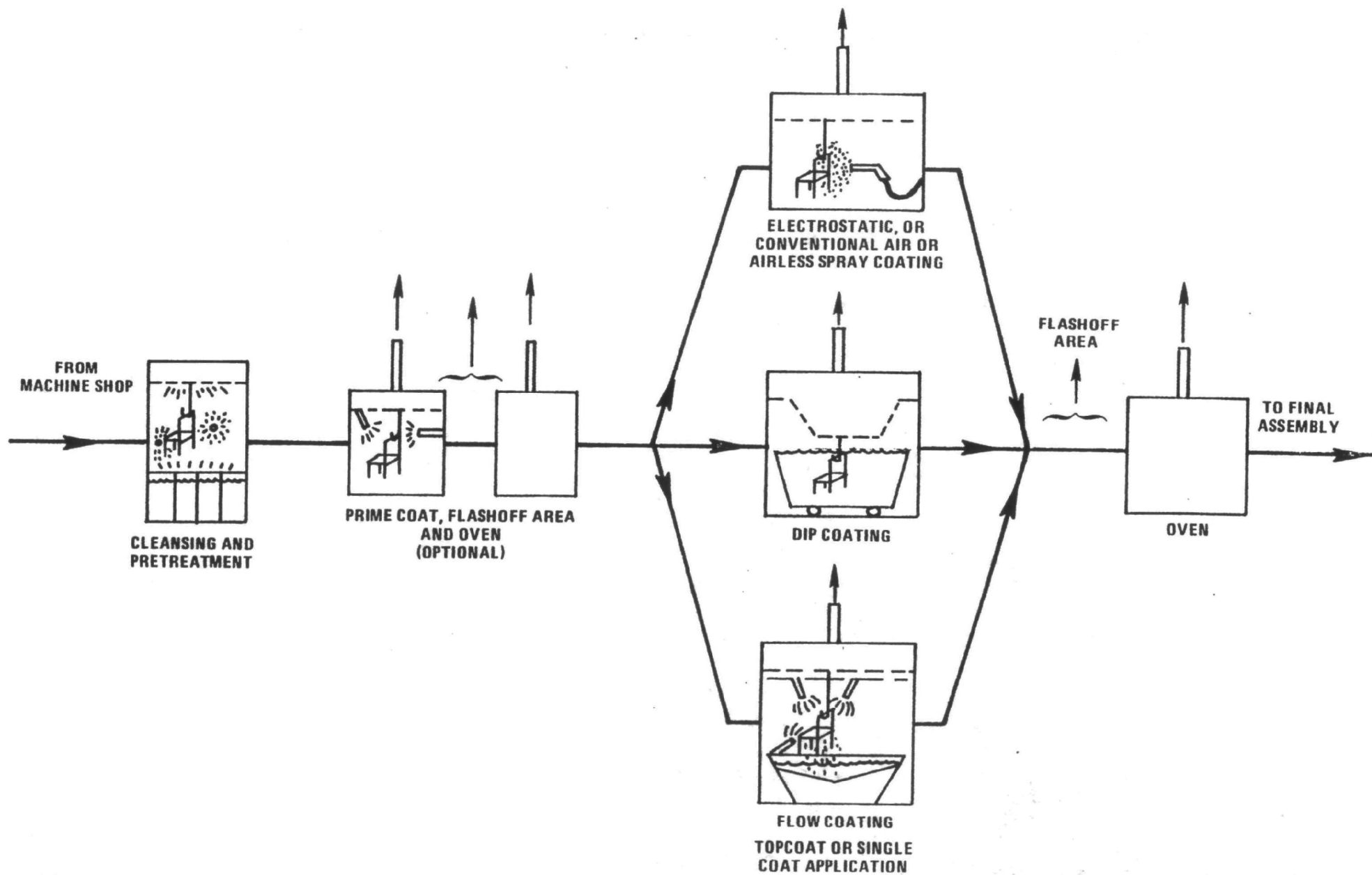


Exhibit 1-2. Common Techniques Used In The Coating of Metal Furniture Pieces.

1.2.1 Cleansing and Pretreatment

The cleansing and pretreatment employed in metal furniture manufacturing consists of a three- to five-stage process. In general, the process contains the following steps:

Process Stage	Three-Stage*	Five-Stage
Alkaline cleaner wash	1	1
Iron phosphate treatment	2a	2
Hot water rinse	2b	3
Chromic rinse	2c	4
Cold water rinse	3	5

* Only one of the treatments or rinses (2a, 2b, 2c) are utilized in the three-stage process.

The alkaline cleaner wash removes mill scale, grease, and oil. Iron phosphate treatments, hot water rinses, and/or chromic rinses are employed to improve coating adhesion and rust prevention. The furniture pieces are then rinsed with cold water. Following a cold rinse, pieces of metal furniture are dried at 130°-180°C (250°-350°F).¹

In some manufacturing facilities, the entire wash section is omitted and the metal pieces are cleaned in a shot blasting chamber or organic solvent cleaning operation.

The pretreatment employed in wood furniture manufacturing consists of initial planing and sanding to prepare the surface for coating applications.

1.2.2 Primecoat, Flashoff Area, and Oven

Although most metal furniture is finished in a single-coat operation, some pieces require a prime coat application due to the topcoat formulation or the end use of the furniture. Prime coats may be applied by spray methods, flow or dip coating techniques. These methods are discussed under top coat application (Section 1.2.3). The substrate with the prime coat then goes through a flashoff period to avoid popping of the film when the prime coat is baked. The prime coat is usually baked in an oven at 160°-200°C (300°-400°F).¹

Before a topcoat can be applied to wood furniture, several "primers" must be applied. The finishing sequence of wood furniture varies considerably, but the main priming steps include staining, applying a washcoat, filling, sealing, glazing, and shading. Some of these steps may be omitted in the manufacture and finishing of low and medium end furniture.

- **Stains:** Stains add initial color to the wood. They serve to even out and accent the natural wood grain.
- **Washcoats:** Washcoats aid in coating adhesion, filling, and color uniformity. They also help seal the wood from subsequent staining operations. In addition, washcoats prepare the wood surface for sanding after stain applications.
- **Fillers:** Fillers are highly-pigmented wiping stains containing oil which are use to "fill" open pore woods such as oak and mahogany.
- **Sealers:** Sealers, like washcoats, provide adhesion, enable sanding, increase build, and seal the wood.
- **Glazes:** Glazes, shading stains, and spatter add highlights or character to wood.

In most cases, the furniture is allowed to air dry, or "flash off," in between each priming application step. Ovens are increasingly used for this operation. After washcoats and sealers are applied and prior to topcoat application, the furniture is sanded.

1.2.3 Topcoat application

Topcoats (like the primers previously described) may be applied by spraying, dipping, or roll or flowcoating. Manufacturing facilities applying a variety of paints (metal furniture) or stains (wood furniture) usually use spray coating methods. If a plant manufacturers furniture using only one or two paints/stains, they may use flowcoating, dipping, or rollcoating.

1.2.3.1 Spray Coating

Spray coating is the most widely used method of coating application for both metal and wood furniture. Spray systems are often characterized by their transfer efficiency, or the ratio of

the weight of coating solids deposited on an object to the total weight of coating solids used in a coating application step. The material that is not deposited on the object is lost to the surrounding air and is often referred to as overspray. Systems with high transfer efficiencies deliver significantly more material to the substrate than to the surrounding air.

Spray guns operate on the principle of atomization, the process whereby coating materials are separated into particles. The quality of finish improves as the particle diameter decreases. This is partly because film thickness is directly proportional to the diameter of the particle. Thinner films are associated with better quality finishes. However, as particle size decreases, so does transfer efficiency.

Spray coating is normally performed in a booth to contain overspray and prevent surface contamination. Two kinds of spray booths are commonly employed; down draft and side draft. Spray booth air flow rates vary depending on human occupation, the type of booth, and the size of the spray booth and its openings.

The five most common spray application methods are discussed below and summarized in Exhibit 1-3. All of these spray technologies attempt to reduce overspray and waste by increasing transfer efficiency and maintaining quality of finish. Once the finish has been applied, the coated furniture is transferred to a flash-off area or oven for curing.

1.2.3.1.1 Conventional Air

Conventional air spray guns use compressed air to atomize the coating material at pressures ranging from 35,000 to 70,000 kgs/m² (ksm) (50 to 100 psi). Although compressed air results in very fine particle atomization and high quality finishes, it also causes inefficient

EXHIBIT 1-3. FURNITURE FINISHING SPRAY APPLICATION METHODS

Application Method	Transfer Efficiency	Atomization Quality	Industry Application	Coatings Applied	Cost for Base Unit
Conventional Air Spray	30 - 60	Very Fine	Decorative	Nitrocellulose Waterborne	\$250
Airless Spray	40 - 50	Coarse	Primarily Maintenance	Nitrocellulose Waterborne	\$1,700
Air-Assisted Airless	45 - 65	Fine	Functional Decorative	Nitrocellulose Waterborne High-Solids	\$2,800
Electrostatic	80 - 95	Fine	Functional Decorative	Nitrocellulose High-Solids Powder Coatings Waterborne Radiation-Curable	\$2,500
HVLP (High-volume, low-pressure)	65 - 90	Fine	Functional Decorative Industrial	Radiation-Curable Nitrocellulose Waterborne High-Solids	\$1,500

material transfer. Approximately 30 to 60 percent of the material sprayed is delivered to the substrate. The remaining 40 to 70 percent of the material is wasted through overspray or fogging.²

1.2.3.1.2 Airless

Airless units use fluid or hydraulic pressure instead of air to atomize the coating material. They have an average transfer efficiency of 40 to 50 percent and produce less fog than conventional air spray systems.³ The quality of the particle atomization is coarse and the process is used basically for maintenance purposes.

1.2.3.1.3 Air-Assisted Airless

Air-assisted airless units combine the best features of conventional compressed air atomization and airless atomization. The nozzle tip acts to atomize approximately 85 percent of the material by employing the airless methods of fluid or hydraulic pressure.^{4,5} Atomization is then completed with compressed air that is introduced at the nozzle tip. The spray would be coarsely atomized and the pattern poorly defined without the compressed air. The addition of the air allows for a finely atomized coating that approaches that of compressed air atomization. The transfer efficiency for air-assisted airless spray ranges from 45 to 65 percent. The quantity of overspray and fog is similar to that of airless spraying.^{6,7}

1.2.3.1.4 Electrostatic

Electrostatic spraying uses the basic principle of electrostatics, similar or like electrical charges repel each other while unlike charges attract. The atomized paint particles are positively charged and the piece to be coated is grounded or negatively charged. The strength of the attraction not only pulls the coating to the substrate but also causes the spray to wrap around the piece of furniture being finished, and cover all sides including most indented and recessed areas. Spraying from many angles is unnecessary because of this wrap-around effect. The result is fewer spraying passes and a reduction in both labor and material.

Electrostatic systems have an average transfer efficiency of 80 to 95 percent.⁸ While metal furniture is naturally conductive, wood is not. To use electrostatic spray methods with wood furniture, the furniture must first be coated with a sensitizing agent which renders it humidity sensitive and, therefore, conductive.

1.2.3.1.5 High-volume, low-pressure (HVLP)

HVLP units atomize material at less than 7,000 ksm (10 psi) by using a high volume of warm, dry, atomizing air. The low pressure air passes through large passages in the spray gun with few restrictions. The air in HVLP systems contains enough energy and atomization potential to carry the coating to the substrate instead of rapidly expanding as it does when released from most spray systems. This enables HVLP systems to coat a substrate without significant fog, resulting in less overspray. Consequently, HVLP units deliver a consistently high transfer efficiency between 65 and 90 percent.⁹

1.2.3.2 *Dip Coating*

After spray coating, dip coating is the most common method of finish application. Conducted either manually or automatically, items to be coated are loaded onto an overhead conveyor which lowers them into a tank containing the finish. Once coated, the pieces are raised from the tank and suspended in a flash-off area over a drainboard.

1.2.3.3 *Flow Coating*

Flow coating involves conveying the furniture pieces to be coated into an enclosed flow coating chamber. In the chamber, the coating material is directed at the object from all angles through many nozzles. The spray from the nozzles forms a curtain through which the furniture must pass. Once the furniture has been coated, it is held over a drainboard in a flash-off area. The excess coating drains back into the chamber where it is filtered and eventually pumped back into a coating holding tank.

1.2.3.4 Roll Coating

Roll coating involves transferring the finish to a substrate by a roller or a series of rollers. Roll coating techniques may be used to coat flat furniture components prior to assembly. Because the majority of furniture consists of non-flat pieces, roll coating is not a frequently used coating method. A roll-coating diagram is schematically illustrated in Exhibit 1-4.

1.2.4 Flashoff Area

The flashoff area is defined as the area between two spray booths or between a booth and an oven. Facilities may have one or several flash-off areas in which the volatiles in the coating are allowed to evaporate and the film is allowed to cure or partially cure before the next finishing step. Some flashoff areas utilize forced air circulation or a separate exhaust system which removes the volatiles (fumes) from the working area.

1.2.5 Ovens

Once the coated pieces have passed through the flashoff area, they enter the baking oven. Baking ovens are used in the metal furniture industry to bake or cure the coatings that have been applied, and may contain several zones with temperatures ranging from 160° to 230°C (300° to 450°F)¹. The ovens that are used in the wood furniture industry operate at lower temperatures (typically less than 55°C (130°F)) because at higher temperatures, the natural moisture in the wood may be driven out resulting in damage to the coating. These ovens are used mainly to flash off and dry the solvent since the oven temperature is not hot enough to bake or cure the coating.

1.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS AND WASTE STREAMS

The primary waste streams generated at furniture finishing facilities using traditional solvent-based coatings include solvent cleaning wastes and volatile organic compound (VOC)

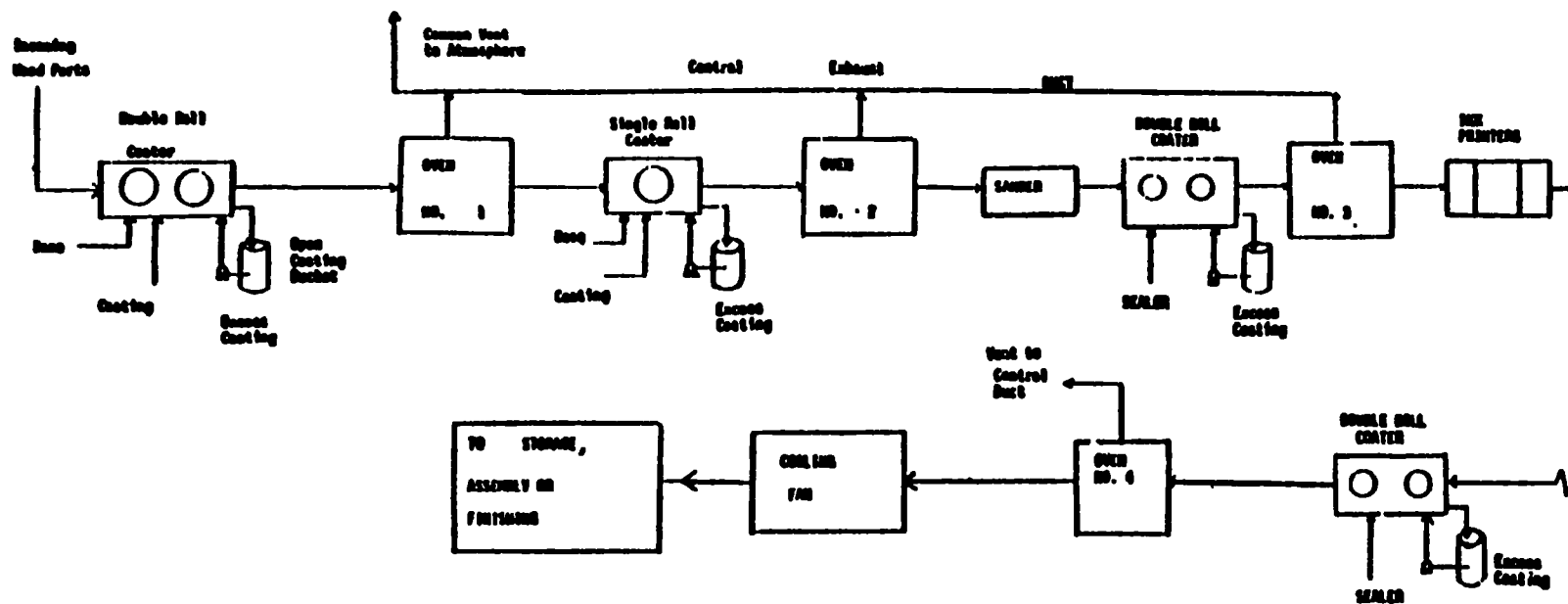


Exhibit 1-4. Schematic Drawing of a Roll Coating Operation (ink printing)³.

The four main sources of VOC emissions are spray booths, flashoff areas, ovens, and cleanup operations.

The preparation of metal furniture is an involved process requiring chemical treatment. This complicated preparation process also generates wastes that require treatment prior to disposal.

1. Alkaline cleaner wash
2. Iron phosphate treatment
3. Hot water rinse
4. Chromic rinse
5. Cold water rinse

This preparatory process produces a wastewater stream containing several constituents which must undergo treatment before disposal. The likely contaminants and the expected average concentrations include:

		Average Concentration
Phosphates (total)	-	9.5 mg/L
Hexavalent chromium	-	1.5 mg/L
Total chromium	-	20.1 mg/L
Oil and grease	-	550 mg/L

The cleansing, pretreatment, and rinsing steps apply only to metal furniture. An in-depth discussion of these wastes, minimization measures, and treatment options involved in the metal furniture pretreatment processes is found in Section 2.5 and 2.7 of the Electroplating chapter.

The preparation of wood furniture is far simpler than that of metal furniture and consists of initial planing and sanding to prepare the surface for the application of coatings. The wastes produced from these processes include wood chips, filings, and sawdust, which are non-hazardous and may be disposed of along with any other non-hazardous solid waste (e.g., garbage) that may be generated at the facility.

1.3.2 Coating Application

In the furniture industry, coatings are usually applied in spray booths using various types of spray equipment. Spray booths generally do not have any temperature or humidity control and are maintained at ambient conditions. Finishing operations may use either manual or automatic spray booths. In order to control particulates, many booths are equipped with dry filters, typically made of paper material. In the past, water curtains were used to control particulates; however, since the spent water was a hazardous waste, hazardous waste disposal costs had to be considered. As these costs increased, the cost effectiveness of water curtain filtration decreased. Therefore, most new and modified spray booths that use filters are equipped with dry filters.

The furniture industry uses a variety of sizes and types of spray booths. Residential furniture manufacturers usually apply coatings manually in booths that are approximately 2.4 meters (8 feet) high, 5.8 m (19 ft) wide, and 2.7 m (9 ft) deep. Typical exhaust rates from these booths range between 283 and 850 cubic meters per minute (m^3/min) (500 cubic feet/sec (cfs), with an average exhaust rate of 540 m^3/min (315 cfs). Most booths used by residential furniture manufacturers consist of only a backside.

Spray booths used by office/cabinet manufacturers applying coatings manually to preassembled furniture are approximately 2.1 m (7 ft) high, 6.1 m (20 ft) wide, and 3.6 m (12 ft) deep. Typical exhaust rates from these booths range between 198 and 566 m³/min (115 and 330 cfs), with an average exhaust rate of 397 m³/min (232 cfs). These booths often consist of only a backdrop. If, however, pieces are coated prior to assembly, they can enter a four-sided booth through slots in the sides. Manufacturers using the more efficient automatic spray equipment can use smaller spray booths with an average exhaust rate of 105 m³/min (61 cfs).

The waste streams generated in the coating application/spray booth area are solvents, excess paint, and waste filters. Exhibit 1-5 compares VOC emissions from conventional and waterborne coatings in a sampling of North American furniture manufacturing facilities. Suppliers of the furniture finishes are also indicated in the table.

1.3.2.1 Filters

The filters in spray booths provide a mechanical means of filtering the air by passing it through a form of filter media. As the filter removes the paint particulates in the air stream, the buildup will gradually restrict the air flow and require a change in the filter media. Paper or pad type filters with accumulated paint or varnish solids are often disposed of in a dumpster as solid waste. Cloth filters may be washed and reused. The wash water may then require proper treatment.

Water wash spray booths flush paint particulates out of an air stream by drawing the air through a continuous curtain of moving water. The solid paint particles are flung off of the water curtain and into a collecting pan. The water is then treated by compounding causing the paint particles to coagulate and float on the surface where they are then skimmed off of the top.

Neither the water wash spray booth systems nor the dry filter booths remove any solvent vapors.

EXHIBIT 1-5. ESTIMATED HYDROCARBON EMISSIONS REDUCTION POTENTIAL

Furniture Manufacturers-Finish Supplier	Estimated kg of Hydrocarbon Emitted per 100 m ₂ of Surface Covered ^a		Potential Percent Reduction
	Conventional	Waterborne	
Drexel Heritage-Inmont	99.8	5.9	94
Bassett-Spruance	120	89.0 ^b	26
Bassett-Guardsman	87.1	34	61
Bassett-Mobil	43	30.0 ^c	30
Broyhill-Mobil	71.4	12.0 ^d	83
Bernhardt-Reliance	98.8	7.3	92
Bernhardt-Guardsman	-	58.7 ^e	-
Stanley-Reliance	160	12	93
American-Lilly	136	29	79
American-Inmont	-	11	-
American-Guardsman	-	24	-
Henredon-Reliance	120	16	87
Thomasville-Guardsman	81.2	36	55

^aAverage values taking into account supplier-estimated overspray values and different furniture pieces.

^bTrial goal was to replace wash coat and sealer only with waterborne substitutes and keep the balance conventional.

^cTrial goal was to replace color coats only with waterborne substitutes but keep conventional clear coats.

^dCalculated values based on actual finish usages.

^eValues appear high, based on other trial data.

Source: Participating finish suppliers.

1.3.2.2 Solvents

Because the coatings employed in furniture finishing contain a wide variety of volatile substances with a wide range of concentrations, the solvent streams emitted during the finishing process also contain a variety of VOC concentrations and components. The organics in these streams consist of alcohols, ketones, cellosolves, acetone, toluene, xylene, and other volatile compounds. Some of the coating organics volatilize as the material is being applied. An additional amount volatilizes once the spray reaches the substrate or the spray booth filter.

It is estimated that 85 percent of the VOC emissions in the wood furniture coating process occur in the spray booths. The remaining 15 percent of the emissions are released during curing operations in the bake ovens and flashoff areas. The emissions from a variety of metal coating plants is provided in Exhibit 1-6. The majority of VOC emissions from metal furniture coating operation occurs in the application and flashoff areas.

Spent solvents are also produced during the finishing of furniture. The two major sources of spent solvents in furniture finishing are the stripping, or "wash off", of wood furniture and the cleanup of finishing equipment and spray booths. In the wood furniture stripping process, improperly finished furniture is stripped of its defective finish using a lacquer thinner or "stripper" which is reused until it becomes too contaminated for further use. Spray guns, feed lines, and spray booths are cleaned on a regular basis using a lacquer thinner which is discharged into storage containers after being used in the cleanup. In addition, some spent solvent also results from the occasional batch of defective finishing materials.

The virgin stripper that is used in these processes is usually composed of a mixture of toluene, xylene, acetone, ethanol, butanol, isopropyl alcohol, naphtha, methyl ethyl ketone, and esters. The spent solvents from the stripping of furniture and spray booth cleanup may become contaminated with stains, fillers, glazes, and nitrocellulose. The solvents that are used in the furniture industry are normally non-halogenated and have high BTU values and, therefore, are usually much easier to dispose of than spent solvents from industries that use

EXHIBIT 1-6. EMISSION FACTORS FOR TYPICAL METAL COATING PLANTS

Type of Plant	Production Rate	Emissions		Estimated Emissions (%)	
		Hg/hr	ton/yr	Application and Flashoff	Ovens
Large appliances Prime and topcoat spray	768,000 units/yr	315	347	80	20
Metal furniture ^a Single spray ^b	48 x 10 ⁶ ft ² /yr	500	550	65 - 80	20 - 35
Single dip ^c	23 x 10 ⁶ ft ² /yr	160	176	50 - 60	40 - 50
Miscellaneous metal ^a Conveyor single flow ^c	16 x 10 ⁶ ft ² /yr	111	122	50 - 60	40 - 50
Conveyor dip	16 x 10 ⁶ ft ² /yr	111	122	40 - 50	50 - 60
Conveyor single spray ^d	16 x 10 ⁶ ft ² /yr	200	220	70 - 80	20 - 30
Conveyor two coat, flow and spray	16 x 10 ⁶ ft ² /yr	311	342	60 - 70	30 - 40
Conveyor two coat, dip and spray	16 x 10 ⁶ ft ² /yr	311	342	60 - 70	30 - 40
Conveyor two coat, spray	16 x 10 ⁶ ft ² /yr	400	440	70 - 80	30 - 30
Manual two coat, spray and air dry	8.5 x 10 ⁶ ft ² /yr	212	233	100	0

Source:

halogenated solvents or produce low BTU wastes. In the past, these spent solvents were disposed of in secure landfills. However, landfilling liquid wastes is prohibited in the United States under RCRA. Due to these restrictions, furniture manufacturing facilities have had to explore other means by which to manage their spent solvents. One of the options commonly practiced by furniture companies in managing their spent solvents is recycling, both onsite and offsite. Other options exercised by some furniture manufacturing facilities in the management of their spent solvents is the incineration of these spent solvents onsite or using them as fuel. Recycling, however, has proven to be a more economical means of managing the spent solvents than incinerating these wastes or using them as a fuel.

1.3.2.3 Coating waste

Most of the coating waste generated during the coating application process is captured by the spray booth filters and is handled as described in Section 1.3.2.1.

1.3.3 Flashoff Area

The wastes generated in flashoff areas are solvents. The flashoff area serves as a staging area between two finishing steps where volatiles in the coating are allowed to evaporate and the film is allowed to cure or partially cure before the next finishing step. Some flashoff areas have forced air circulation which forces the excess coating solvent to evaporate.

1.3.4 Bake Oven

Solvents are also the primary waste stream resulting from the oven curing process. The elevated temperatures in the oven cause any remaining solvent in the coating to volatilize from the furniture surface. Oven temperatures can range from 38° to 121° C (100° to 250°F) depending on the type of coating used, while the exhaust rate can range from 21.2 to 425 m³/min (750 to 15,000 ft³/min).

1.3.5 Equipment Cleaning

The primary process waste generated from equipment and spray booth cleaning is spent solvents which are usually contaminated with paints, stains, fillers, glazes, and nitrocellulose.

1.4 POLLUTION PREVENTION, WASTE TREATMENT, AND CONTROL SYSTEMS

Much of the waste generated in furniture finishing is a result of using solvent based coatings. Exhibit 1-7 summarizes the finishing processes and their corresponding waste streams. If finishers moved to alternative product formulations (i.e., high-solids, waterbornes, radiation curables, or powder coatings), then a significant amount of waste would be eliminated (pollution prevention). VOC emissions would be reduced as would equipment cleaning wastes. Spray guns, dip tanks, and roller mills used to apply solvent based material must be cleaned with solvents thereby generating solvent cleaning wastes. However, when applying waterbornes and many other finish formulations, alkaline or water washes can be used effectively in cleaning equipment. In many cases, the treatment and handling measures for these wastes are simpler and more cost effective than actions taken for solvent cleaning wastes.

If solvent based materials must be used, air emissions and finishing wastes can be reduced by increasing the transfer efficiency of the application equipment. Increased transfer efficiency results in more material on the substrate and less in the air or on spray booth filters.

In addition to reformulating products and increasing transfer efficiency, furniture manufacturers can reduce waste by improving operating procedures and implementing recycling and good housekeeping techniques.

Add-on control devices should serve as a last means of reducing wastes. In the furniture industry, add-on control devices to control air emissions are not always applicable because of

EXHIBIT 1-7. SUMMARY OF FURNITURE FINISHING WASTE STREAMS

Process Stream	Industries Using	System Constituents	Waste Stream Constituents
Cleansing and Pretreatment	Metal Furniture	Acid solutions Alkaline solutions Abrasives Organic compounds Chelating agents	Low or high pH Dissolved metals Complexed metals Metal chips and fines
Rinsing	Metal Furniture	Water	Low or high pH Dissolved metals Organic compounds Waste chemicals Chelating agents
Coating Application	Wood and Metal Furniture	Coating materials Organic vapors Water	Particulates Organic compounds
Flashoff Area	Wood and Metal Furniture	Organic vapors	Organic compounds
Bake Oven	Wood and Metal Furniture	Organic vapors	Organic compounds
Equipment Cleaning	Wood and Metal Furniture	Organic vapors Liquid organics Coating materials	Organic compounds Waste chemicals Coating particulates

the low concentration of VOCs and the varied constituents in the emission streams. Many traditional control devices such as carbon absorption (scrubbers) and condensation are most efficient in removing higher concentration, single component waste streams. As such, they are not be very efficient in controlling the low concentrations and varieties of VOCs found in furniture finishing emissions. In addition, some of the constituents in the finishing waste streams could act as poisons to catalysts used in catalytic incinerators.

1.4.1 Material Substitution

Pollution prevention opportunities for reducing waste and emissions through material substitution and process modifications are summarized in Exhibit 1-8 and described in the following section.

1.4.1.1 Coatings

The most effective way to eliminate or reduce solvent waste generated during the coating application process is to change to alternative coating formulations with lower solvent contents. Although low solvent coatings exist and are successfully used in many facilities, other furniture finishing plants are reluctant to invest the time and effort required to change to new and developmental technologies. The following sections discuss several low solvent coating alternatives. A summary of these options is presented in Exhibit 1-9.

1.4.1.1.1 High Solids

The normal solids content for conventional coatings ranges from eight to 30 percent, while high-solids coatings typically contain 40 to 100 percent solids.^{10,11} Because high solids coatings contain less solvent and more solids, they help to lower VOC emissions. In addition, less material must be shipped, stored and sprayed to achieve the desired film build. In short, this means less potential to generate waste. Two coatings which fall into the high solids category are radiation-curable and powder coatings.

EXHIBIT 1-8. SUMMARY OF FURNITURE POLLUTION PREVENTION OPTIONS

Coating/Process Type	Industries Using	Penetration within Industry	Plant Size	Advantages	Disadvantages	Potential for Furniture Use (Issues)
UV-Curable Coatings	Wood and Metal Furniture	Slight	Large	Durable, less material used, low VOC emissions	Application problems, toxicity problems, cost	Possible (application difficulties, equipment and coating costs)
Waterborne Coatings	Wood and Metal Furniture	Currently used	Medium Large	Low VOC emissions, H ₂ O clean-up, reduce fire hazard	Wood surface raising, quality of finish, longer drying time, Increase oven temp., need humidity control	Currently used in larger facilities
Powder Coatings	Metal Furniture	Currently used	Medium Large	Quality finish, durable, low VOC emissions, less material required to coat, excess recyclable	Faraday effect, cost, difficult touch-up, requires oven curing, color change	Possible (application and cure difficulties--high cure temps.)
High-Solids Coatings	Wood and Metal Furniture	Currently used	Small Medium Large	Low VOC emissions, less material required to coat, good color matching, potential energy reduction	Reduced shelf-life, short pot-life, Faraday effect	Yes (currently used)
High Volume/Low Pressure Units	Wood and Metal Furniture	Currently used	Small Medium Large	Low VOC emissions, quality finish, increased transfer efficiency, minimized waste disposal	No electrostatic wrap, difficult to use on parts with many open spaces	Yes (currently used)
Flat Line Finishing	Wood and Metal Furniture	Currently used	Large	Efficient, good material utilization, low VOC emissions, good transfer efficiency, quality finish	Can use only with long, flat stock	Yes (currently used in some industries)

EXHIBIT 1-8 (CONTINUED)

Coating/Process Type	Industries Using	Penetration within Industry	Plant Size	Advantages	Disadvantages	Potential for Furniture Use (Issues)
Electrostatic Units	Wood and Metal Furniture	Common in metal furniture, not as frequent in wood	Small Medium Large	Increased transfer efficiency, good material utilization, quality finish, low VOC emissions	Wood requires sensitizing agent, difficult to use in low humidity, not good with case goods, parts must be grounded	Yes (currently used)
Pressure Atomized Units (Airless)	Wood and Metal Furniture	Currently used in many facilities	Small Medium Large	Low VOC emissions, reduced material consumption, less coating rebound	Limited coat thickness, high pressure requires increased operator care	Yes (currently used)
Air-Assisted Airless Units	Wood and Metal Furniture	Currently used operations	Small Medium Large	Operates at low pressure, less rebound, low VOC emissions, reduced material consumption		Yes (currently used)

EXHIBIT 1-9. SUMMARY OF COATING CATEGORIES

Coating Category	Volume Percent Solids	Volume Percent Solvent	VOC Content (lbs/gal)	Quality of Finish	Cure Temperature Required (°F)	Available Film Thickness (mils)	Method of Application
High-Solids Coatings	40 - 100	0 - 60	0 - 5	High Quality Very Durable	Air Dry - 400	0.5 - 2.0	Electrostatic Air Assisted Airless HVLP
Radiation-Curable Coatings	20 - 100	0 - 80	0 - 5	High Quality Very Durable	UV-Cure EB-Cure	2 - 10	Rollcoating Electrostatic HVLP
Powder Coatings	98 - 100	0	0	High Quality Very Durable	350 - 400	< 1	Electrostatic
Waterborne Coatings	25 - 80	5 - 20	1 - 3	Varies	66 - 241	1.0	Conventional Air Spray Air-Assisted Airless Electrostatic Airless HVLP
Nitrocellulose Based Coatings	8 - 30	70 - 92		High Quality Durable	Air Dry - 165	1.0	Conventional Air Spray Air-Assisted Airless Airless HVLP Electrostatic

1.4.1.1.2 Radiation Curables

Radiation curable coatings are coatings formulated to cure at room temperature with the assistance of a radiation source, either an ultraviolet (UV) light or an accelerated electron beam (EB). The electromagnetic radiation energy effects a chemical and physical change in the coating materials by forming cross-linked polymer networks. Radiation-curable coatings typically have higher solids contents than their conventional solvent-borne counterparts. The majority of current radiation-curable systems contain none of the organic solvents found in conventional coatings. The film-forming components in a radiation-curable system may be considered 100 percent reactive, which means all of the material is converted into the polymer network and nothing evaporates before the coating or ink is considered dry. The coatings are most often applied to the substrate by a roll coating station, although spray devices may be used with some types of radiation-curable components. Radiation curable coatings have been used successfully in both metal and wood furniture applications. Some disadvantages associated with radiation curable systems are the initial start-up and conversion costs and toxicity classifications of the materials utilized.

1.4.1.1.3 Powder

Powder coatings are mixtures of dry synthetic resins, pigments, solid additives, and from zero to ten percent entrapped volatiles. The application of powder coating is based on the principle that charged particles attract. Negatively charged atomized powder particles are sprayed onto the positively charged (grounded) part to be coated. The powder is pneumatically fed from a supply reservoir to a spray gun which renders a low amperage, high voltage charge to the powder fragments. These particles, which have become negatively charged, are readily attracted to the positively coated surface of the part. This attraction results in a wrap-around effect which not only pulls the coating to the substrate but also causes the spray to wrap around the piece and cover all sides, including most indented and recessed areas. The powder particles are then held on the surface of the part until melted and fused into a smooth coating in the baking ovens.

Any overspray resulting from the coating process can be collected and recycled using a powder recovery system. These systems range in size depending on user needs, but all operate by separating unused powder from its carrying air stream by incorporating vacuum and filtration methods to return the powder to a feed hopper for reuse. Employing this method allows the user to approach a 100 percent efficiency-use rate.

Although powder coatings may be used in coating wood furniture, they are better suited to metal furniture as metal is naturally conductive.

1.4.1.1.4 Waterbornes

Waterborne coatings contain water as the main solvent or dispersant, although most contain five to 20 percent organic solvent for coating property enhancement. Waterborne formulations reduce or eliminate solvent emissions and improve worker and operation safety. Waterborne formulations reduce fire hazards and explosion potential in storage and application areas which lowers insurance rates. Hazardous waste handling is minimal because water is used for clean-up. Waterborne coatings allow for rapid color changes and quick and simple clean-up because of their solubility in water.

Waterborne coatings are a very feasible waste reducing alternative in the metal furniture industry, but somewhat less feasible for wood furniture finishing. The application of waterborne finishes to wood substrates may result in grain raising. Although quality waterbornes for wood furniture are produced, they may be difficult to find or of limited availability.

1.4.1.2 Cleaning materials

Like coatings, cleaning materials may be reformulated to reduce solvent waste and air emissions. Air VOC emissions may also be reduced if high boiling point solvents are used

instead of highly volatile materials. Although materials with high boiling points and low volatility will eventually evaporate when exposed to air, they will not volatilize during pouring and agitating to the extent that highly volatile materials will. In some instances, aqueous, detergent-type cleaners can be substituted for solvent-based materials.

1.4.2 Process Modifications

1.4.2.1 Coating application

The wastestreams generated during the coating application process include waste solvent and waste paint. One way to effectively reduce these wastes is to reduce the amount of overspray produced. This can be accomplished by increasing the transfer efficiency of the application equipment either by using more efficient equipment or by moving to automatic spray devices. Because spray technologies are the most common application techniques used in furniture finishing, the two most efficient spray application methods are discussed below.

1.4.2.1.1 Electrostatic

Electrostatic systems have an average transfer efficiency of 80 to 95 percent.⁸ Electrostatic methods may be used to apply conventional solvent-based coatings, powder coatings, and high-solids materials. Recent equipment developments also make the application of waterborne coatings possible. In the past this method was unsafe because the conductivity of the materials presented a shock hazard. Current practices isolate material supplies to prevent physical contact with this part of the system and allow for quality coating.

1.4.2.1.2 HVLP

HVLP systems produce considerably less overspray than conventional systems with transfer efficiencies measured between 65 and 90 percent. This can result in significant waste reduction. Water-wash booths may be replaced by dry filter media reducing water pollution

and hazardous waste generation. Less overspray and migration also reduce necessary booth and equipment cleaning, sludge removal, and filter changing while increasing material usage. HVLP systems may be used to apply radiation curable, waterborne, and high-solids coatings.

1.4.2.2 Spray booth modifications

The most common spray booths in the furniture industry are used to apply a finish with manual spray equipment. These booths, which are open on all sides, require large volumes of ventilating air which are normally supplied by a side draft system. Side draft booths incorporate a fan which moves air past the operator, over the piece being coated, and through the spray booth filters. The filters remove the overspray (i.e., particulates) and direct the air out of the booth stack (usually to the atmosphere). Enclosing the spray booth by minimizing the openings needed for furniture to enter and exit would allow recirculation ductwork to be installed. Recirculating spray booth air reduces uncontrolled emissions and reduces the amount of fresh air which is required to be supplied to the operator.

1.4.2.3 Enclosed finishing lines

Enclosing finishing lines allows for a higher capture efficiency of the organics released during the finishing sequence (e.g., emissions from spray booths, flash-off areas, and ovens). Total enclosures may be constructed over a spray booth, an oven, or over the entire finishing line. Total enclosures are very important if add-on control equipment is used. The emissions from these enclosed areas are captured and exhausted through a stack or a duct to a control device.

1.4.3 Modified Operating Practices

1.4.3.1 Reduction and recycling in cleanup solvent use

Modified operating practices are often considered by industry to be the lowest-impact approach to reducing waste. Because no change in solvent is involved, there is no

compromise in cleaning efficiency. The idea is to restrict the movement of air across containers of solvent and to limit the amount of solvent exposed to air. Containers of cleaning materials (i.e., rags and towels) saturated with solvents must be closed tightly to prevent solvent evaporation.

To be an effective pollution prevention technique, the cleaning of small parts should be conducted in a closed unit to prevent splashing and spraying which creates emissions. Equipment is currently being manufactured which will clean spray equipment without requiring the operator to spray cleaning solvent through the air. Cleansing of the internal parts is accomplished by submerging the gun in a tank which is able to pump solvent through the gun. The solids in the cleaning solvent settle out and the solvent is recycled. The solids are removed for disposal.

Another method to limit the use of cleanup solvents is to issue a limited amount of solvent to each operator during a shift. This administrative action limits the total solvent consumption and requires the operators to monitor solvent use, but may adversely affect equipment conditions if equipment cleanliness is not properly monitored. Such administrative actions require a good operator training session prior to implementation.

A third waste minimizing method is to use countercurrent rinsing sequences. This method uses recycled "dirty" solvent to initially clean equipment. Following this step, "clean" recycled or virgin solvent is used to rinse away the "dirty" solvent. The countercurrent sequence extends the life of cleaning solvents and, in some cases, permits the spent solvent can be used as a thinner for the finishing material.

1.4.3.2 Housekeeping

One waste-reducing housekeeping method which has been used successfully in many plants is the segregation of waste streams. After use, rather than combining all cleaning materials, such as solvents or cleaning materials from a single or variety of finish lines, the waste

materials are separated and stored by type. This increases the useful life of the cleaner and reduces ultimate disposal or off-site recycling costs.

1.4.3.3 Proper spray techniques

The least expensive way to reduce overspray and VOC emissions generated during the coating application process is to practice proper spray techniques. These techniques can improve transfer efficiency without incurring the cost of new or modified equipment. Implementing a spray techniques program involves adjusting equipment to the proper settings, training the operators on proper techniques, and developing a system for inspecting and maintaining the spray equipment at maximum efficiency. The basic fundamentals of a good spray technique include the following:

- A 50 percent overlap of the spray pattern
- A distance from gun to workpiece of 16 to 20 cm (6 to 8 in.)
- A gun delivery volume of approximately 7.1 m³/min (250 ft³/min.)
- Holding the gun perpendicular to the surface
- Triggering the gun at the beginning and end of each pass

A training program that incorporates these techniques, if implemented correctly, can reduce finishing material usage, reduce waste generated from overspray, reduce air emissions, and improve the quality of the product.

1.4.4 Add-On Controls/Treatment

The two add-on control techniques which are considered to be technically feasible for both the metal and the wood furniture industry are carbon adsorption and thermal incineration.

1.4.4.1 Carbon adsorption

Almost 50 to 80 percent of the volatile organic compounds from furniture finishing are released during the application and flashoff processes. Carbon adsorption techniques can reduce emissions from these areas by 75 to 90 percent depending on the capture efficiency of the control device.

In the carbon adsorption process, VOC emission streams are passed through a bed of activated carbon in which the VOC molecules are captured on the porous carbon surfaces by non-chemical Van der Waals forces. The adsorptive capacity of the carbon bed tends to increase with the gas phase VOC concentration, molecular weight, diffusivity, polarity, and the boiling point of the VOC. After the working VOC capacity of the carbon is reached, the VOC can be desorbed from the carbon and collected for reuse.

Desorption of the VOC from the used carbon bed is typically achieved by passing low-pressure steam through the bed. In the regeneration cycle, heat from the steam forces the VOC to desorb from the carbon where it is entrained in the steam. After the carbon bed has been sufficiently cleared of VOC, it is cooled and replaced on line with the emission stream. Meanwhile, the VOC-laden steam is condensed, and the VOC is separated from the water by decanting or, if necessary, by distillation. If the VOC is not recovered for reuse or reprocessing, it may be incinerated.

The size of a carbon adsorption unit is dependent on the exhaust flow rate, its desorption period, and VOC concentration. The flow rates and volatile organic concentrations will vary in each furniture facility because of the wide variety of coatings employed in the finishing process. In order to optimize the efficiency of the carbon adsorber, the finishing line should be enclosed.

Carbon adsorption is considered a viable control option for the application and flashoff areas because exhaust gases are at ambient temperature and contain only small amounts of particulate matter that could contaminate the carbon bed.

1.4.4.2 Thermal incineration

Thermal incinerators pass the emission stream through a combustion chamber where the VOCs are burned at temperatures typically ranging from 700 to 1,300°C (1,300 to 2,370°F). Initially, burning is started with the assistance of a natural gas flame or similar heat source. If the VOC in the emission stream has a sufficient heating value and concentration, ignition temperatures can be sustained by the combustion of the VOC, and the auxiliary heat can be turned off. If the ignition temperature cannot be maintained by combustion only, the auxiliary heat must be left on. Auxiliary heat can be provided by fuels such as natural gas and from recovery of heat released during combustion. The waste gases from the thermal incinerator are usually vented to the atmosphere.

Incinerators are more efficient than carbon adsorbers for reducing VOC emissions from furniture finishing operations. The concentration of organic vapors is usually higher in the oven exhaust (5 to 15 percent of the lower explosive limit (LEL)) than in the application and flashoff areas and provides some fuel for the incinerator.

Thermal incineration is widely used to control continuous, dilute VOC emission streams with constituents from a number of compounds. Thermal incinerators can achieve VOC removal efficiencies of 98 percent or a 20 ppm exit concentration. For safety considerations, VOC concentrations are usually limited to 25 percent of the LEL (lower explosive limit) for the VOC. If the VOC concentration is higher in the waste gas, dilution may be required.

Thermal incinerators remove particulates and other organics in addition to VOCs, thus enhancing their utility.²⁵

1.4.4.3 Solvent Stills

For those solvents that have become too soiled for reuse, some manufacturing facilities have determined that it is cost effective to install stills that will recycle their spent solvents.

The installation of solvent stills allows manufacturers to lengthen the life of cleaning solvents and to reduce the purchase of virgin solvent by implementing in-house recycling. Spent solvent is pumped or poured into the boiling chamber where it is boiled. Vapors form and pass through the vapor tube into a water-cooled condenser. The vapors are condensed into a liquid state and flow into a container or drum. When a visual check through a sight glass indicates that no additional distillate is available, the unit is allowed to cool. Once cooled the material remaining in the boiling chamber is removed and disposed of as hazardous waste.

By recycling spent solvents in-plant, out-of-plant recycling costs can be avoided. These costs can include recycling fees, transportation charges, and insurance premiums. In addition, in-plant recycling eliminates the risk of any spills or accidents that could occur during transportation of these wastes.

Recycling solvents presents some limitations. Because the composition of the solvent changes with distillation, it is not possible to reuse the reclaimed solvent in stripping, or "wash-off" operations. Acetone is added to this reclaimed solvent and this reconstituted mixture is then used for thinning coatings in the facility's spray operations. This reuse results in a reduction in the quantity of virgin solvent that is purchased for the spray mix.

There are several types of distillation equipment available that handle a wide variety of solvents with varying capacities. Perhaps the most important design parameter to be considered in selecting a still to recover spent solvents is the type(s) of solvent(s) that are to be recycled. The presence of nitrocellulose lacquer residues, which many furniture industry solvents contain, poses special problems because nitrocellulose can become explosive when heated. The manufacturers of these stills recommend that special design features be included in those stills that will be utilized to recover spent solvents containing nitrocellulose. These features may include vacuum distillation, a water-flush quick cooldown mechanism, a caustic neutralizing flush, or explosive protection casings with the still placed in an isolated location.

When recycling solvents, efforts should be made to keep solvents segregated. In facilities that utilize several different solvents in various stages of their operation, these solvents should be kept segregated in order to be able reclaim them for reuse. If solvents are not kept segregated, the material that is reclaimed will be a mixture of the various solvents that are used, which may render it unsuitable for reuse in any of the facility's processes thereby leaving disposal as the only remaining alternative of handling this material. Segregation of solvents is, therefore, always required for those facilities that wish to recycle their spent solvents in-house, or offsite.

One of the disadvantages to solvent recycling through distillation is the still bottoms that remain after the solvent has been reclaimed. These still bottoms are usually composed of unrecovered solvents and any contaminants that soiled the solvent, including paints, stains, fillers, glazes, and nitrocellulose. The types and levels of constituents present in these still bottoms vary depending on production processes. These still bottoms must be managed as a hazardous waste and disposed of accordingly. In the United States, some solvent recyclers have discovered that it is more cost effective to send these wastes to RCRA-type facilities that practice fuel blending programs (e.g., to cement kilns and industrial boilers), rather than sending the resulting bottoms to commercial incinerators.

When a facility has determined that in-house recycling is not feasible, it may opt to send its spent solvents to outside recyclers for distillation. Most outside recyclers will reclaim spent solvents for approximately three-quarters the cost of virgin solvents. Two basic types of off-site or commercial solvent recycling are available: custom toll recycling and open market recycling.

In custom toll recycling, the generator's spent solvents are kept segregated, batch processed to the generator's specification, and then returned for reuse. The custom toll system reduces the chances of the recycled solvent being contaminated with substances foreign to the manufacturing process of the generator.

The second form of commercial reclamation is known as open market recycling, where the

spent solvents are co-mingled with like or similar wastes from many generators, and processed for resale and reuse in the marketplace as refined solvent. This option is available to virtually all generators of spent solvents, so long as the recycling facility offers the service (some companies specialize only in custom toll recycling), and there is a resale market for the refined product. One of the potential limitations to this type of recycling involves waste segregation. If a generator is using several different solvents in the various steps of its operation, and co-mingles the waste, it is likely that the refined solvent from the waste may be unsuitable for resale, leaving disposal as the only alternative.

The disadvantages of outside recycling are the transportation costs and the damages and cleanup liability associated with a possible spill. Also to be considered is the possibility of liability the generator may assume from any actions the recycler may take that lead to liability. One such problem of particular concern is the means of disposing of still bottoms, which may be classified as a hazardous waste.

1.4.4.4 Pretreatment of Waste Water

The only significant water-based waste stream associated with furniture manufacturing is that from the prefinishing operations of metal furniture. The wastewater stream that is generated during the preparation of the metal furniture must undergo pretreatment before discharge into the sewage system to protect public-owned treatment works (POTW) from the adverse impacts that may occur from hazardous or toxic wastes. Pretreatment is conducted to prevent interference with the POTW, "pass-through" of contaminants, and contamination of municipal sludges, and improve opportunities to recycle and reclaim industrial wastewaters and sludges.

The spent alkaline solution that may be discharged to the wastewater stream requires neutralization. Any salts that are precipitated during this neutralization step must be separated and, subsequently, dewatered. For more information regarding the treatment of this waste, refer to the Electroplating chapter.

Any hexavalent chromium that is present in the waste stream must be reduced to the trivalent

form before precipitation out of solution. The Electroplating chapter also presents a detailed discussion of the treatment technologies that are available to accomplish this reduction and removal.

Any other solids (e.g., oil, grease, particulates, etc.) that are present in the waste stream produced by these prefinishing processes can be removed through microfiltration (see Section 2.8.4 of the Electroplating chapter) and subsequently treated for disposal. Disposal options include stockpiling (temporary), incineration, or landfilling. Prior to disposal, wastes that are classified as hazardous may be encapsulated or stabilized by the addition of binders, as described in Section 2.8.

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APPENDIX A
CONTACTS

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CHAPTER 2
ELECTROPLATING PROCESSES

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CHAPTER 2

ELECTROPLATING PROCESSES

2.1 INDUSTRY DESCRIPTION

Electroplating operations are performed by many industries involved in forming and finishing metal products. Plating involves altering the surface properties of a metal in order to increase corrosion or abrasion resistance, alter appearance, or otherwise enhance the utility of the metal product. Plating operations are normally batch processes where metal objects to be coated (workpieces) are dipped into and then removed from baths containing various reagents for achieving the required surface condition. The workpieces may be transported through the process manually on racks or in barrels or automatically by conveying racks.

Most plating operations have three basic process steps: surface cleaning or preparation, surface modification, and workpiece rinsing and finishing. These sections are covered in detail below, followed by a discussion of pollution prevention opportunities, waste stream treatment and control technologies.

2.2 PROCESS DESCRIPTION

2.2.1 Surface Cleaning/Preparation

The preparation of a metal surface involves several stripping and cleaning operations which are inherent steps in industries involved with the manufacture of metal parts and equipment. Almost all fabricated metal products require some form of cleaning. Most machined parts are cleaned with solvents, while paint and old plating materials are stripped from workpieces using caustics and abrasives. During the plating process workpieces are cleaned several times using water, acids, caustics, and detergents.

Most industries performing plating operations use one of five types of cleaning media:

- solvents (halogenated and nonhalogenated)
- alkaline cleaners (aqueous cleaners)
- acid cleaners (aqueous cleaners)
- nonchemical, abrasive materials
- water

Other frequently used cleaning materials include mixtures of solvents and alkalines and mixtures of water-immiscible solvent emulsified in water (i.e., emulsions).

Cleaning methods depend upon three factors: the nature of surface contamination, the type of metal substrate, and the degree of cleanliness required. Cleaners, except for abrasives, are normally contained in large open tanks. The parts to be cleaned are mounted on racks or contained in perforated horizontal barrels.

2.2.1.1 Solvent Cleaning

Solvents, the most widely used class of cleaners, are used in removing oil-based contaminants, by either cold cleaning or vapor phase cleaning (vapor degreasing) methods. A third, less common cleaning method is dipphase cleaning.

2.2.1.1.1 Cold Cleaning

Cold cleaning is the simplest and least expensive method of solvent cleaning. As a result, it is also the most common. The solvents used in cold cleaning are usually at room temperature although they may be slightly heated, and always remain well below the solvent's boiling point.

Cold cleaning solvents account for almost all of the aliphatic, aromatic, and oxygenated degreasing solvents and about one-third of halogenated degreasing solvents. The average cold cleaning unit generally emits only about one-third ton per year of organics, with about one half to three-fourths of that emission resulting from evaporation of the waste solvent at a disposal site.

The four types of cold cleaning are wipe cleaning, soak cleaning, ultrasonic cleaning, and steam gun cleaning. A typical cold cleaner is illustrated in Exhibit 2-1.

2.2.1.1.2 Vapor Degreasing

The vapor degreasing process cleans parts through the condensation of hot solvent vapors on colder metal parts. The cleaning cycle involves lowering parts into the vapor zone (i.e., the vaporous area above the boiling solvent). The condensing solvent dissolves surface contaminating oils and provides a washing action to clean the parts. After condensation ceases, the parts are slowly withdrawn from the degreaser. The residual liquid solvent on the parts quickly evaporates as the parts leave the vapor zone. The cleaning action may be increased by spraying the parts with solvent or by immersing them into the liquid solvent bath.

The solvents selected for vapor degreasing boil at much lower temperatures than do the contaminants, thus the solvent/soil mixture in the degreaser boils to produce an essentially pure solvent vapor. Most vapor degreasers are batch loaded, cleaning only one work load at a time. A typical vapor degreaser is illustrated in Exhibit 2-2.

2.2.1.1.3 Dipphase System

Dipphase systems use both water and solvent for cleaning purposes. The parts to be cleaned pass through a water bath prior to passing through a solvent spray.

Exhibit 2-1
Typical Cold Cleaner

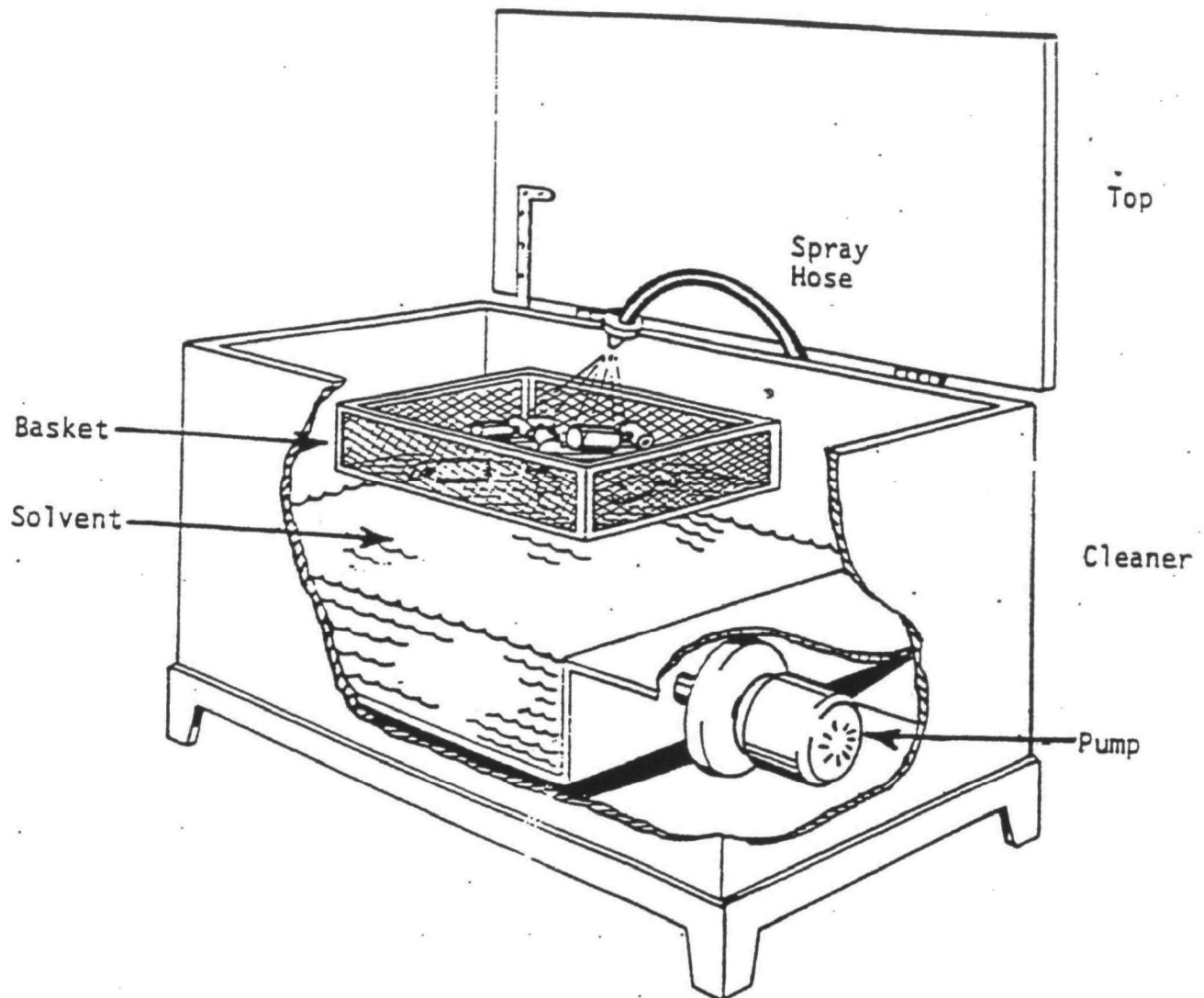
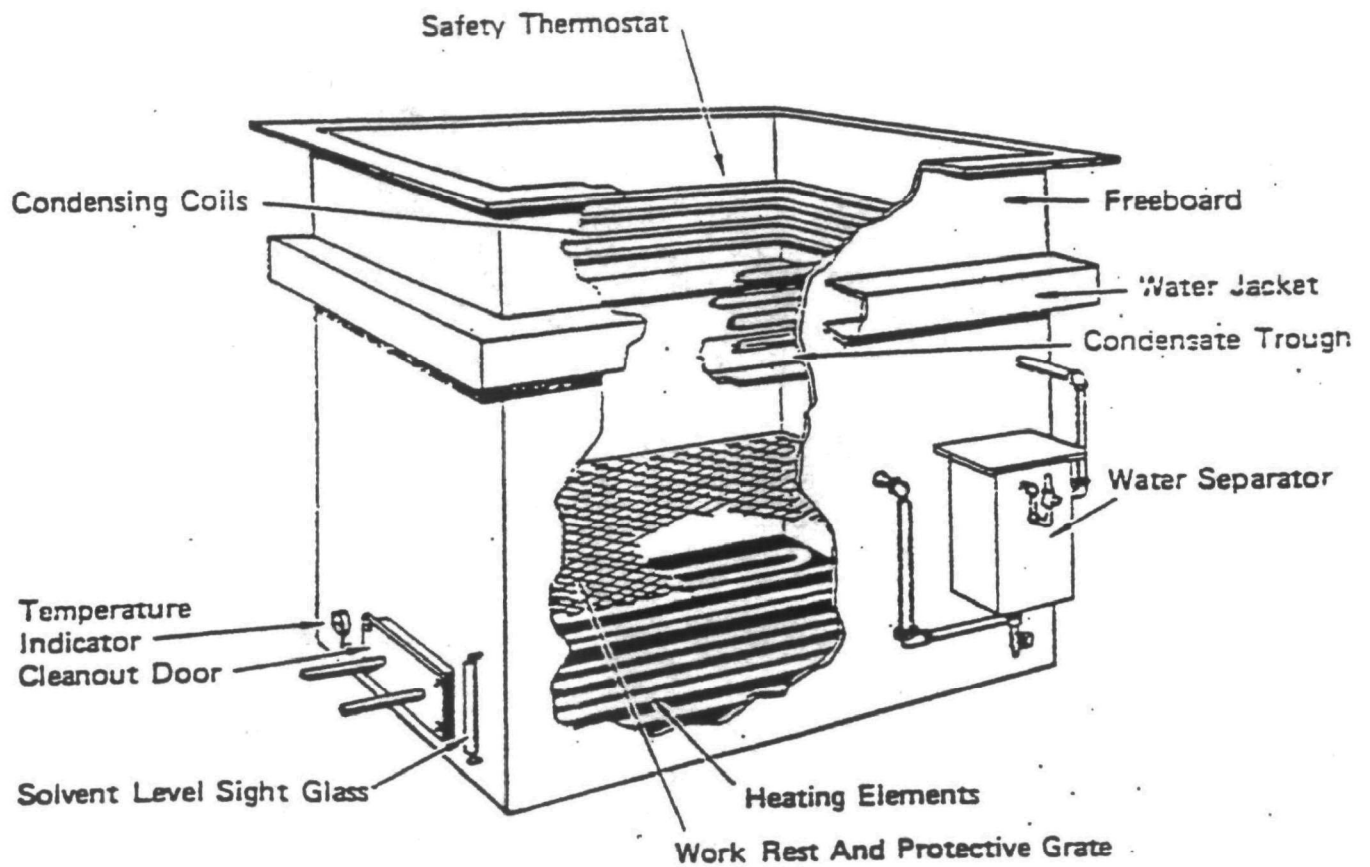


Exhibit 2-2

Typical Open Top Degreaser



2.2.1.2 Aqueous (Acid and Alkaline) Cleaning

Alkaline and acid cleaning are both accomplished using soak tanks similar to those used with solvent cleaning. Aqueous cleaning serves to displace soils from metal surfaces rather than dissolve them as is the case with solvent cleaners. Alkaline solutions contain builders (sodium salts of phosphates, carbonates, silicates, and hydroxides) and surfactants (detergents and soaps) and are used to remove soil as well as old plating and paint. Acidic cleaning solutions may contain mineral acids (nitric, sulfuric, and hydrochloric), organic acids (sulfamic, acetic, oxalic, or cresylic), detergents, and chelating agents. Acid cleaners are used to remove rust scale and smut from metal parts. The chelating agents reduce the chemical activity of metal ions while increasing their solubility, thus allowing more ions to be held in suspension in a process bath.

2.2.1.3 Abrasive Cleaning

Abrasive cleaners are designed for creating smooth surfaces and for removing rust, oxides and burrs, and old plating and paint. Typical abrasives are aluminum oxide or silicon carbide mixed with an oil or water based binder. This abrasive-binder mixture is applied to a buffing wheel made from an absorbent material such as cloth. The metal part is held against the spinning wheel until surface contamination is eliminated.

Other methods of abrasive cleaning involve blasting the part with either sand, plastic media, or in some cases, crystallized sodium bicarbonate.

2.2.2 Surface Modifications (Electroplating Processes)

Electroplating is achieved by passing an electric current through a solution containing dissolved metal ions and the object to be plated. The metal object acts as a cathode in an electrochemical cell and attracts metal ions from the solution. Ferrous and nonferrous metal objects are typically electroplated with aluminum, brass, bronze, cadmium, chromium, copper, iron, lead, nickel, tin, or zinc. Precious metals such as gold, platinum, and silver are also used to plate ferrous and nonferrous pieces. A typical electroplating process involves cleaning, stripping of old plating or paint, electroplating, and rinsing between each of the previously mentioned steps. Several common electroplating materials are discussed in the following sections.

2.2.2.1 Cyanide Plating

There are many electroplating baths which contain cyanide as a component. The most common are listed in Exhibit 2-3.

During the electroplating process cyanide dissociates from its metal ion. The metal ion is attracted to the workpiece, while the cyanide is released in the waste stream. In some facilities, the cyanide-containing plating solution is filtered continuously to ensure that the plating baths remain free of the solids that form during the plating operation.

EXHIBIT 2-3. ELECTROPLATING BATHS CONTAINING CYANIDE

Electroplating Bath Name	Composition
Cadmium Cyanide	Cadmium Cyanide Sodium Cyanide
Copper Cyanide	Copper Cyanide Sodium Cyanide
Fluoride-Modified Copper Cyanide	Copper Cyanide Potassium Cyanide

A general process flow diagram for cyanide plating is depicted in Exhibit 2-4. This diagram also represents the typical process flow for most plating operations.

2.2.2 Chromium Plating

There are two types of chromium electroplating: hard, in which a relatively thick layer of chromium is deposited directly on the base metal (usually steel) and decorative, in which the base material is plated with a layer of nickel prior to the addition of a relatively thin layer of chromium. The industrial or hard chromium coating processes have desirable engineering properties such as heat, wear, corrosion, and erosion resistance and a low coefficient of friction. Some of the uses of hard and decorative chromium plating processes are listed in Exhibit 2-5.

Chromic acid anodizing, a second electroplating operation, consists of the immersion of the base metal, usually aluminum, in a chromic acid solution. Electricity is applied to produce a film of chromium deposit on the base metal. The uses of chromic acid anodizing include aircraft parts and architectural structures that are subject to high stress and corrosion.

Chromium coatings are deposited mainly from a highly toxic, chromic acid solution containing chromic acid, sulfuric acid, and sometimes a fluoride catalyst.

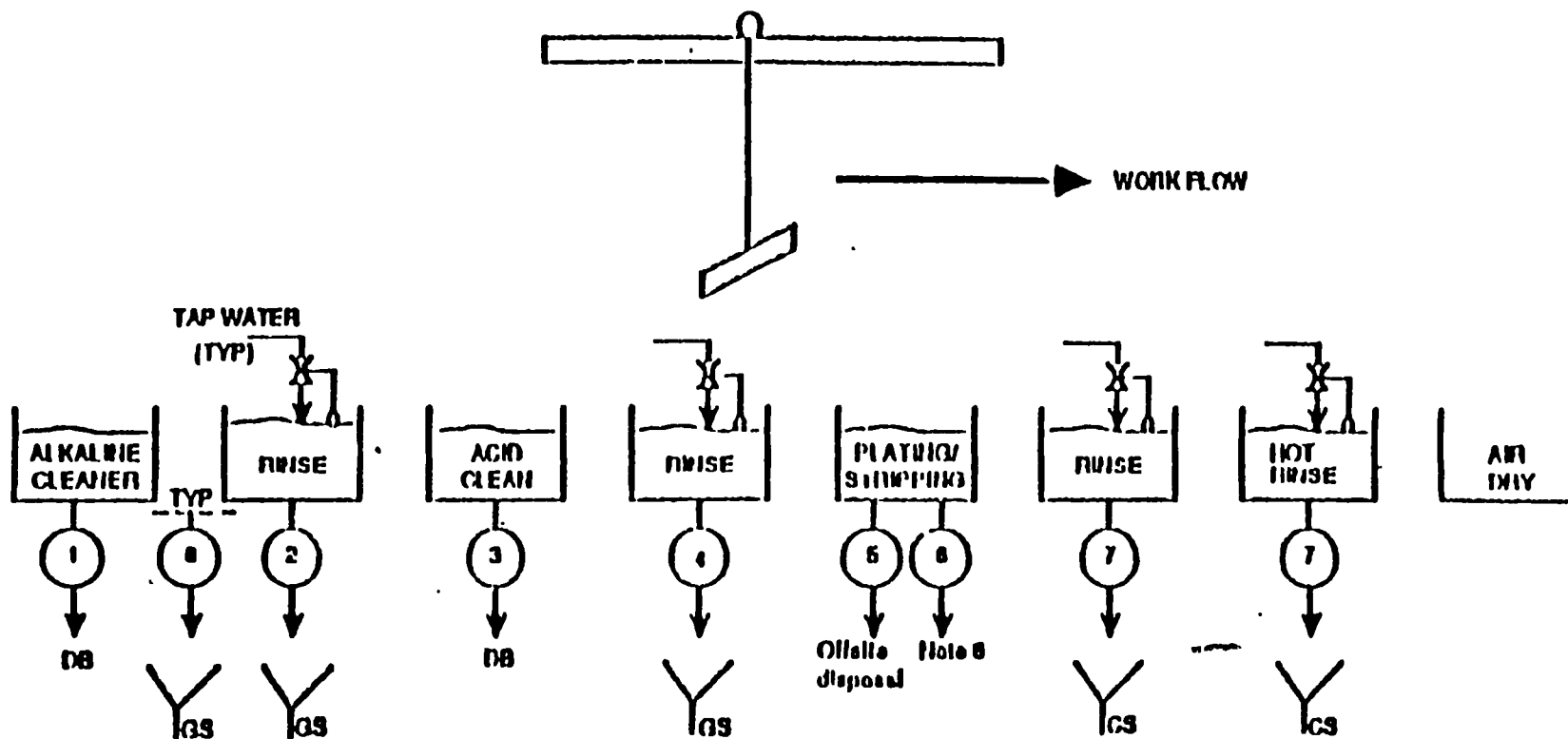
2.2.3 Workpiece Rinsing and Finishing Operations

2.2.3.1 Water Rinsing

Water cleaning and rinsing is an integral part of every parts cleaning process. Most of the cleaning operations previously mentioned require a water rinse before and after each operation. Water washing is normally done in a soak tank or with a spray unit. Some soak tanks are equipped with air or mechanical agitation devices which enhance the effectiveness of the rinsing operations. The agitation is done either by spraying compressed air at the bottom of the tank or by mechanical propellers.

Overflow from rinse tanks may be routed to a specific sump (i.e., a cyanide sump in rinse tanks associated with cyanide plating) or to a general waste sump. The flow of make-up water into the plating or stripping baths may be level-controlled which allows the water to be continually replenished.

Typically the last rinse step in a plating sequence is done with a warm water bath 50-60°C (120 to 140°F) to thoroughly clean the plated parts and to facilitate subsequent drying operations.



Notes: 1. Chemical make up streams are not shown

2. CS - Cyanide Sump

3. GS - General Waste Sump

4. TYP - Typical

5. DB - Dry basin at WWT

6. Replacement of spent plating solutions is not currently required. Spent silver stripping solutions are sent to an offsite waste treatment facility for silver reclamation.

(1) Spent alkaline solution

(2) Alkaline rinsewater

(3) Spent acid solution

(4) Acidic rinsewater

(5) Filter waste

(6) Spent plating/stripping solution

(7) Cyanide containing rinsewater

(8) Spills

Exhibit 2-4. Electroplating Operation and Associated Waste Streams

EXHIBIT 2-5. HARD AND DECORATIVE CHROMIUM PLATING USES

Hard Electroplating Uses	Decorative Electroplating Uses
Engine Components	Automotive Trim
Marine Hardware	Metal Furniture
Plastic Molds	Bicycles
Zinc Die Castings	Hand Tools
Industrial Rolls	Plumbing Fixtures
Hydraulic Cylinders and Rods	

2.2.3.2 Machining

Machining processes use cutting tools that shear metal from the surface of the workpiece. Much of the power consumed in cutting is transformed into heat. Most of this heat is carried away by the sheared metal chips while the rest is split between the tool and the workpiece. Temperatures at the tool to workpiece surface interface may reach 93°C (200°F).

Machining operations involve a variety of metal cutting processes including turning, drilling, milling, reaming, threading, broaching, grinding, polishing, planing, and cutting and shaping. Many turning and some drilling processes are completed on lathes which hold and spin the workpiece against the edge of the cutting tool. Drilling tools are used both for making holes and for enlarging existing holes (reaming). Milling involves cutting unusual or irregular shapes into the workpiece. Broaching is the finishing of internal holes with a machine called a broach.

Machining operations also involve applying metalworking fluids to the workpiece and cutting tool in order to facilitate the cutting process. These fluids act as lubricating, cooling, finishing, and rinsing materials. They may be water (with or without an alkali), emulsions of a soluble oil or paste, or oils (e.g., mineral, sulphurized, or chlorinated).

2.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS AND WASTE STREAMS

All of the processes associated with plating operations have specific waste streams and emission points. Most of the sources of air emissions occur during metal cleaning and surface preparation operations. These emissions consist of organic vapors from solvent cleaners and acid and alkali fumes from aqueous cleaning materials. In addition, particulates are released during finishing and machining operations.

2.3.1 Surface Cleaning and Preparation

The primary waste streams associated with surface cleaning of metal parts are summarized in Exhibit 2-6 and include abrasives, solvents, alkalines, acids, and rinse water. The specific composition of these streams depends on the cleaning media used, the type of substrate, and the type of surface contaminant removed (e.g., oils, greases, waxes, metal particles, or oxides).

Cleaning solutions may be acidic or basic and may or may not contain organics. Normally, significant levels of heavy metals are not present, although some aqueous cleaning streams may contain cyanide. The pollutants expected from the acid/alkaline cleaning waste stream might be as follows:

Copper	3 mg/l
Nickel	3 mg/l
Zinc	3 mg/l
Lead	3 mg/l
Iron	36 mg/l

Another waste stream from cleaning processes is stripping waste which results from the stripping off of old plated material.

Rinse water waste streams are often combined with acid and alkaline cleaning solutions (which tend to neutralize each other) and treated at wastewater treatment facilities. If a facility employs blasting, the rinse water may be contaminated with sand, sodium bicarbonate, or plastic pellets.

2.3.1.1 Emissions from Cold Cleaners

The sources of solvent emissions from cold cleaners include bath evaporation, solvent carry-out, agitation, waste solvent evaporation, and spray evaporation. These are depicted in Exhibit 2-7. Solvent emissions are estimated to be approximately 0.3 metric tons (.33 tons) per year with a range from 0.17 to 0.5 metric tons (.19 to .55 tons) per year.

2.3.1.2 Emissions from Vapor Degreasers

Most of the emissions resulting from vapor degreasing operations are those vapors that diffuse out of the degreaser. Unlike the cold cleaners, vapor degreasers do not lose much solvent through waste solvent evaporation or liquid carry-out. The average open top vapor degreaser emits about 2.5 kilograms (5.5 lbs) per hour per meter² of opening. Assuming an open surface area of 1.67 m² (18 ft²), a typical emission rate from a vapor degreaser would be 4.2 kilograms (9.25 lbs) per hour or 9,500 kilograms (20,950 lbs) per year. Emissions from a vapor degreaser are illustrated in Exhibit 2-8.

2.3.2 Surface Modification

Some of the common waste streams from surface modification processes are noted in Exhibit 2-9 and described in more detail in the following sections. The exact composition of the process wastes will depend on the specific plating process and the removed surface contaminant. In certain cases, specific process waste streams, such as concentrated cyanide wastes and filter sludges, may be combined.

Both spent alkaline cleaning solutions and spent acid cleaning solutions are generated by the periodic replacement of contaminated process solutions. Rinse waters are generated from overflow of rinse tanks and contamination by drag-out from cleaning baths. The waste removed from plating tanks by the continuous filtering of the baths results in filter sludges.

2.3.2.1 Metal Baths and Rinses

Most spent plating solutions contain high concentrations of metals. Because of this, the plating solutions are not as easily disposed of or treated as are cleaning solutions. As impurities build, the bath is purged. Wastewaters resulting from electroplating processes also contain a variety of heavy metals and cyanide.

EXHIBIT 2-6. METAL PARTS CLEANING WASTES

No.	Waste Description	Process Origin	Composition
1	Abrasive	Removal of rust, scale polishing of metal	Aluminum oxide, silica metal, water, grease
2	Solvents	Removal of oil-based soils	Halogenated and non- halogenated solvents, oil- based contaminants
3	Alkalines	Removal of organic soils, descaling	Alkaline salts, additives, organic
4	Acids	Removal of scale, smut	Acids, additives, dissolved metal salt, water
5	Rinse water	Removal of previous	Water with traces of cleaners and cleaning material additives

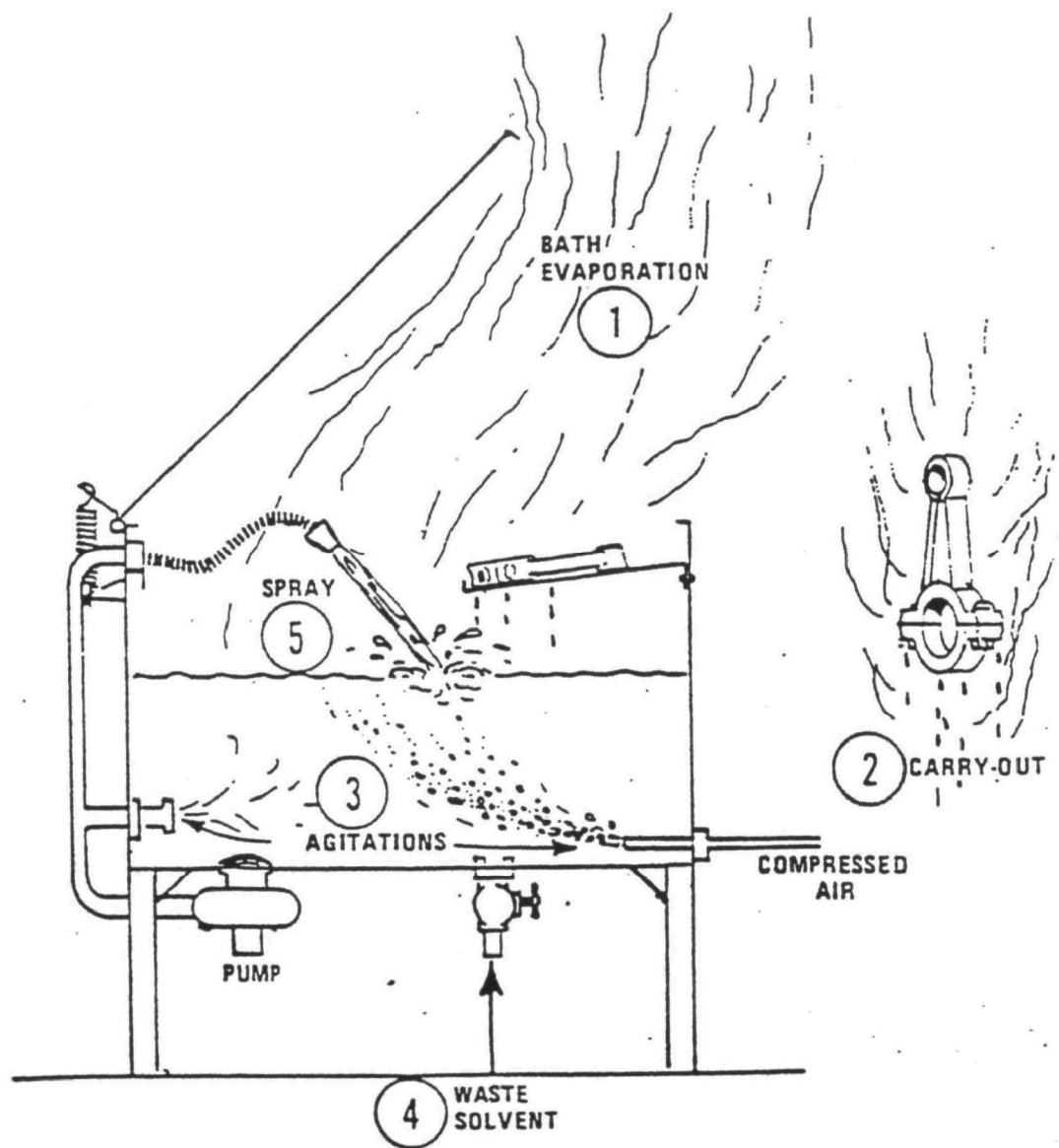


Exhibit 2-7. Cold Cleaner Emission Points

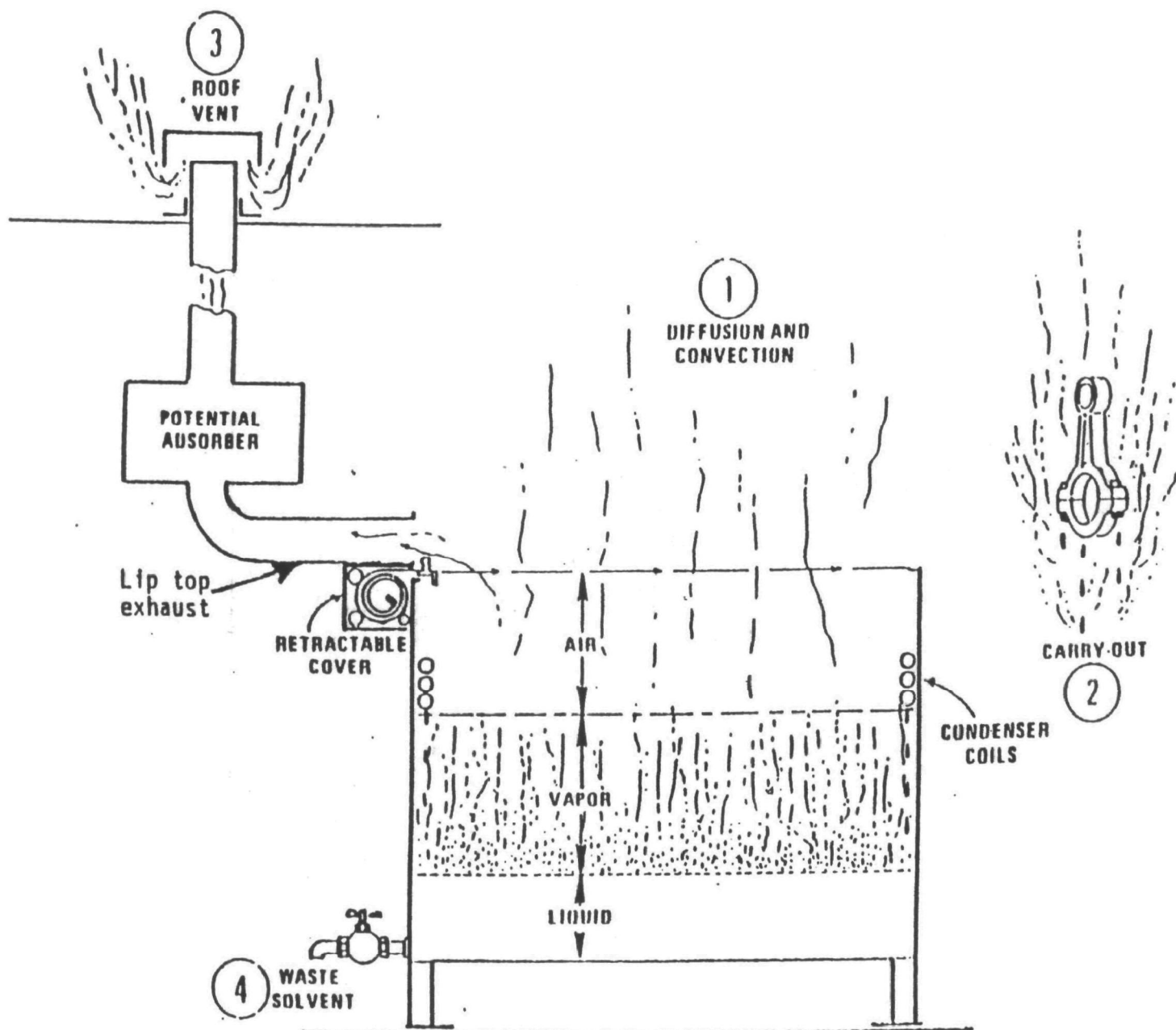


Exhibit 2-8. Open Top Degreaser Emission Points

EXHIBIT 2-9. PROCESS WASTES

Waste Description	Process Origin	Composition
Spent process solutions	Plating and chemical conversion	Specific to the process solution
Filter sludges	Plating and chemical conversion	Silica, silicides, carbides, ash plating bath constituents
Quench oils and quench oil tank cleanup wastes	Case hardening	Oils, metal fines, combustion products
Spent salt bath	Carburizing, nitrating, cyaniding	Sodium cyanide and cyanate. Potassium cyanide and cyanate.
Wastewater treatment sludge	Wastewater treatment	Metal hydroxides, sulfides, carbonates
Vent scrubber wastes	Vent scrubbing	Similar to process solution composition
Ion exchange resin reagents	Demineralization of process water	Brine, HCl, NaOH

For example, in a chromium plating operation, the rinse water stream might contain the following contaminants:

Chromium(6+)	12 mg/l
Chromium(total)	18 mg/l
Copper	3 mg/l
Nickel	3 mg/l
Iron	36 mg/l

The level of chromium could be significantly higher if multiple rinse streams are utilized. The chromium 6+ ion is particularly hazardous and must be reduced to the 3+ ion.

2.3.2.2 *Wastewaters from Spills*

Wastes produced from spills and leaks are usually present to some extent in an electroplating process. Water is used to wash away floor spills resulting from tank leakage, from accidental overflow of the plating/stripping tanks, and from the dripping of solutions from parts during their transfer between tanks. The resulting wastewater contains all of the contaminants present in the original plating or cleaning solutions.

2.3.2.3 *Metal Cyanides*

The primary sources of cyanide waste come from operations associated with cadmium, copper, and silver plating and stripping. These waste streams normally occur from the overflow of associated rinse tanks.

For metal plating involving cyanide eg:cadmium, zinc or copper, the rinse water stream would contain the metal contaminant and cyanide:

Metal	20 mg/l
Cyanide	25 mg/l

2.3.2.4 *Chromic Acids*

Emissions of chromic acid mist occur due to the inefficiency of the chromium plating process. Only about ten to twenty percent of the electric current applied to the solution is actually used in the deposition of the chromium on the item. The vast majority of the electric current is consumed in the evolution of hydrogen gas, with the resultant liberation of gas bubbles, which burst at the surface of the plating solution, forming a fine mist of chromic acid droplets.

2.3.2.5 *Tank Dumpings*

Once a plating solution is spent, the process tank is often emptied or "dumped." The chemical bath dumps containing heavy metals and sludges are another source of hazardous waste.

2.3.2.6 Rinse Waters

Contaminated rinsewater accounts for the majority of plating process waste as numerous rinsing steps occur during the plating operations. Rinse water is used to wash off the drag-out or excess solution that remains on the workpiece surface after the workpiece is removed from the plating bath. Typically, more drag-out results from plating pieces in perforated barrels than from rack plating. Drag-out that is carried into the next process bath is treated as a contaminant and is referred to as drag-in.

2.3.3 Workpiece Rinsing and Finishing Operations

Like the electroplating rinse waters, the rinse water generated during the finishing operations contains heavy metals and cyanides.

2.4 SOLVENT AIR EMISSIONS - POLLUTION PREVENTION, WASTE TREATMENT AND CONTROL SYSTEMS

2.4.1 Solvent Stills

The installation of solvent stills allows manufacturers to lengthen the life of cleaning solvents and to reduce the purchase of virgin solvent by implementing in-house recycling. Stills consist of a boiling chamber, a condenser, a reclaim container, and a ventilation device. Spent solvent is pumped or poured into the boiling chamber where it is boiled. Vapors form and pass through the vapor tube into a water-cooled condenser. The vapors are condensed into a liquid state and flow into a container or drum. When a visual check through a sight glass indicates that no additional distillate is available, the unit is allowed to cool. Once cool, the material remaining in the boiling chamber is removed and disposed of as hazardous waste.

2.4.2 Reducing Emissions from Solvent Cleaning Operations

Solvent cleaning operations are the primary source of volatile organic compound (VOC) air emissions. The five main devices which are used to reduce these emissions include covering the still, increasing the freeboard height, installing refrigerated chillers, using safety switches, and using carbon adsorbers.

2.4.2.1 Covers

Covers are the most important control device for open top degreasers. Although most degreasers already have covers, they can be more effectively and frequently used if they are automated or assisted by mechanical devices.

For vapor degreasers, the cover should open and close in a horizontal motion so that the air/vapor interface disturbance is minimized. These types of covers include rolled plastic covers, canvas curtains and guillotine covers.

The covers on cold cleaners are often mechanically assisted by means of spring loading or counterweighing. In certain applications, submerged and water covers may be used. The submerged cover is a horizontal sheet of material which is submerged approximately two inches below the surface of a liquid solvent that is vigorously pump agitated. The water cover is a layer of water between two and four inches thick over a halogenated solvent. Water covers cannot be used in applications where the water would corrode the metal surface of the parts to be cleaned or where it would degrade the solvent.

Covers are also used to control acid and alkali fumes resulting from aqueous cleaning processes.

2.4.2.2 Freeboard Height

The freeboard reduces the drafts near the air/solvent interface. An acceptable freeboard height is normally determined by the freeboard ratio, the freeboard height divided by the width (not length) of the degreaser's air/solvent area. The freeboard ratio is normally 0.5 to 0.6 for the open-top vapor degreasers, except for very volatile solvents where a minimum freeboard ratio of 0.75 is used. Increasing the freeboard ratio from 0.5 to 0.75 often reduces emissions by 25 to 30 percent, while increasing the freeboard ratio from 0.5 to 1.0 may result in a 50 percent reduction in emissions. The freeboard height does not have much effect on cold cleaners using low volatilizing solvents, but it does benefit cold cleaners using higher volatility solvents.

2.4.2.3 Refrigerated Chillers

Condenser coils and a freeboard water jacket can help prevent solvent vapors in a vapor degreaser from overflowing. These primary condenser coils control the upper limit of the vapor zone. The addition of refrigerated freeboard chillers above the primary condenser coils impede the diffusion of solvent vapors from the vapor zone into the work atmosphere by chilling the air immediately above the vapor zone and creating a cold air blanket. The blanket of cold air results in a sharper temperature gradient which reduces the mixing of air and solvent by narrowing the air/vapor mixing zone. The chilling also produces a stable inversion layer which decreases the upward convection of solvent laden air.

Another type of refrigerated chiller is the refrigerated condenser coil which replaces the primary condenser coils. If the coolant circulating through the condenser coils is refrigerated enough, it will create a layer of cold air above the air/vapor interface. These coils are normally used only on small open-top vapor degreasers.

2.4.2.4 Safety Switches

Safety switches are devices used on vapor degreasers to prevent emissions during malfunctions and abnormal operation. The five main types of safety switches are as follows:

- Vapor level control thermostat
- Condenser water flow switch and thermostat

- Sump thermostat
- Solvent level control
- Spray safety switch

The first four safety switches turn off the sump heat while the fifth turns off the spray.

The most important safety switch is the vapor level control thermostat. This device is activated when solvent vapor rises above the designated operating level. If the coolant flow is interrupted and hot vapors are sensed, the sump heater is turned off thereby minimizing vapor escape. The condenser water flow switch and thermostat turn off the sump heat when either the condenser water stops circulating or the condenser water becomes warmer than specified. The sump thermostat and the solvent level control prevent the sump from becoming too hot resulting in solvent decomposition. Although the safety spray switch is not used as often as the other devices, it can also help to control solvent vapors. When the vapor level drops below a specified level, the pump for the spray equipment will shut off until the normal level is attained.

2.4.2.5 Carbon Adsorbers

Carbon adsorbers are widely used to capture solvent emissions from metal cleaning operations. A typical adsorber is illustrated in Exhibit 2-10. When applied correctly to solvent cleaning processes, adsorbers can achieve high levels of emission control capturing in excess of 95 percent of the organic material input to the system and reducing total emissions by 40 to 65 percent. The actual and theoretical emission values differ because the ventilation equipment in the adsorber cannot capture all of the solvent vapors and deliver them to the adsorption bed. Solvent vapors occurring from parts drag-out, leaks, spills, and waste solvent disposal, are not significantly affected by a ventilation system. The effectiveness of the ventilation system (and the effectiveness of the adsorber) can be improved by improving ventilation design and by using drying tunnels or other devices to decrease the solvent losses due to drag-out. Additional methods of reducing drag-out are discussed in Section 2.6.4.

In the carbon adsorption process, solvent emission streams are passed through a bed of activated carbon in which the VOC molecules are captured on the porous carbon surfaces by non-chemical Van der Waals forces. The adsorptive capacity of the carbon bed tends to increase with the gas phase VOC concentration, molecular weight, diffusivity, polarity, and boiling point of the solvent. After the working solvent capacity of the carbon is reached, the VOC can be desorbed from the carbon and collected for reuse. The adsorption and desorption cycles are illustrated in Exhibits 2-11 and 2-12.

Desorption of the VOC from the used carbon bed is typically achieved by passing low-pressure steam through the bed. In the regeneration cycle, heat from the steam forces the VOC to desorb from the carbon where it is entrained in the steam. After the carbon bed has been sufficiently cleared of VOC, it is cooled and replaced on line with the emission stream. Meanwhile, the VOC-laden steam is condensed, and the VOC is separated from the water by decanting or, if necessary, by distillation.

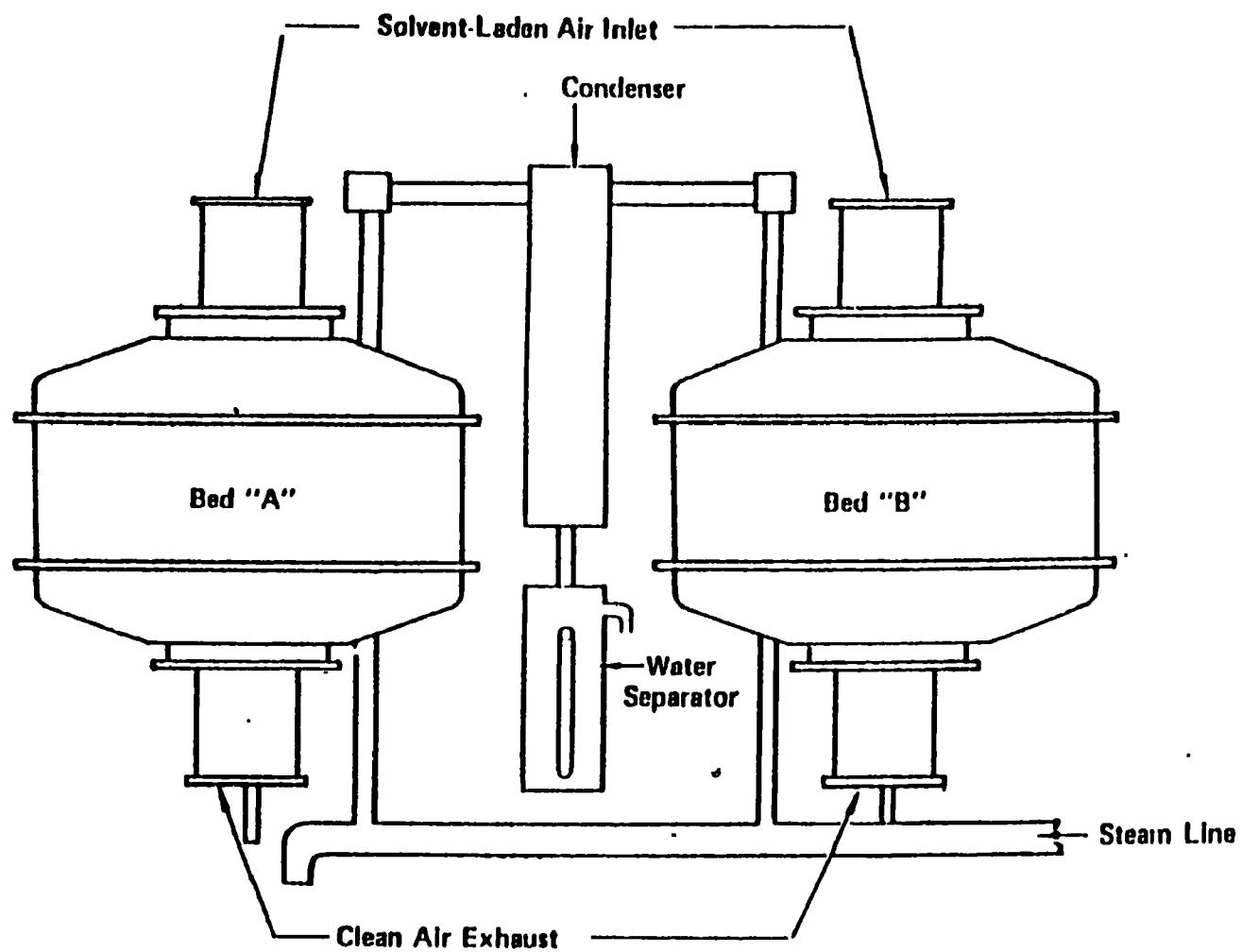


Exhibit 2-10. Carbon Adsorber

Exhibit 2-11. Adsorption Cycle

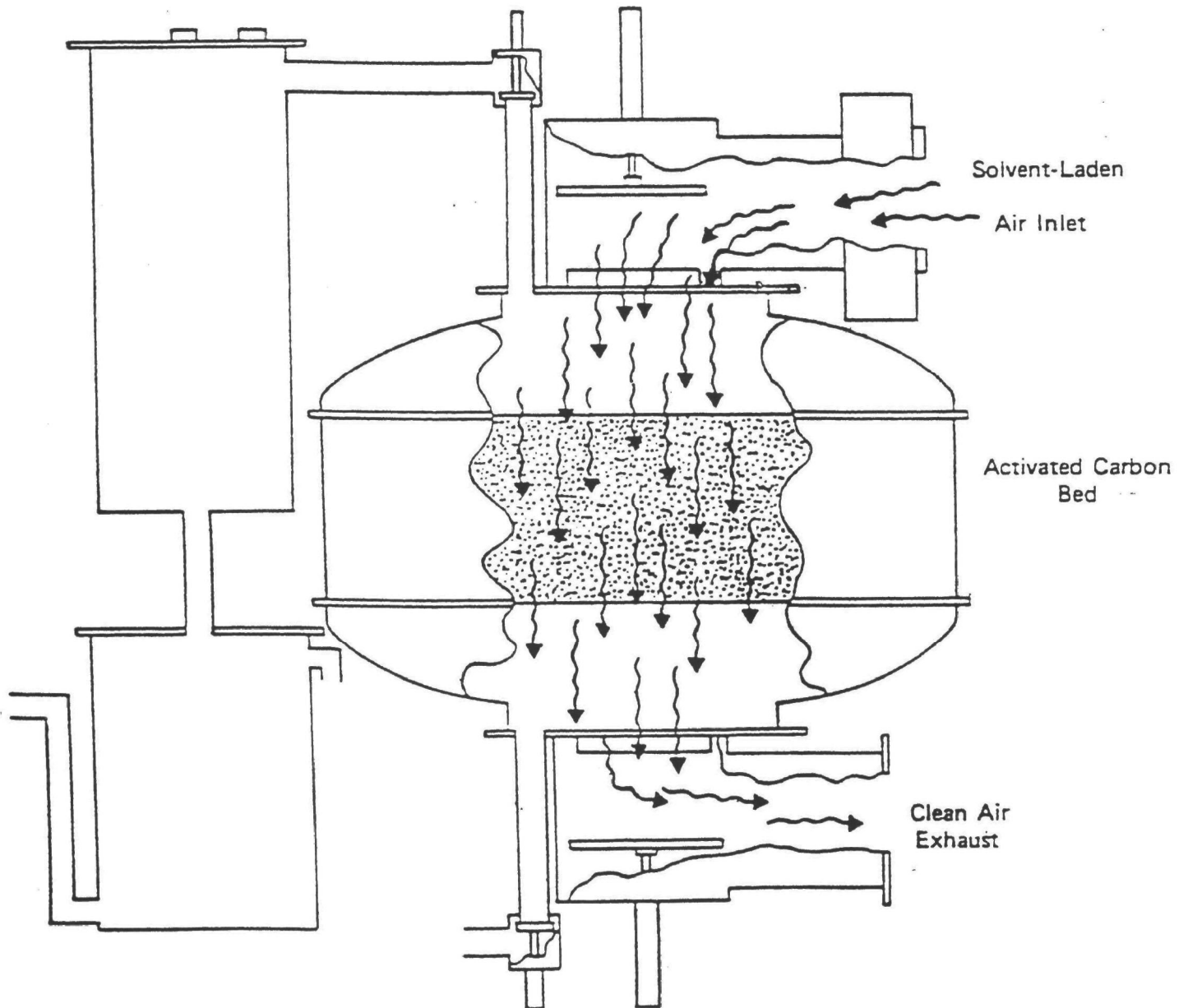
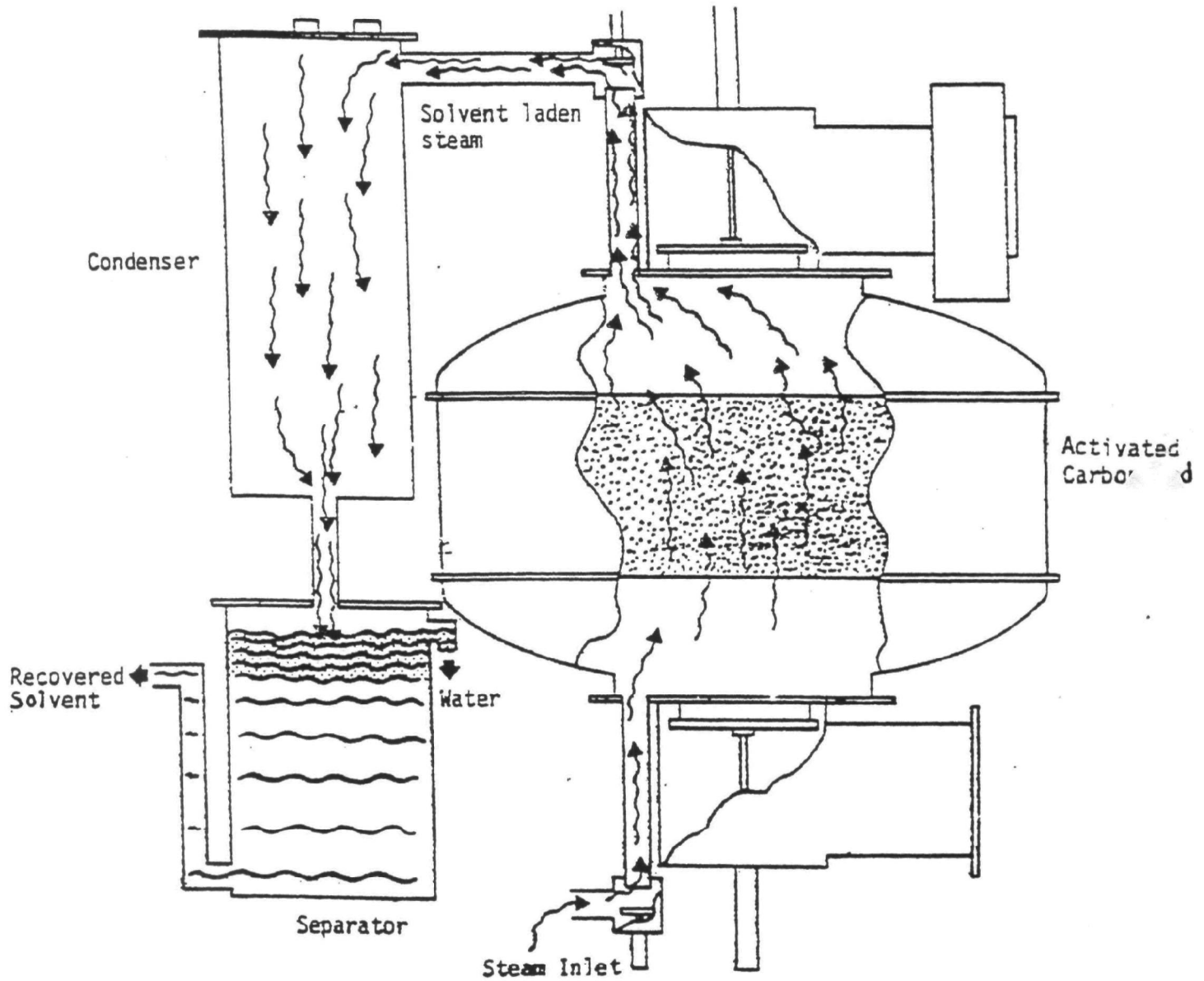


Exhibit 2-12. Desorption Cycle



The principal advantage of carbon adsorption is that it is very cost effective with low concentrations of VOCs. VOC recovery offsets operation costs, and operation of the adsorber is relatively simple for both continuous and intermittent use.

Certain types of VOCs such as those which are difficult to strip from carbon or those which are miscible with water may not be candidates for carbon adsorption. If the VOC involved is miscible with water, additional distillation measures are necessary to recover the VOC. If steam-stripping is conducted with chlorinated hydrocarbons, corrosion and wastewater treatment problems may occur. Also, carbon adsorption is relatively sensitive to emission stream humidity and temperature. Dehumidification is necessary if the emission stream has a high humidity (relative humidity > 50 percent) and cooling may be required if the emission stream temperature exceeds 49-54 degrees C (120-130 degrees F).

Two commonly used adsorption systems are the fixed-bed system and the fluidized-bed system. In the fixed-bed system, non-moving beds of carbon are alternately placed on-line and regenerated. In the fluidized-bed system, loose, clean carbon is constantly metered into the bed while loose, VOC-laden carbon is removed for regeneration.

Fixed-Bed Systems. In a continually operating fixed-bed system, the VOC emission stream is passed through two or more non-mobile carbon beds. In a two-bed system, one bed is on-line with the emission stream while the other bed is being regenerated or on standby. When the first bed reaches its working VOC capacity, the emission stream is redirected to the second bed, and the first bed is regenerated. While two beds are common, three or more beds can be used in a variety of configurations, with more than one bed on-line at a time.

Fluidized-Bed Systems. The fluidized-bed adsorber system contains one or more beds of loose, beaded activated carbon. The VOC emission stream is directed upward through the bed where the VOCs are adsorbed onto the carbon. The flow of the emission stream stirs the carbon beads causing it to "fluidize" and flow within the adsorber. The VOC-cleaned air exiting the adsorber is passed through a dust collector and then released into the atmosphere. Fresh carbon is continually metered into the bed while VOC-laden carbon is removed for regeneration.

Fluidized-bed adsorbers can capture more VOC with a given quantity of carbon because the fluidized bed mixes newly regenerated carbon and VOC more thoroughly, and because the system continually replaces used carbon with regenerated carbon. This increased VOC-capacity reduces costs for steam regeneration.

2.5 WATER BASED POLLUTION PREVENTION AND WASTE TREATMENT

There are numerous methods to reduce water based of pollution. The following methods have been discussed:

2.5.1 Good Housekeeping

2.5.2 Reducing Water Usage

2.5.3 Alternative Sources of Materials

2.5.4 Reducing Drag-out
2.5.5 Metal Recovery
2.5.6 Plating Bath Regeneration

2.5.1 Good Housekeeping

The following housekeeping practices are generally easy to implement for any manufacturer and require little or no capital investment:

- Repair all leaking tanks, pumps, valves, et.
- Inspect tank and tank liners on a regular basis to prevent liner failures that may result in bath dumps.
- Inspect steam coils and heat exchangers on a regular basis to prevent accidental contamination of steam condensate and cooling water or leakage of condensate and cooling water into the plating bath. Inspecting coils for scale buildup is also important.
- Install high-level alarms on all plating and rinse tanks to avoid accidental bath overflows.
- Maintain plating rocks and anodes to prevent contamination of baths. Remove racks and anodes from baths when not in use.
- Minimize the volume of water used during cleanup operations.
- Properly train plating personnel so that they understand the importance of minimizing bath contamination and waste generation, and preventing spills.
- Properly clean and rinse parts prior to plating to minimize contamination of the plating bath. Areas that are not to be plated should be masked or stopped off with tape and wax to limit corrosion from these areas. Parts should be removed from the bath at the optimum time.

2.5.2 Reducing Water Usage

Reducing water usage can be accomplished by various process changes or additional control devices such as

- multiple rinse tanks
- surface evaporation
- conductivity cells
- flow regulators
- water re-use
- spray rinse

2.5.2.1 Multiple Rinse Tanks - see process Exhibit 2-13

2.5.2.1.1 Counter Current Flow

In a counter current system, the parts pass through the rinse tanks in a direction counter to the flow of rinse water. Fresh water is fed into the final rinse tank to ensure the parts are properly cleaned. The water then passes through the other tanks and progressively becomes more concentrated with the contaminants. The volume of water required to obtain the same concentration of contaminants in the final rinse as would be achieved using only one rinse tank can be reduced by up to 99 percent using this simple process.

advantage: may reduce water usage by 99 percent

2.5.2.1.2 Parallel Flow

Fresh water is introduced to each rinse tank and the overflow is discharged to waste. This flow system also significantly reduces the volume of water required although not to the extent of counter current flow.

2.5.2.2 Surface Evaporation

Evaporation from the plating tank means that continual topping off is required. A standard (2.8 sq m (30 square feet)) surface area tank could expect to lose 18.9 liters/hour (5 gallons/hour) through evaporation operating at a temperature of 65°C (150° F). Agitation of the tank contents can double evaporation rates. Likewise, temperature increases from (27° to 71° C (80° to 160° F) will increase evaporation by a factor of 10.

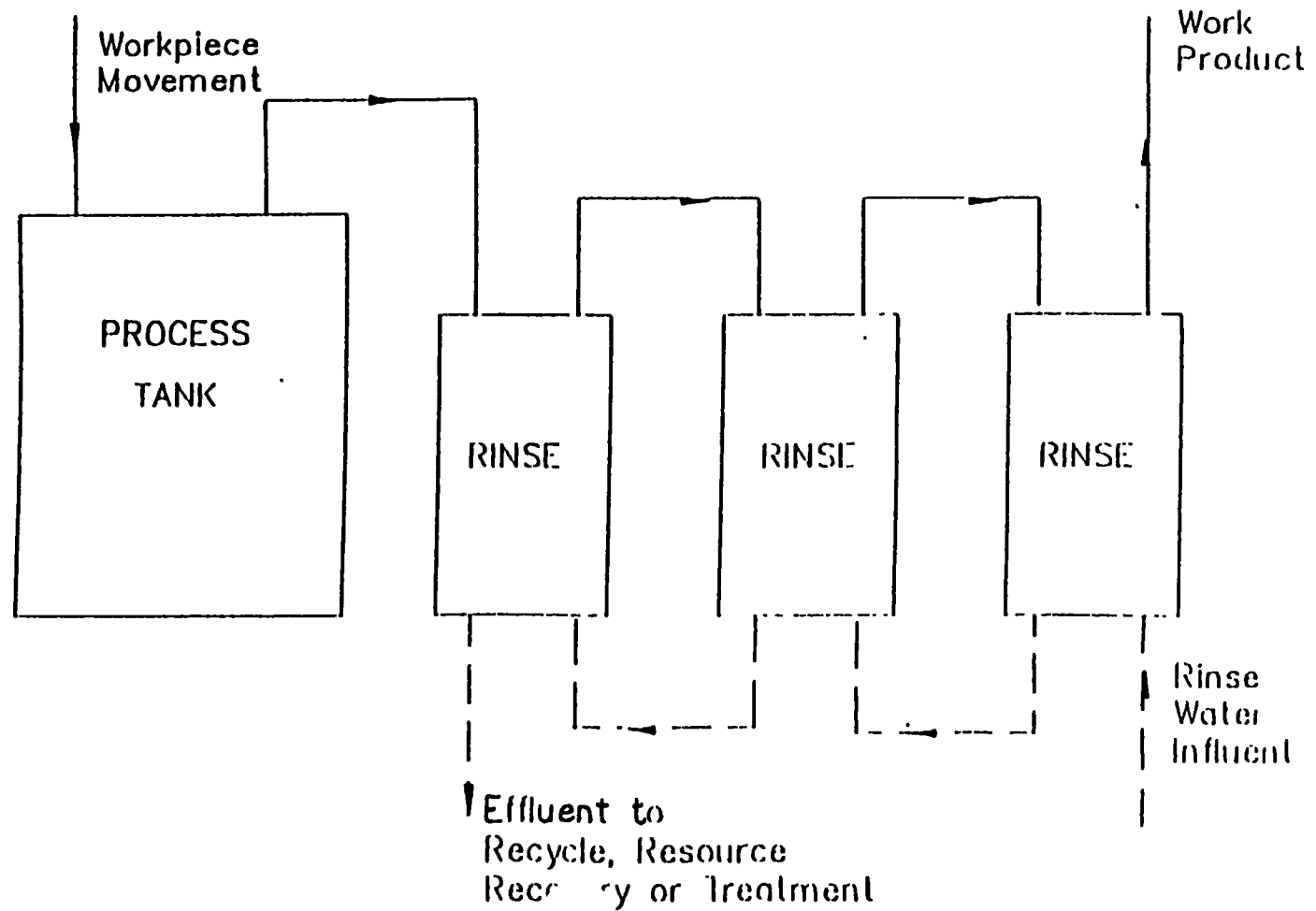
If evaporation is significant, the waste rinse water can be used to top off the plating tank. Indeed, if the rate of wastewater flow equals the rate of evaporation then all wastewater can be used up in this way and no further treatment processes are required. The temperature of the plating tank can be raised in order to increase the rate of evaporation, but it is necessary to ensure that the additives will not be degraded at the higher temperatures.

In the case of multiple rinse tanks, the upstream rinse tank contents may be recycled and the final rinse would be a free rinse containing a much reduced level of contaminants requiring little or no further treatment.

advantage: reduces wastewater
 recycles valuable metals

Exhibit 2-13

TRIPLE STAGE COUNTER-CURRENT RINSE SYSTEM



2.5.23 Conductivity Cells

The allowable maximum concentration for a rinse tank is known before the contents must be subjected to treatment. A simple conductivity probe, controller unit and automated valve can be utilized to automate the procedure of providing fresh solution. When the level of contaminant reaches a preset level, the valve is automatically opened and fresh water is introduced to the rinse tank until dilution reaches a preset minimum. A reliable probe is required and the control box should be housed in a non-corrosive material.

advantage: simple, cheap process
 reduces excess water usage

2.5.24 Flow Regulators

After establishing the appropriate flow rate into a rinse tank, this level can be accurately maintained using flow regulators.

advantage: do not need to reset flow rate each time
 valve is opened

2.5.25 Water Re-use

Final rinse water generally has a low level of contaminants and can therefore be re-used as an intermediate rinse. Alternatively it can be used as rinse water for another process step where the level and type of contaminants do not affect the rinsing operation e.g., rinse water from acid dipping can be used as rinse water for alkaline dipping.

advantage: reduces wastewater generation

2.5.26 Spray Rinse or Air Knives

As the work piece is removed from the plating tank, it is suspended above it while a spray rinse or air knife (mounted on the lip of the plating tank) is sprayed over the work piece. Up to 75 percent of chemicals can be returned to the tank in this manner. It is especially suitable for lengthy plating processes where the work piece spends many hours or days in the tank e.g., hard chromium plating.

advantage: reduces chemical drag-out and hence the need for large volumes of
 rinse water.

2.5.3 Material Substitution

If the toxic substances found in waste streams can be prevented from entering the system, wastewater treatment may not be required. Several alternative feed chemicals can be utilized as described below.

2.5.3.1 *De-ionized Water*

De-ionized water can be substituted for tap or softened water for both rinsing and topping up plating tanks.

advantages: reducing contaminants to the plating process, providing a better rinsing function, reducing waste build up in the effluent stream.

2.5.3.2 *Zinc Plating*

In zinc plating, cyanide based solutions are conventionally used. An alternative is to use a low cyanide bath, an alkaline bath or a proprietary neutral chloride bath. With the latter, ammonium or potassium ions are required for complexing the zinc. While substitution has the advantage of eliminating toxic cyanide from waste these methods appear to reduce ductility and therefore are really only suitable for cosmetic zinc applications.

2.5.3.3 *Cadmium Plating*

Chemical substitutes in cadmium plating can include acid baths consisting of cadmium oxide, sulfuric acid, distilled water, and anionic compounds.

2.5.3.4 *Copper Plating*

Copper sulphate can be used as a substitute.

2.5.3.5 *Tin Plating*

Acid tin chloride can be used as an alternative.

2.5.3.6 *Trivalent Chromium*

Trivalent chromium can replace hexavalent chromium in some circumstances.

2.5.3.7 *Cyanide*

Cleaners can be replaced by ammonia or trisodium phosphate. Chromic acid used for pickling purposes can be replaced by sulfuric acid or hydrogen peroxide.

2.5.4 *Reducing Drag-out*

Drag-out refers to the plating solution that adheres to the parts after they are taken out of the plating bath and is carried-over into the rinsewater. Drag-out represents the largest volume source of wastewater in electroplating operations. Minimizing drag-out will reduce the amount of contaminants entering the next process bath or rinsewater, thus reducing the volume of waste that must be treated and disposed.

Several techniques have been developed to control drag-out. These drag-out reduction methods are inexpensive to implement and are repaid through savings in recovered plating chemicals. Techniques to control drag-out include:

- Modifying properties of the plating bath to improve drainage of the plating solutions back into the plating baths or reduce the concentration of dissolved metals in the drag-out. These methods include:
 - Decreasing bath viscosity: by reducing the chemical concentration of the bath or by increasing the bath temperature.
 - Decreasing bath surface tension: by adding non-ionic wetting agents or increasing bath temperature.
- Lowering the withdrawal rate of parts from a bath. This method can reduce the thickness of a drag-out layer because of surface tension effects.
- Increasing the drain time over the plating tank.
- Installing drain boards, drip bars, and drip tanks to capture the drag-out. The collected drag-out can be fully or partially returned to the plating bath to make up for evaporative losses. These devices save chemicals, reduce rinse requirements, and prevent unnecessary floor wettings.
- Proper racking: By careful racking and parts removal, entrapment of bath materials on surfaces and in cavities is minimized. Methods to accomplish this include:
 - parts should be racked with major surfaces vertical.
 - parts should not be racked directly over one another.
 - parts should be oriented so that the smallest surface area of the piece leaves the bath surface last.
- Designing parts to promote drainage, e.g, parts with no cups or shelves.
- Designing plating racks with a minimum surface area, minimum horizontal surfaces, no pockets, and an effective orientation to promote drainage.
- Using air knives with oil-free compressed air to knock plating films off parts and back into the plating tanks.
- Using fog and spray rinses, parts can be spray rinsed with deionized water over the plating tanks. This method is used when tank evaporation rates are sufficient to accommodate the added volume of spray water.

- In rack plating: Provide drain bars over the plating tank from which the rack can be hung to drain for a brief period.
- In barrel plating: Rotate the barrel over the plating tank to remove excess plating solution.

2.5.5 Metal Recovery

Metals recovered from the waste stream can be recycled. The resulting detoxified (waste) stream can then proceed to disposal, further minor treatment, or it can be recycled to the rinse tanks if the required purity levels have been achieved. There are obviously two major advantages to this type of treatment:- 1) expensive chemicals are recycled 2) the wastewater volume is minimized or even eliminated. Several major methods for recovering metals are available and are discussed below. The methods are:

- 2.5.5.1 Evaporation
- 2.5.5.2 Ion Exchange
- 2.5.5.3 Electrolytic Cell Process
- 2.5.5.4 Reverse Osmosis
- 2.5.5.5 Electrodialysis
- 2.5.5.6 Freeze Crystallization

Exhibit 2-14 identifies which metal recovery application is suitable for each electroplating process.

2.5.5.1 Evaporation

This process is suitable for plating operations where high drag-out levels are experienced. It is best used with multistage rinse tanks where the volume of water is reduced and the concentration of contaminants is high. Such plating operations would include metal cyanide baths, hot chromium baths, and ambient temperature nickel baths.

Wastewater entering the evaporator is distilled, the distillate is recycled to the third rinse tank and the plating metals are returned to the plating tank. There are several types of evaporators described in the following sections.

2.5.5.1.1 Rising Film Evaporators - see Exhibit 2-15

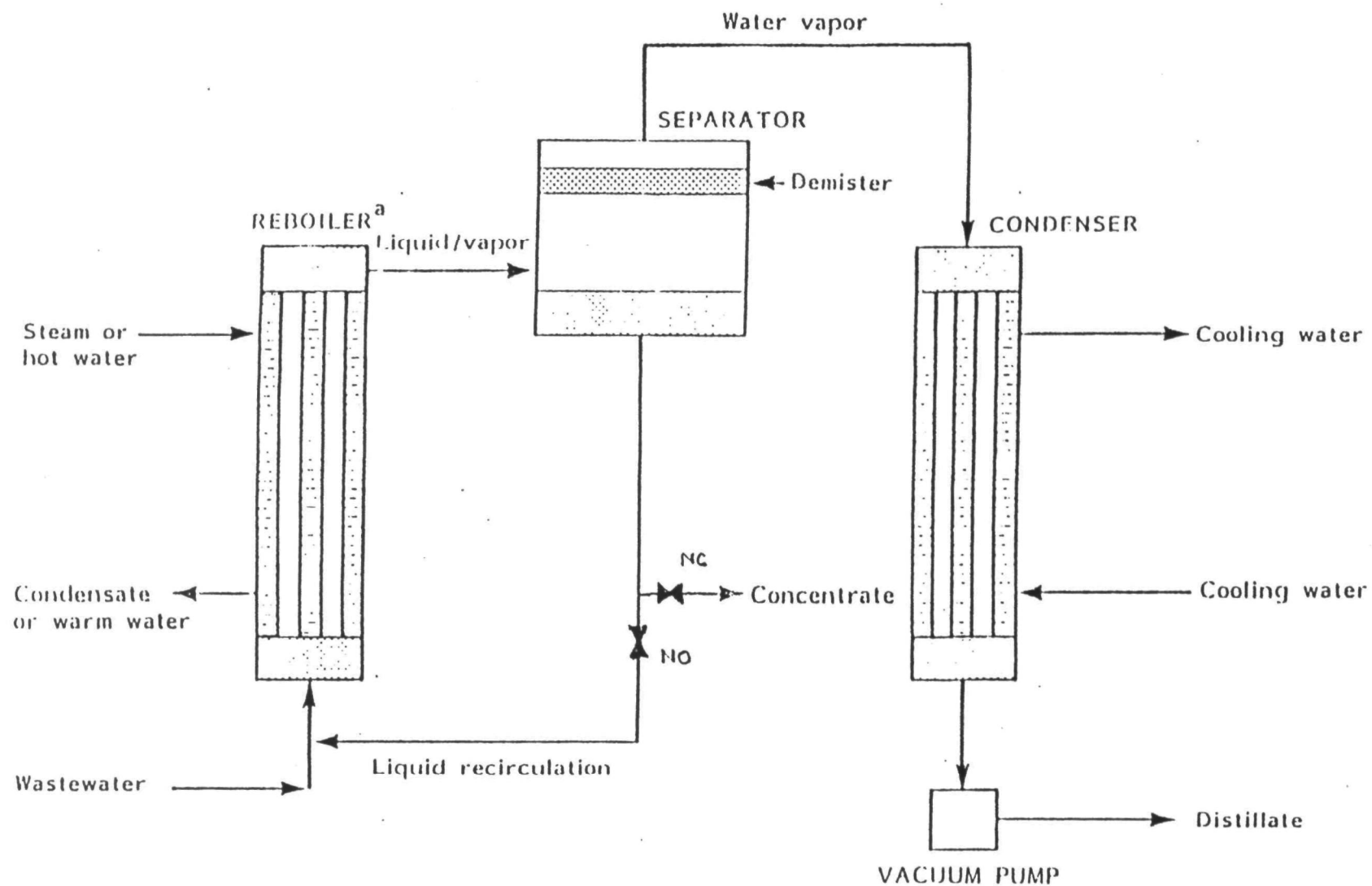
Wastewater enters the reboiler (a shell and tube heat exchanger with wastewater either within the tubes or within the shell on the surface of the tubes) and forms a vapor/droplet mixture. The mixture enters the separator and the water vapor passes to the condenser and hence to the third rinse tank. The concentrate is recycled to the reboiler until the concentration reaches a preset level. Once this level is attained, the valve opens and passes the concentrate to the plating bath.

EXHIBIT 2-14. SUMMARY OF RECOVERY TECHNOLOGY APPLICATION

Metal Recovery Techniques	Plating Baths									
	Decorative Chromium	Hard Chromium	Nickel	Electro-less Nickel	Cadmium (CN)	Zinc (CN)	Zinc (Cl)	Copper (CN)	Tin (BF ₄)	Silver
Evaporation	X		X		X	X	X	X	X	X
Reverse Osmosis			X			X		X		
Ion Exchange	X		X	X						X
Electrolysis					X	X	X	X	X	X
Electro-dialysis			X		X	X	X	X	X	X

Source: (U.S. Environmental Protection Agency, 1985. Environmental Pollution Control Alternatives - Reducing Water Pollution Control Costs in the Electroplating Industry).

NOTE: An "X" identifies which metal recovery process is suitable for the noted electroplating process.



^aThe heating medium and wastewater may be interchanged in the shell and tubes, depending on the manufacturer.

Exhibit 2-15. Rising Film Evaporation

2.5.5.1.2 Flash Evaporators - see Exhibit 2-16

This process is very similar to the rising film evaporator except that some of the plating bath is continuously recycled through the evaporation system. Some of the plating solution flashes off in the separator and provides heat to the wastestream. This reduces the overall energy

2.5.5.1.3 Submerged Tube Evaporators - see Exhibit 2-17

This process involves only a single unit, which minimizes capital expenditure. The submerged tube unit operates under a vacuum 492-914 kg/m² (0.7 - 1.3 lb/in²) created by diverting some of the cooling water through an external educator. Heating coils are immersed in the boiling wastewater. Distillate passes through a demister and is condensed via the cooling coils. It is then passed to the final rinse tank. The concentration of chemicals in the boiling wastewater becomes steadily more concentrated until a preset level is achieved, at which time the solution is returned to the plating tank. Unlike the rising film and flash evaporators, the wastewater is not continually recirculated.

2.5.5.1.4 Atmospheric Evaporators - see Exhibit 2-18

Wastewater passes through a heat exchanger (shell and tube). The vapor mixes with ambient air and is discharged to the atmosphere as saturated air. The contaminated rinse water is recirculated until it reaches a preset concentration level, at which stage it is returned to the plating tank. With this process, no condenser unit is required as the water vapor is discharged to atmosphere. However because of this, water needs to be added to the rinse tanks. De-ionized water should be used to avoid build-up of minerals in the plating tanks.

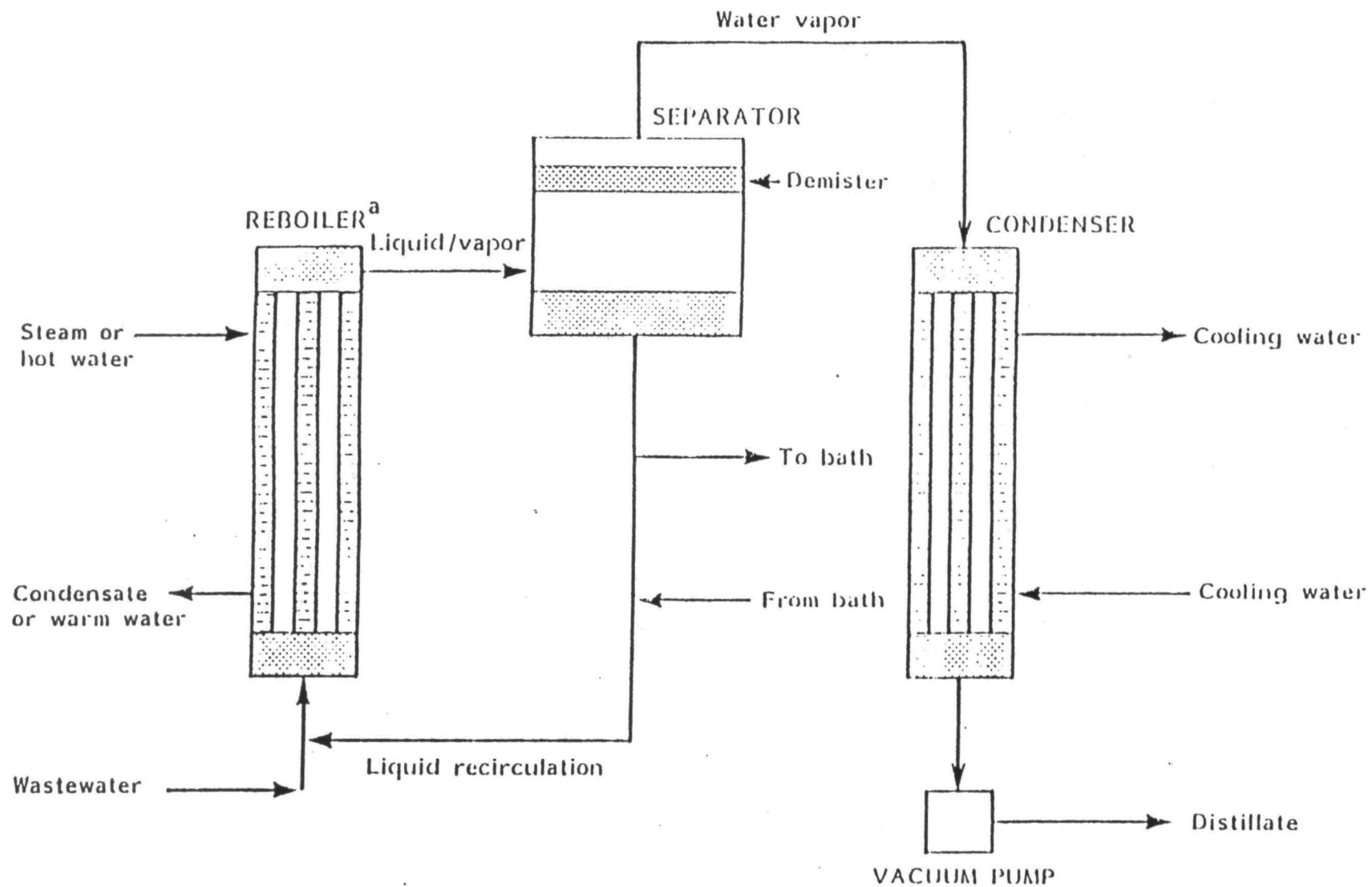
2.5.5.1.5 Double Effect Evaporators - see Exhibit 2-19

The wastewater stream is split between two reboilers. The vapor from the first stream enters the second reboiler and hence supplies thermal energy as it condenses. This process requires extra capital expenditure, yet does provide a method of treating two separate waste streams. The steam requirements are also reduced.

2.5.5.1.6 Mechanical Vapor Recompression - see Exhibit 2-20

The mechanical compressor superheats the vapor and increases pressure before it is passed to the boiler. This process avoids the need for any external steam source.

In the case of all evaporators, careful choices need to be made for the material of construction of the condenser and evaporator units, in order to resist the corrosive properties of the plating chemicals eg: use titanium, tantalum, borosilicate glass, FRP (fibre glass reinforced plastic), stainless steel, or PVC (polyvinyl chloride). Carbon steel is suitable for use in alkaline cyanide recovery.



^aThe heating medium and wastewater may be interchanged in the shell and tubes, depending on the manufacturer.

Exhibit 2-16. Flash Evaporation

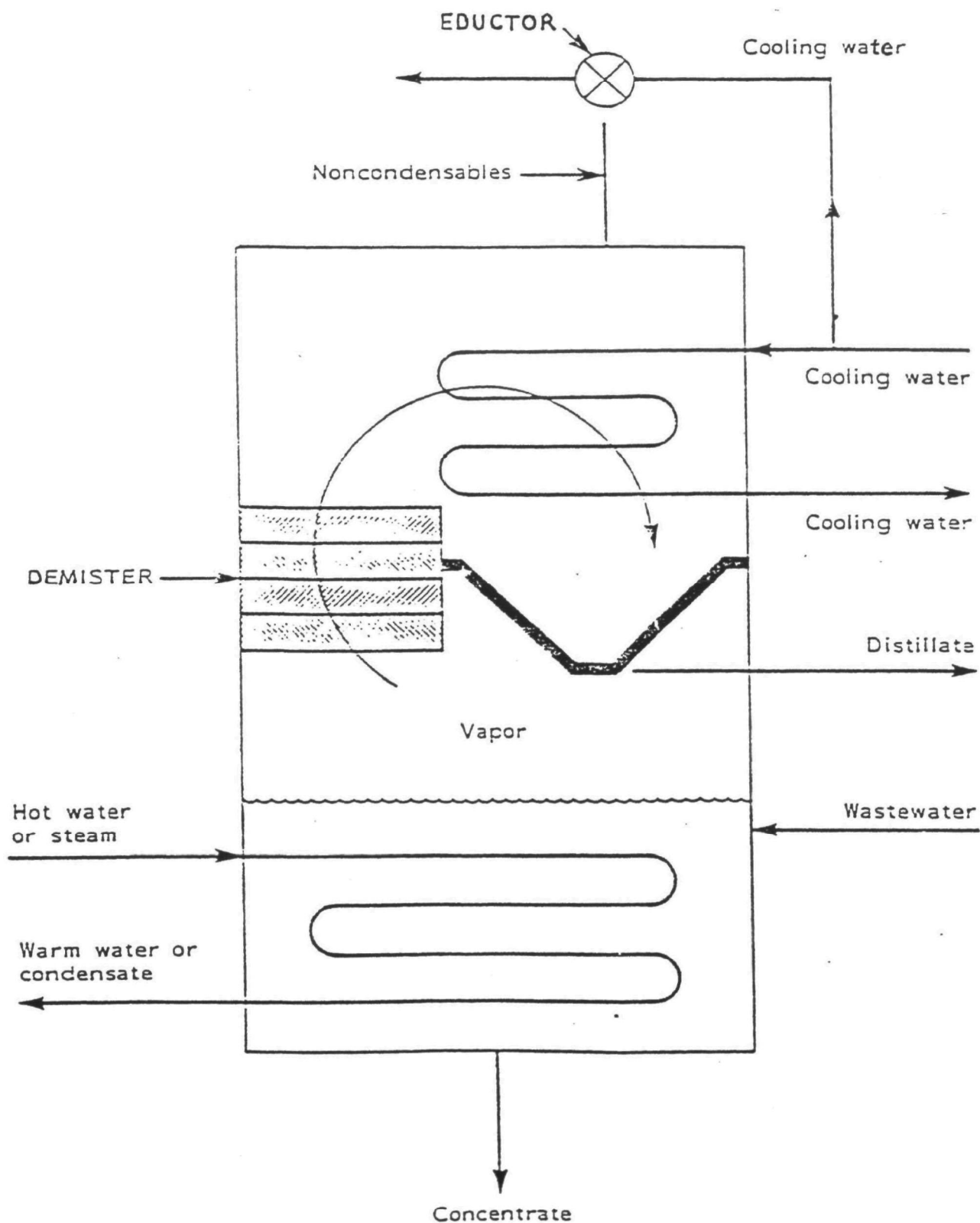


Exhibit 2-17. Submerged Tube Evaporation for Chemical Recovery

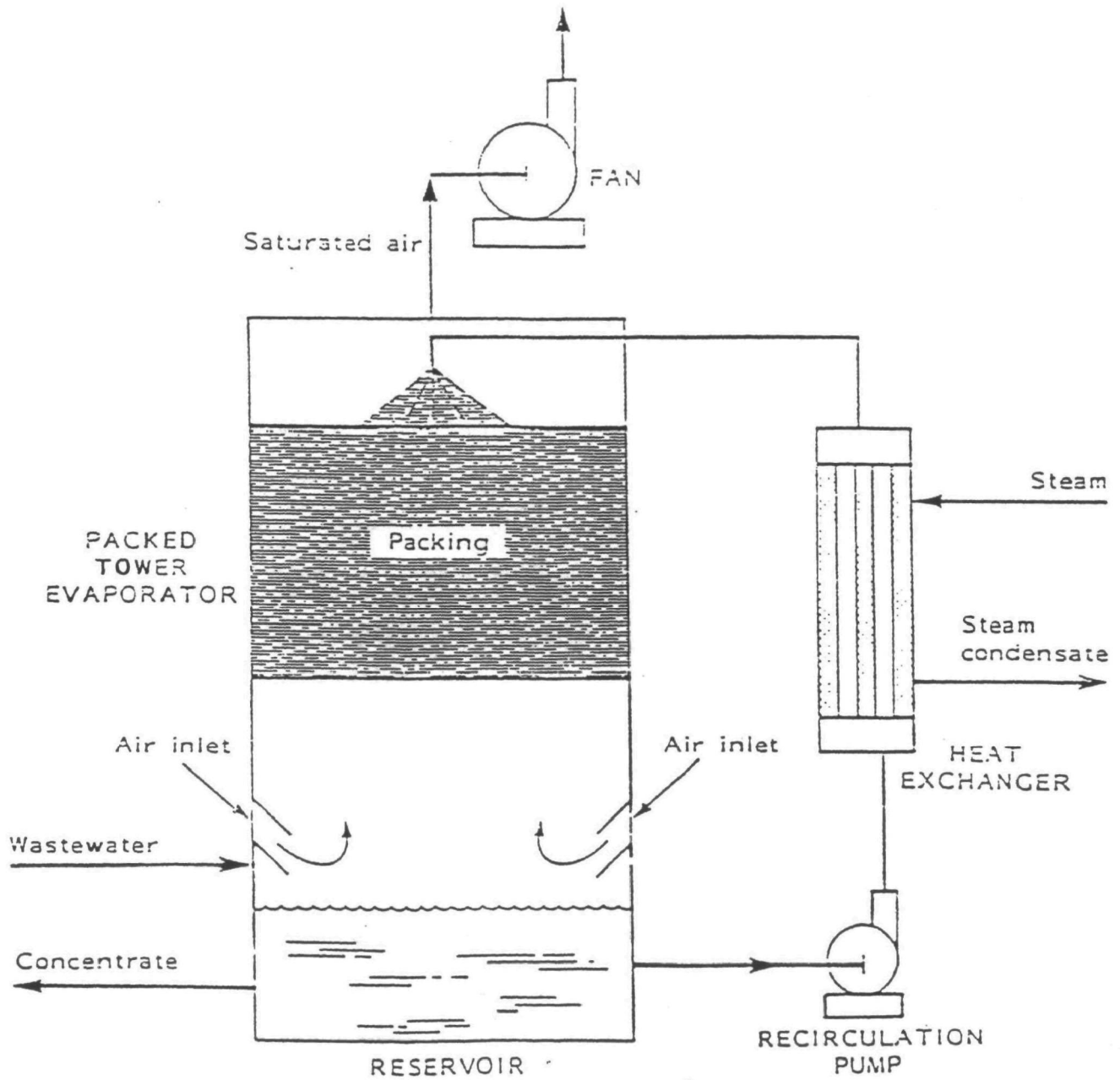
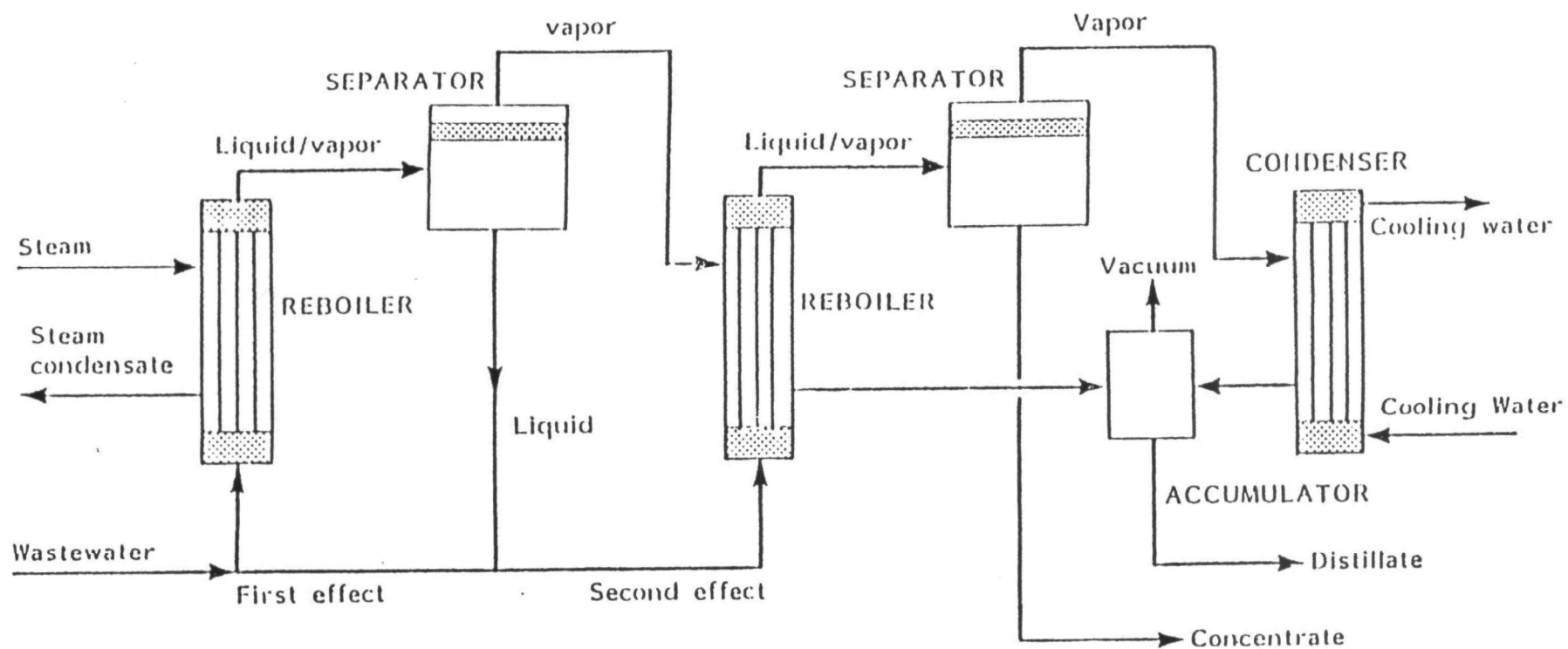


Exhibit 2-18. Atmospheric Evaporation for Chemical Recovery



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Exhibit 2-19. Double-effect Evaporation for Chemical Recovery

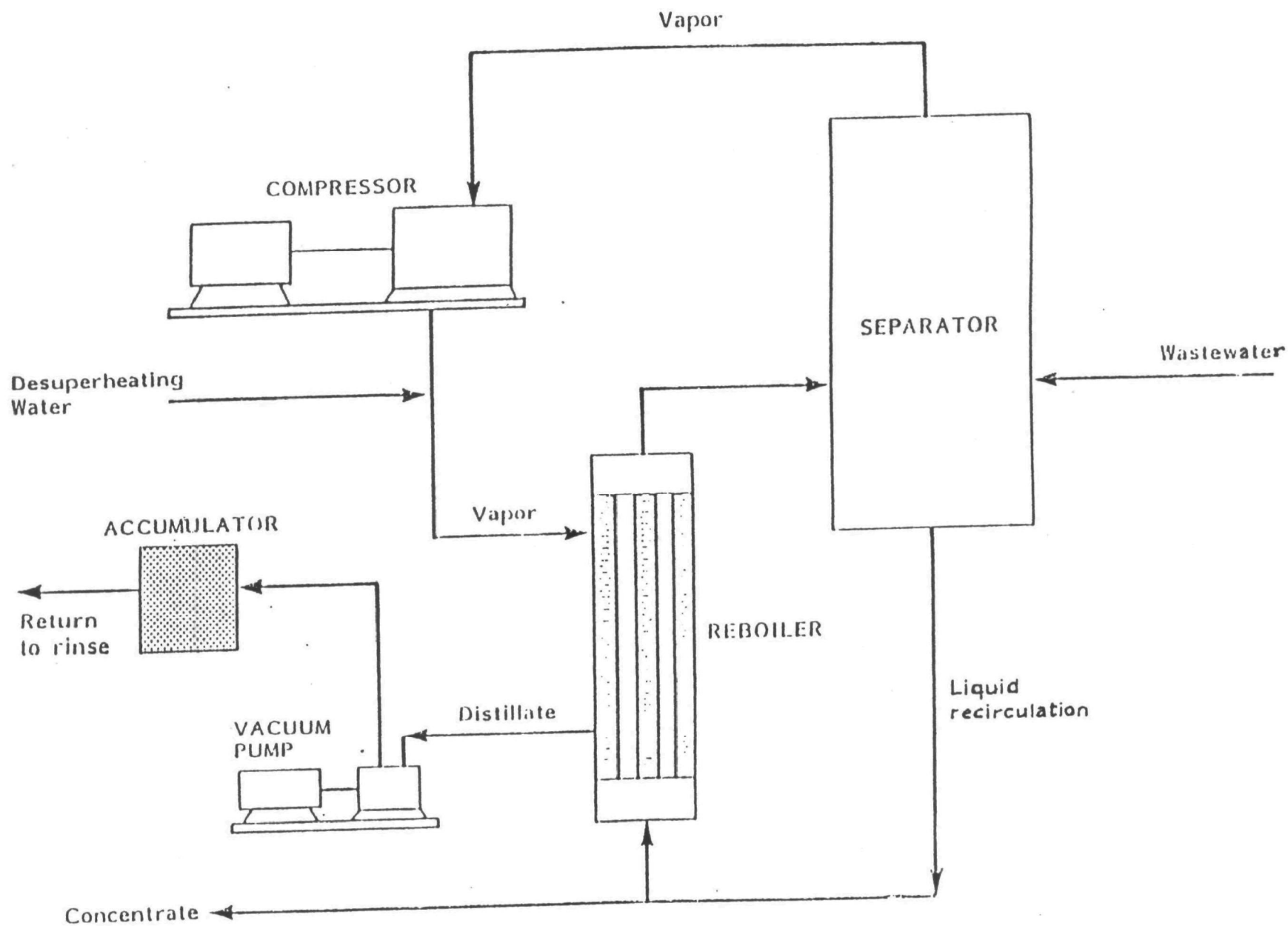


Exhibit 2-20. Mechanical Vapor Recompression Evaporation for Chemical Recovery

2.5.5.2 Ion Exchange

This process is suitable for purification of spent plating baths, recovery of anodizing baths and the recovery of plating materials from rinse water solutions (copper, zinc, nickel, tin, cobalt and chromium).

Metals and impurities are removed by using polymeric resins which replace harmful or valuable ions in solution with safe, inexpensive ones. The cations removed are generally replaced by hydrogen ions and anions removed are replaced by hydroxide ions. This method reduces the concentration of dissolved metals to less than 0.5 mg/l and is suitable for dilute solutions. The exchange resins are regenerated with acid (for cation regeneration) and alkaline (anions). It is important that the rinse water is prefiltered to remove grease, oil and solids which may foul the resins.

Chromic acid recovery (see Exhibit 2-21) represents a good example of ion exchange. The rinse water from chromic acid plating is collected in a wastewater reservoir. It is then passed through a cation and two anion columns. The cation column removes the heavy metals from the solution. The anion columns remove the chromate ions. The anion resin is regenerated by the addition of sodium hydroxide to the anion columns, resulting in the formation of sodium chromate. The sodium chromate is transported to the second cation column, where it is regenerated to chromic acid, by the addition of hydrochloric acid. (The sodium ion is replaced with a hydrogen ion.)

2.5.5.3 Electrolytic Cell Process

This process is suitable for the recovery of metals, oxidation of cyanide (by addition of sodium chloride to the rinse water), and the reduction of hexavalent chromium. It is also suitable for the regeneration of ammoniacal and chloride etch solutions during metal recovery. These systems recover 90-95 percent of the available metals.

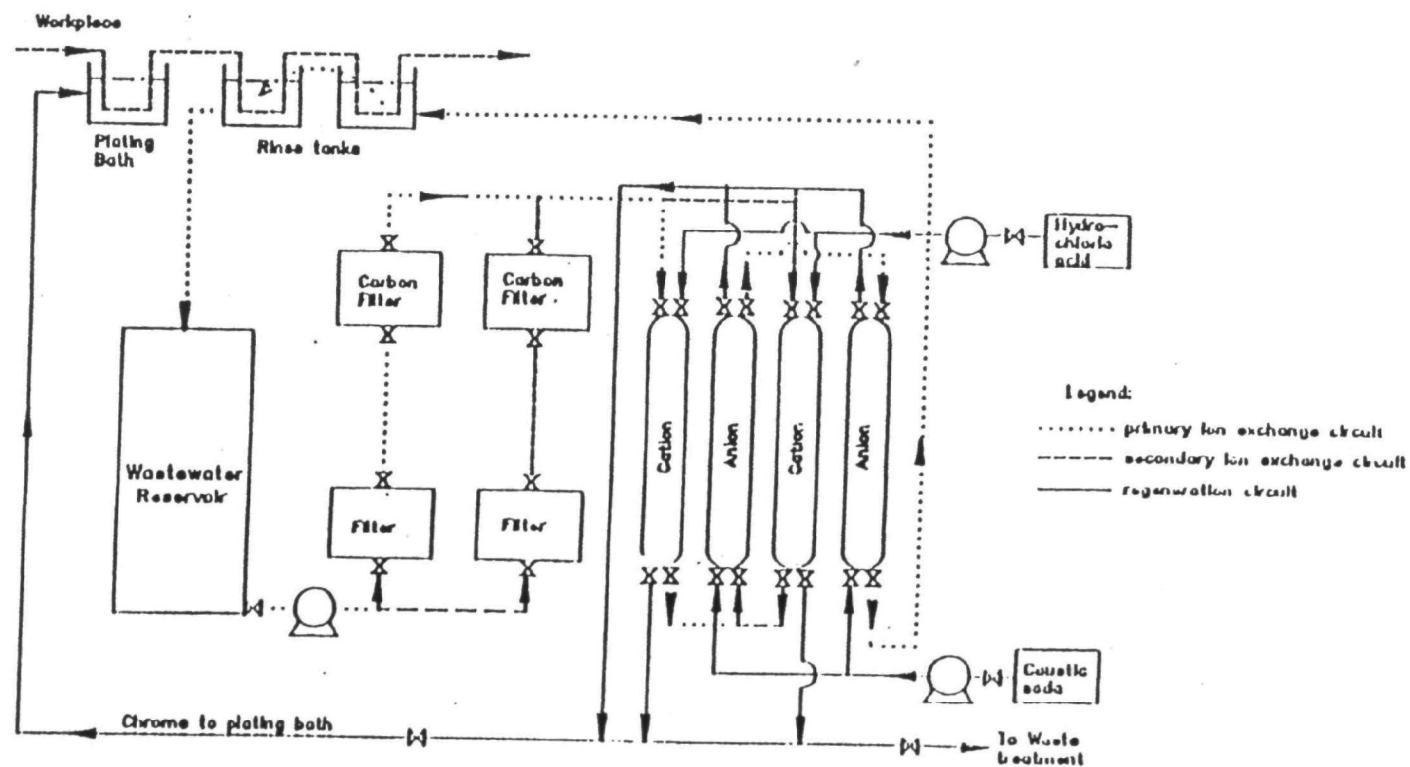
Rinse water is passed through the electrolytic cell. The metal ion is plated onto the cathode. Once a certain thickness has been reached, the metal is removed (usually by scraping). Good agitation is required. The rinse water concentration should generally be in the range of 2 - 10 g/l for homogenous metal deposition. This process, known as electrowinning, is illustrated in Exhibit 2-22.

High surface area cathodes can be utilized for more dilute concentrations (10 - 50 mg/l). Strips of metal up to a half inch thick are formed on the cathode. In this situation the treated rinse water can be disposed to the sewer.

Planar cathodes are flexible and as such the deposited metal can be removed simply by flexing the cathode.

Exhibit 2-21

ION EXCHANGE SYSTEM FOR CHROMIC ACID RECOVERY



(Source: U.S. EPA, Environmental Pollution Control Alternatives: Reducing Water Pollution Control Costs in the Electroplating Industry, September, 1983)

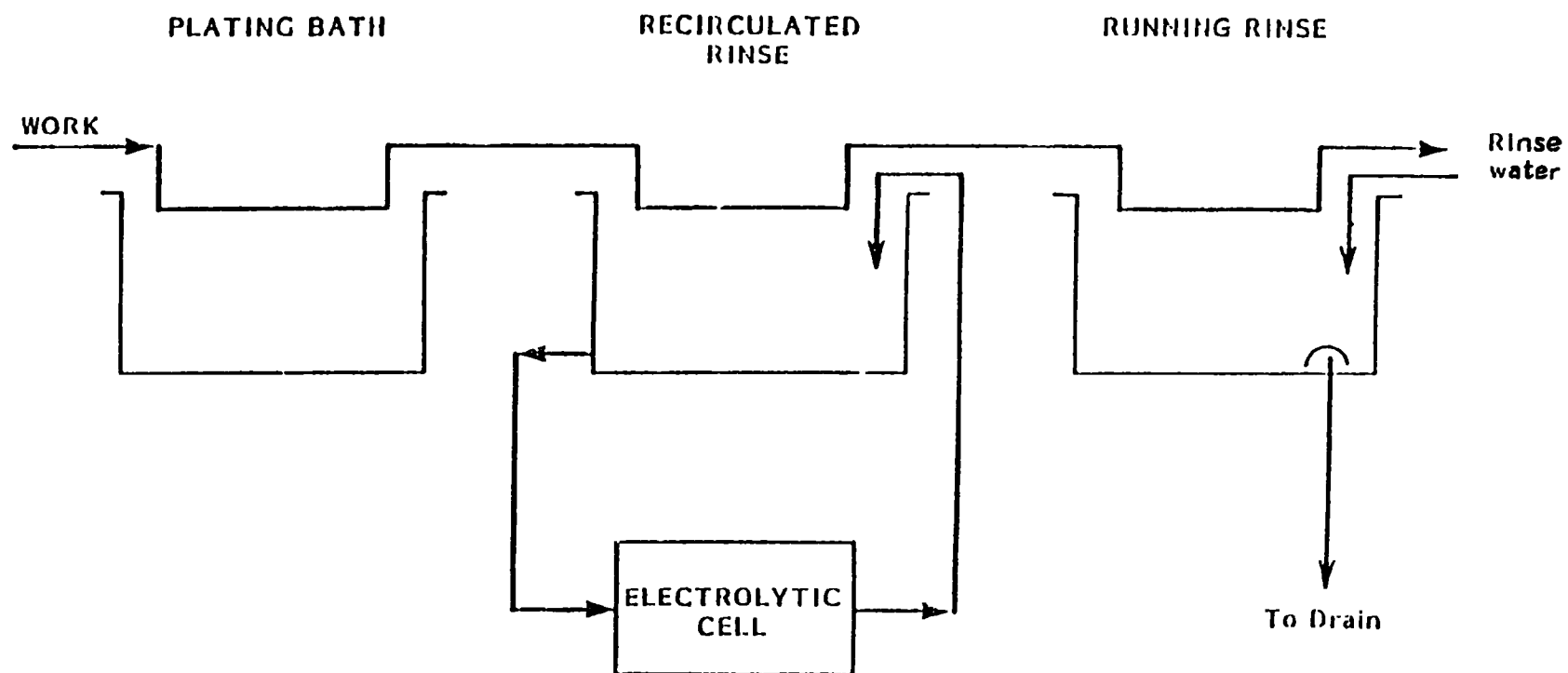


Exhibit 2-22. Drag Out Recovery From A Recirculated Rinse: Electrolytic Cell

A fluidized bed electrochemical reactor is also suitable for dilute solutions of cadmium, nickel, nickel-iron alloy, copper and zinc. The cell has a set of apertured, expanded-metal-mesh electrodes immersed in a bed of small beads. The bed is fluidized to twice its original depth. The glass beads continually scrub the surface of the electrode and thus promote mixing, ensuring fresh solution is continually brought to the surface of the electrode.

2.5.5.4 Reverse Osmosis

This process is suitable for recovery in many different electroplating applications - acid nickel plating; cyanide copper, zinc and cadmium plating; copper sulfate. It is not suitable for solutions with a high oxidation potential eg: chromic acid or extreme pH solutions where the membrane can be destroyed.

The process employs a semi-permeable membrane (tubular, spiral wound or hollow fibre) within a pressure vessel. The feed stream enters under pressure 281,200 - 562,500 kg/m² (400 - 800 lb/in²). Selective permeation of the ions produces a purified permeate stream and a concentrated stream. The concentrated stream can then be recycled to the plating tank, while the purified stream can be re-used as a rinse stream.

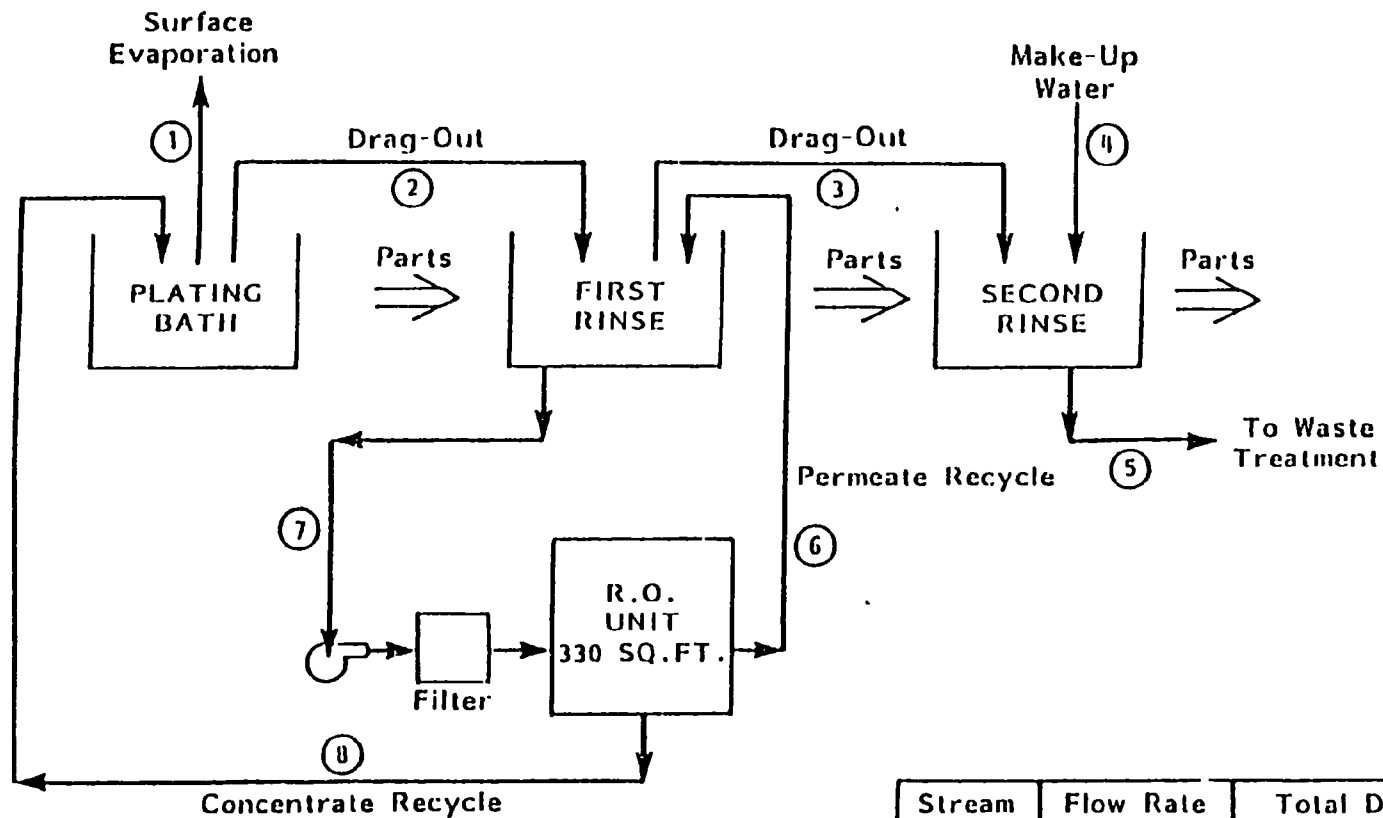
This can be used for either plating drag-out recovery (see Exhibit 2-23) or wastewater stream metal recovery illustrated in Exhibit 2-24. It is expected that 90 percent of metals should be recovered in this manner, which greatly reduces any end-of-pipe treatment. The unit generally functions continuously and has low operating costs with electricity the only operating cost. The membrane can however become plugged up by suspended solids or precipitate products. This can be avoided by upstream filtration prior to reverse osmosis processing.

A modification of the typical reverse osmosis process is advanced reverse osmosis. This process can achieve concentration ratios of up to 10,000 : 1 using lower performance membranes. The difference is that while the clean water is returned to the rinse tanks, the concentrate is held in a storage tank for further passes in order to achieve the required concentration. The system is fully automated and controlled by a microprocessor which directs the flow of the various streams without operator assistance. The membrane materials and system components are specially designed to suit the environment and thus enhance the life of the membrane.

Exhibit 2-25 illustrates the concentration ratios that can be achieved with advanced reverse osmosis, the number of passes required and the life of the membrane for various plating operations.

2.5.5.5 Electrodialysis - see Exhibit 2-26

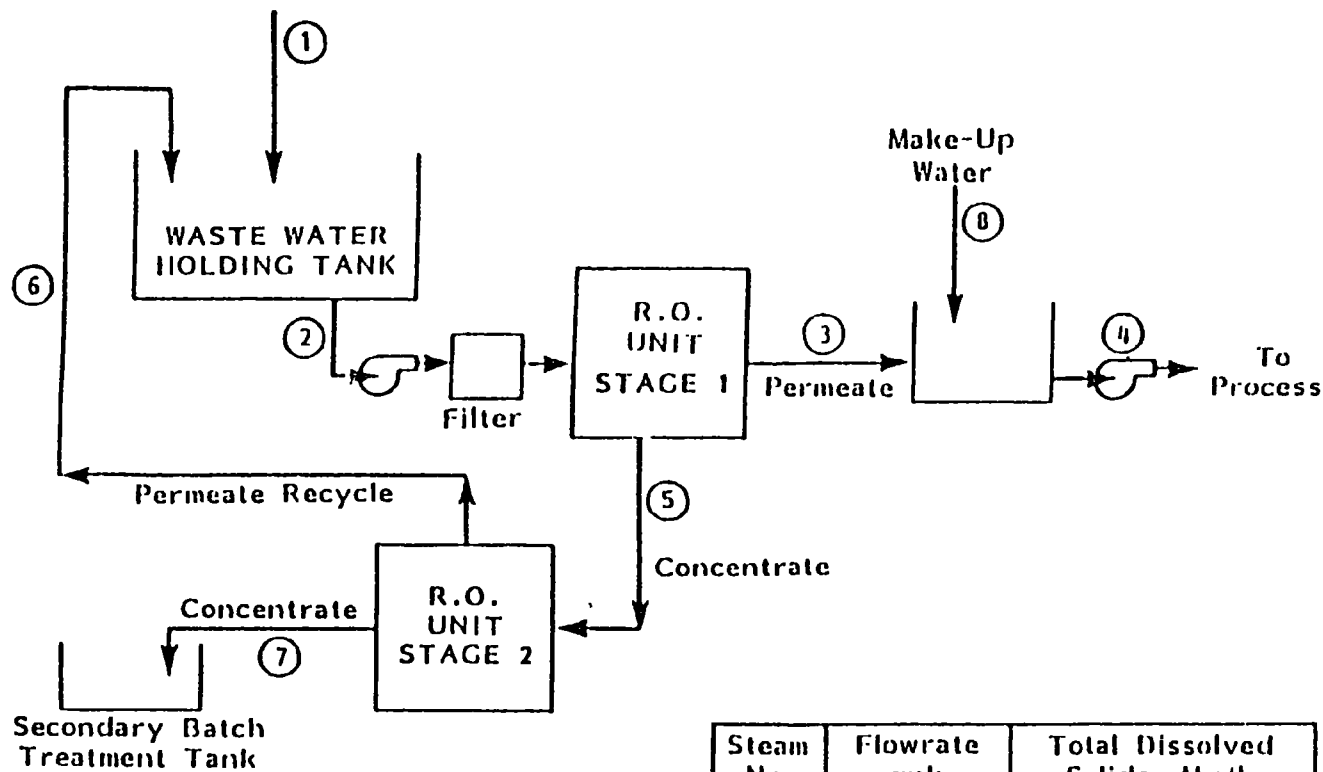
This process is suitable for recovering drag-out plating constituents from rinsewater eg: from nickel, acid zinc, zinc cyanide and chromium plating operations and also for regenerating chromic acid etchant.



Note: Reverse Osmosis Unit Performance Based on 90%
 Solids Rejection and 95% Product Recovery
 Flux Rate = 0.18 Gal/h/Ft²
 Drag-Out Recovery = 99%

Stream No.	Flow Rate gph	Total Dissolved Solids--Mg/l
1	3.0	--
2	1.0	252,500
3	1.0	4,300
4	15.0	30
5	15.0	300
6	57.0	86
7	60.0	4,300
8	3.0	84,000

Exhibit 2-23. Plating Dragout Recovery Using Reverse Osmosis



Notes: Stage 1 R.O. Unit--Solids Rejection = 95%
 Product Recovery = 90%
 Stage 2 R.O. Unit--Solids Rejection = 90%
 Product Recovery = 90%

Purified Rinse Water Savings = 1365 Gal/h
 Based on 99% Recycle

Steam No.	Flowrate gph	Total Dissolved Solids--Mg/l
1	1365	1,004.5
2	1500	1,000
3	1350	50
4	1365	50
5	150	9.550
6	135	955
7	15	86,900
8	15	30

Exhibit 2-24. Mixed Waste Water Recycle Via Reverse Osmosis

EXHIBIT 2-25. ADVANCED REVERSE OSMOSIS

Plating	Bath pH	Concentration Ratios	Passes to Required Strength	Membrane Life (mos)
Acid Copper Sulfate	0	40	3	6+
Copper Pyrophosphate	8	200	2-3	6+
Tin/Lead Fluoborate	0	10	4	6+
Tin and Tin/Lead Methane				
Sulfonic	3.6	100	2-3	6+
Electroless Copper	12	1000*	1*	6+
Electroless Nickel	10	250	2	6+
Bright Nickel	4.3	110	2-3	6+
Nickel Sulfamate	4	250	2-3	6+
Watts Nickel	4.4	100	2-3	6+
Zinc Chloride	4.9	30	3	6+
Zinc Cyanide	12	25	3	6+
Copper Cyanide	13.5	30	3	6+
Cadmium Cyanide	12	25	3-4	6+
Hexavalent Chrome	-14	100	2-3	1
Etchants				
Peroxy-Sulfuric	0	30	4	1-2
Ammonium Chloride	8	60	3	6+
Chromic-Sulfuric Acid	-.5	70	2-3	1
Sulfuric Acid	0	40	3-4	6+
Hydrochloric Acid	.5	20	4	6+
Coatings/Sealers/ Passivators/Cleaners				
Chelated Lead				
Brightener	13.5	80	2	4+
Chrome Iridite	2	10.8	2-3	1+
Nickel Acetate	5.5	150	2	6+
Nitric Acid	1	30	4	1
Sodium Hydroxide	13.5	20	4	3+

*Special membrane, selective separation.

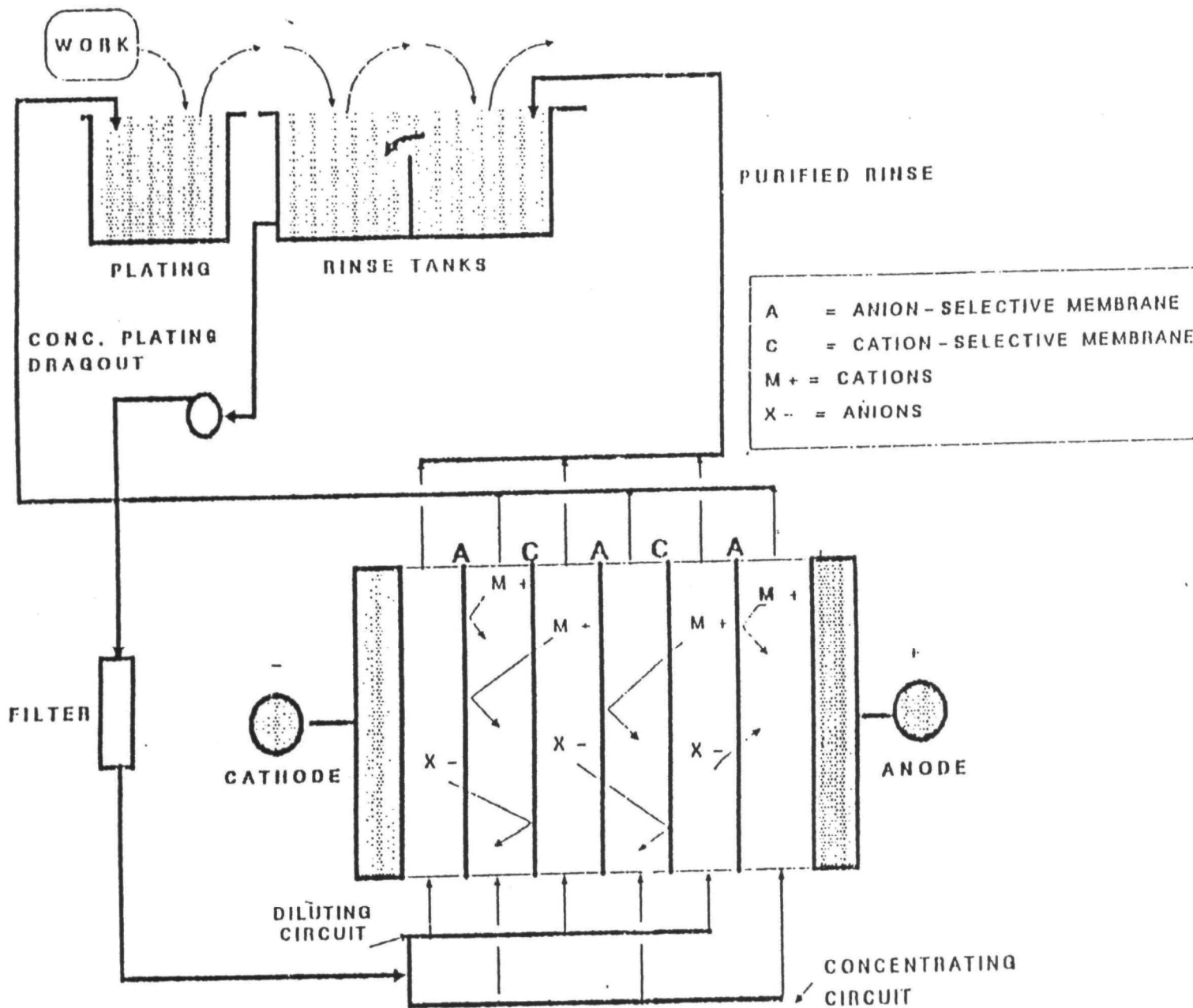


Exhibit 2-26. Electrolysis System

Anion-permeable or cation-permeable membranes are employed. Electrodes create an electrical potential which causes anions and cations to move across the respective membranes. The ions move from the dilute circuit to the concentrating circuit. Multiple passes may be required. It is important to maintain turbulent flow for efficiency. A high recovery rate of up to 95 percent is expected. There is no residual to be disposed of as both streams are recycled.

2.5.5.5.1 Electrodialytic Ion Exchange Cell (EDIX) - see Exhibit 2-27

In this process, wastewater enters the regenerate chamber. The hydrogen and metal ions migrate across the cation-permeable membrane to the concentrate chamber. There now remains an excess of negative ions in the regenerate chamber. Water is broken down to a hydrogen and hydroxide ion. The hydrogen replaces the migrating ions and the hydroxide is discharged at the anode as oxygen with further formation of water.

The concentrate chamber now has an excess of positive ions. Again water breaks down into the hydrogen and hydroxide ions. Hydrogen migrates to the cathode and is released to the atmosphere, while the hydroxide ion neutralizes the positive ions that have migrated across the membrane. More than one pass is usually required in order to achieve the desired concentration levels.

2.5.5.6 Freeze Crystallization

In this process, wastewater is mixed with an immiscible refrigerant eg: Freon. As the refrigerant evaporates, the solution forms a mixture of pure ice water crystals and concentrated contaminants. The crystals are separated, washed and melted to give pure water. The contaminant stream containing the metals can be recycled to the plating tank.

This process has both high capital and operating costs and is therefore only suitable for treatment of a very small volume of water.

2.5.6 Plating Bath Regeneration

Plating tank solutions become spent due to a build up of impurities. This is a major source of hazardous waste. The plating bath can be regenerated using activated carbon or dumpling.

2.5.6.1 Activated Carbon

Activated carbon absorbs the products from the breakdown of organic brighteners, polymeric photoresist additives and inorganic impurities. Hydrogen peroxide is added to oxidize the volatile organic contaminants. The used carbon from this process is disposed of at a hazardous waste landfill. Typically, a copper bath needs to be treated every 3 months and a solder electroplating bath needs treatment every month.

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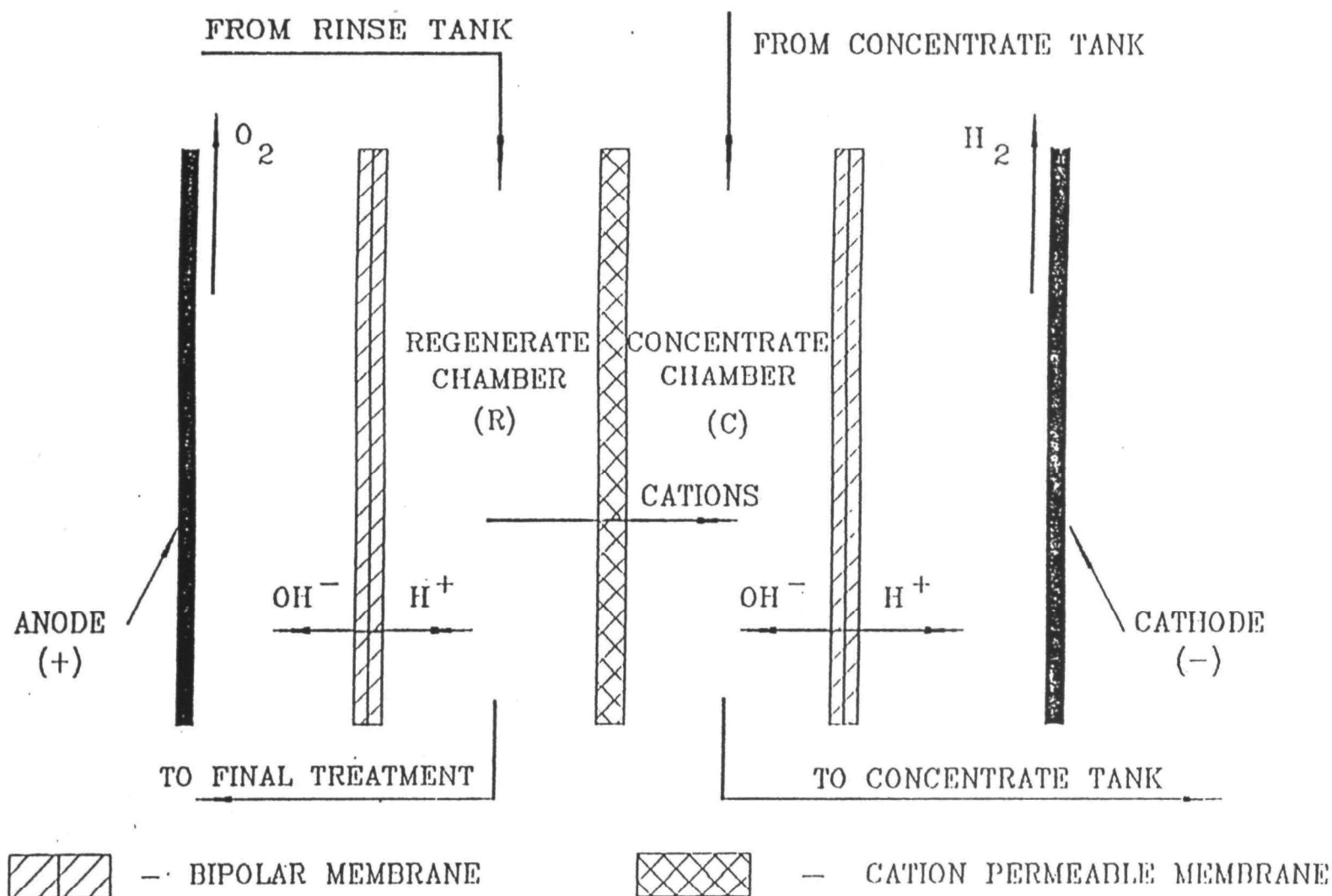


Exhibit 2-27. Schematic diagram of the electrochemical ion exchange (EDIX) cell.

2.5.6.2 Dummyming

This method selectively removes a particular impurity. For example: copper can build up in a zinc or nickel bath. In order to remove the copper, an electrolytic panel is added. A low (trickle) current is applied and the copper is deposited on the electrode. The bath needs to be taken out of process during this operation - usually 1 or 2 days, but the life of the bath can be substantially extended using this simple technique.

2.6 WASTEWATER TREATMENT PROCESSES

Unless one of the previously mentioned metal recovery processes or wastewater elimination methods is employed, the waste stream will require some treatment before disposal. The main toxic contaminants that require removal include hexavalent chromium, cyanide and heavy metals. The treatment processes described below deal with the removal of these three components.

2.6.1 Hexavalent Chromium Reduction

2.6.1.1 Sulfur Dioxide Reduction - see Exhibit 2-28

In order to remove the chromium from the waste stream, it is necessary to precipitate the insoluble hydroxide. To achieve this, any hexavalent chromium present in the waste must first be reduced to the trivalent state. Sulfur dioxide or sodium bisulfite is used as the reducing agent. The pH must be kept low in order to optimize the oxidation reduction potential (ORP), which is achieved by the addition of sulfuric acid. The hydroxide is then precipitated by raising the pH.

This is proven, reliable technology with easy operator control, although it does increase the volume of sludge produced. Hexavalent chromium is reduced to less than 0.05 mg/l

2.6.1.2 Ferrous Sulfate Reduction

The process is very similar to sulfur dioxide reductions discussed above, except ferrous sulfate is added instead of sodium bisulfite. The conditions can be acidic or alkaline. The advantage of using ferrous sulfate is that it is a natural byproduct of steel pickling and as such is readily available. The disadvantage of the process is that it produces additional sludge as the result of the precipitation of the ferrous hydroxide. The advantage of alkaline conditions is that the neutralization step following acidification is no longer required. The residual of hexavalent chromium is reduced to less than 0.05 mg/l.

2.6.1.3 Sacrificial Iron Anodes

A consumable iron electrode is used up in this process. An electric current generates ferrous ions which reduce the chromium to the trivalent form. The reaction proceeds at neutral pH. It is an inexpensive technology, but does increase sludge volume due to the addition of ferrous hydroxide.

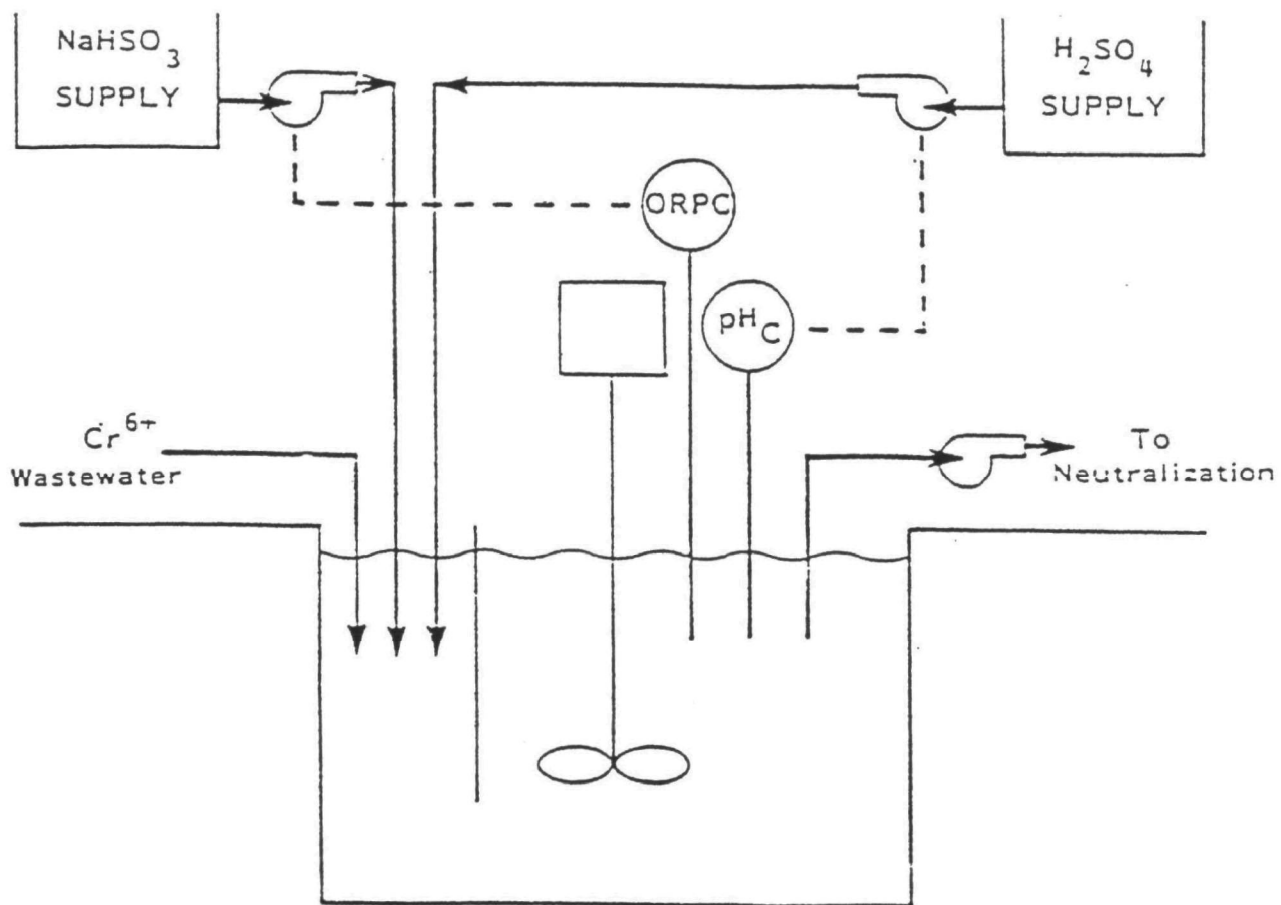


Exhibit 2-28. Chromium Reduction Treatment Unit

2.6.2 Cyanide Oxidation

2.6.2.1 Alkaline Chlorination - see Exhibit 2-29

This two stage process to reduce cyanide in the waste stream operates as follows:

1. Sodium hypochlorite or chlorine gas and sodium hydroxide are added. (The latter is cheaper but chlorine gas requires careful handling) The pH is maintained at 10 or above. In this reaction the cyanide is converted to the cyanate form in only two minutes.
2. Further sodium hypochlorite is added at pH of 8.0 - 8.5 with a residence time of between 30 - 60 minutes. The cyanate forms nitrogen gas and the carbonate.

The cyanide concentration in the waste stream is reduced to less than 1 mg/l. In order to properly control the reaction, it is important to recognize the end point of the cyanide to cyanate reaction and therefore a reliable ORP control system is required. Continual agitation is required to avoid the precipitation of solid cyanides. The process cannot oxidize stable cyanide complexes (e.g., ferrocyanides), which should be separated upstream.

2.6.2.2 Electrolytic Oxidation

This process is suitable for high levels of cyanide waste. A 20,000 mg/l solution can be reduced to 0.5 mg/l - ie: a reduction of 99.99 percent. The cyanide waste stream is subjected to electrolysis at 93°C (200°F) for several days. The cyanide is broken down via the cyanate to carbon dioxide and ammonia. The reaction slows down as the electrolyte is used up and also as the current flow is reduced by scaling on the anode.

2.6.2.3 UV Light/Ozonation

This process is generally used for aqueous wastes that contain a high proportion of oxidizable constituents e.g., the final treatment step of a waste stream. It is also suitable for complexed cyanides. The cyanide stream is mixed with ozone and enters a reaction chamber. The stream passes several UV lamps. The UV radiation enhances oxidation of the cyanide to nitrogen and hydrocarbonate. The destruction rate can be improved by elevating temperatures to 65°C (150°F), increasing the ozone concentration and introducing a catalyst metal ion, such as copper.

2.6.2.4 Wet Air Oxidation - see Exhibit 2-30

This process is suitable for a wastestream concentration of greater than 1 percent, which can be reduced to less than 1 mg/l - a cyanide destruction rate of over 99 percent. The wastewater is combined with oxygen at temperatures and pressures up to 326°C (620°F) and 2.2 million kg/m² (3000 psig) respectively. A feed chemical oxygen demand (COD) concentration of 2 percent is sufficient to cause a temperature rise and liberate volatile

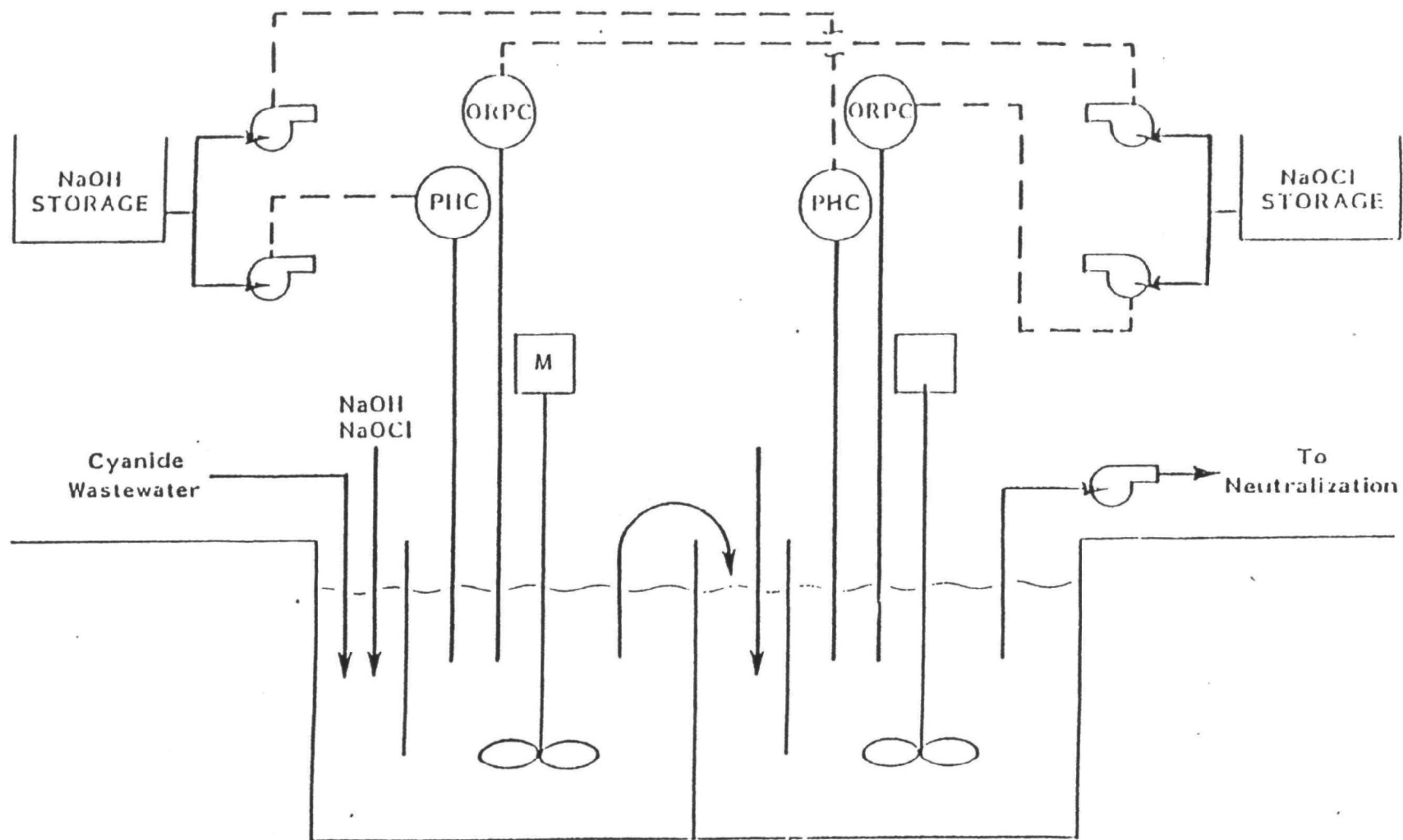


Exhibit 2-29. Two-Stage Cyanide Oxidation System

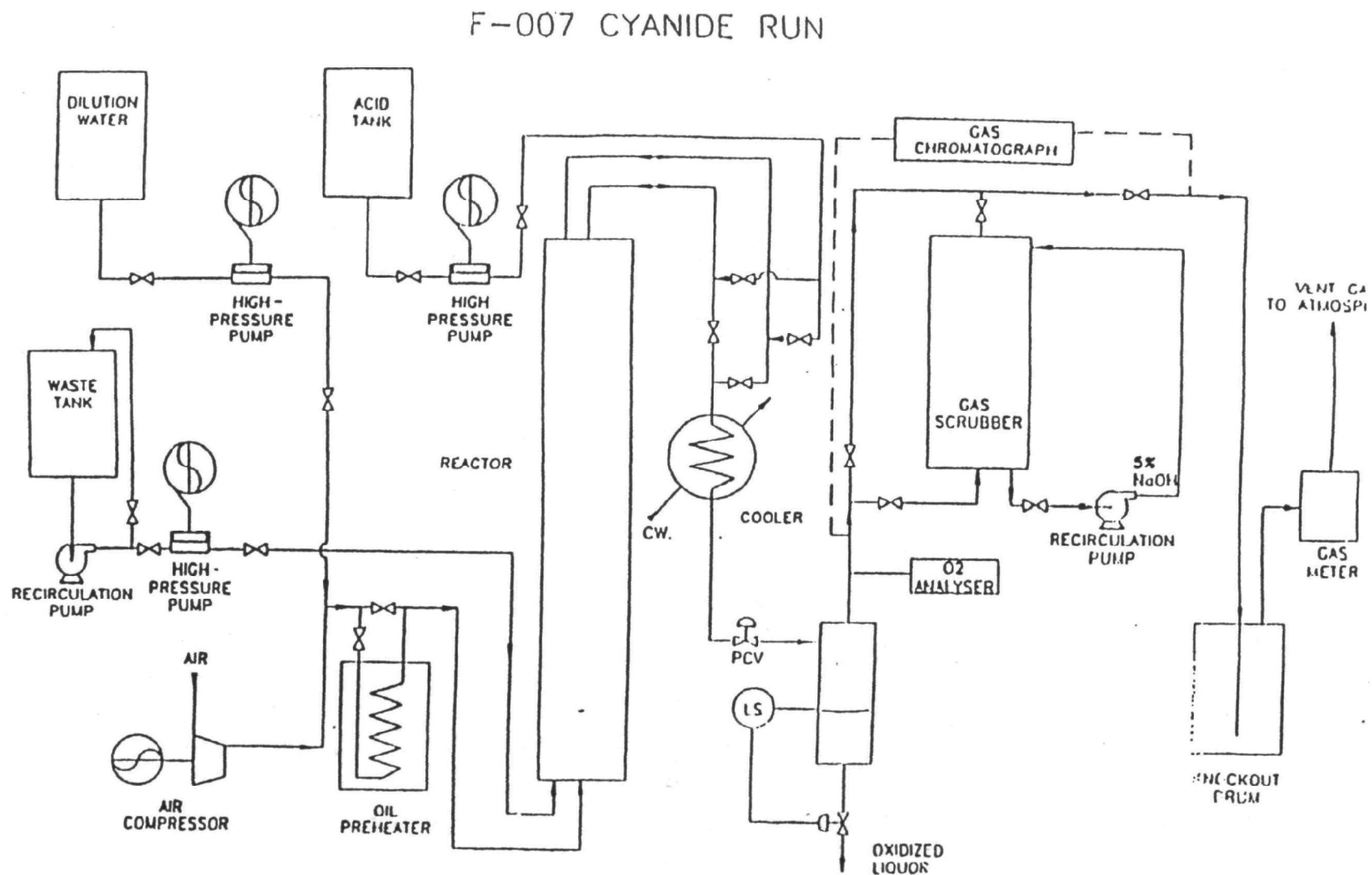


Exhibit 2-30. Cyanide Oxidation: Schematic Diagram of Zimpro/Passavant Wet Air Oxidation Process

components. The solubility of oxygen is enhanced by the elevated pressure and the oxidation is encouraged by higher temperatures. The wastewater/oxygen stream enters the reactor where it is oxidized to the carbonate and ammonium ions. The oxidized liquor proceeds to neutralization and metal precipitation.

There are two main types of reactors: a) the tower reactor is a vertical vessel, where air is introduced from atmosphere to interface with the feed; b) the cascade of completely stirred tank reactors is a series of horizontal chambers within a horizontal cylinder. Air is injected into each chamber as the feed progresses through the chambers.

2.6.2.5 Thermal Oxidation

The thermal oxidation process uses a heated reactor to destroy the cyanides by thermal decomposition. This is ideal for high concentrations of cyanides - e.g., spent baths, cleaners, strippers, and concentrated rinse water.

2.6.2.6 Ozone Oxidation

This process is used as an alternative to alkaline chlorination of cyanides. In this process, the wastewater is shattered into a fine mist within a rotary vacuum filter. The resulting particles have a greater surface area for contact with the ozone gas. When the smaller wastewater droplets are exposed to the ozone, it oxidizes the cyanide content of the waste stream.

2.6.3 Metal Precipitation

2.6.3.1 Hydroxide Precipitation - see Exhibit 2-31

After the chromium stream has been segregated and reduced, the cyanide stream has been segregated and oxidized, all streams are collected and neutralized, at which stage the metals are precipitated and the solid wastes separated.

Hydrated lime (calcium hydroxide) or sodium hydroxide can be utilized for metals precipitation. This is accomplished by control of the pH level in order to minimize the solubility of the metals present. Exhibit 2-32 illustrates the different pH levels for minimum solubility of various metals.

Hydrated lime	vs	Sodium hydroxide
<hr/>		<hr/>
longer reaction time (30 mins)		short reaction time (15 mins)
high solids content (1,370 mg/l)		light, fluffy floc (230 mg/l)
faster settling rate		

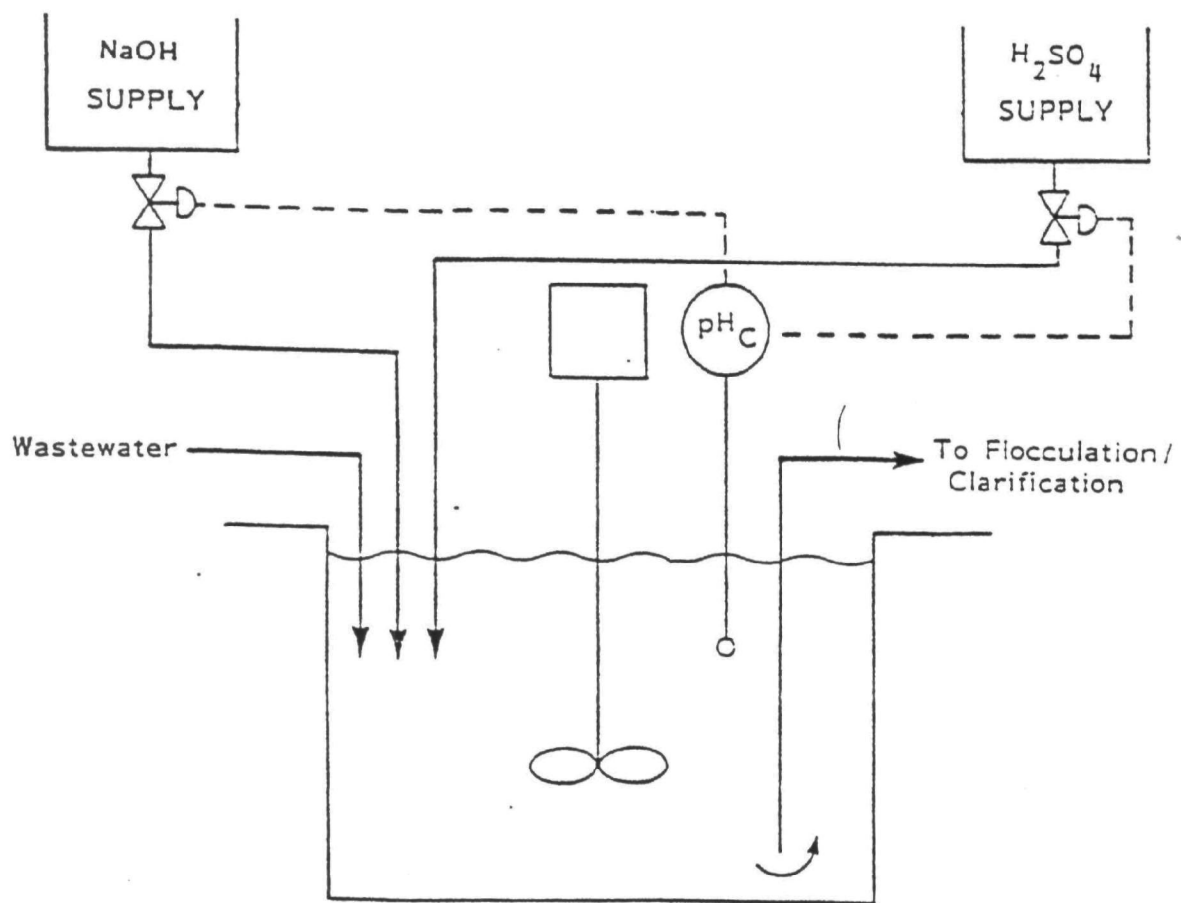


Exhibit 2-31. Hydroxide Precipitation - Stream Neutralization

EXHIBIT 2-32. METAL SOLUBILITY AS A FUNCTION OF PH

Metal	Dissolved Metal Concentration (mg/l)			
	Raw Wastewater	pH 8.4	pH 8.8	pH 9.2
Chromium (total)	45.0	0.1	0.11	0.1
Cadmium	1.0	0.02	0.02	0.02
Copper	25.0	0.02	0.02	0.03
Nickel	10.0	0.20	0.20	0.20
Iron	20.0	NM	NM	NM

Note: NM = not measured.

Each of these neutralizing agents (hydrated lime or sodium hydroxide) has benefits. The comparison above illustrates the differences. A denser floc is desirable as it reduces sludge dewatering requirements.

A one or two stage neutralizer can be utilized. A single stage involves the addition of both acid and base to the same tank. Two stages are utilized for wider swings in reagent demand.

2.6.3.2 Sodium borohydride

Sodium borohydride is a strong reducing agent, capable of precipitating metal ions to elemental metals. Ninety-five percent reduction in total metals can be achieved from a complex waste stream. It also produces a low volume of sludge. The precipitated metals can then be reclaimed. The operating and capital costs are higher than for conventional hydroxide precipitation.

2.6.3.3 Sulfide Precipitation

In this process, the sulfides are precipitated instead of the hydroxides. Sodium sulfide or ferrous sulfide can be utilized. This method is expensive and creates additional sludge volumes. The main advantage of this method is that metal chelates can be removed. Metal ions form chelates with certain other compounds present in the waste stream such as: ammonia, phosphates, and tartrates. The chelates are soluble under alkaline conditions and as such will not precipitate out under hydroxide treatment.

2.7 HAZARDOUS SOLID WASTE MANAGEMENT

During the neutralization step in the waste treatment cycle, many metals will precipitate out. Other suspended solids will also be contained in the waste stream such as: large organic molecules, complexed heavy metals, oil and grease. In order to separate out the solids, coagulation or flocculation need to occur, after which the waste stream will be clarified. The separated solids or sludge will only be between 0.5 - 3.0 percent by weight. In order to reduce the amount of water in the sludge (concentrate it), the sludge needs to be dewatered. See Exhibit 2-33 for a simple schematic of the whole waste treatment process.

For example, the typical levels of pollutants in the sludge from a nickel, chromium and zinc plating operation were found to be:

oil & grease	93,000 mg/kg
nickel	155,600 mg/kg
iron	84,400 mg/kg
chromium	24,620 mg/kg
zinc	11,900 mg/kg
copper	7,100 mg/kg
lead	270 mg/kg
cadmium	7 mg/kg
other	623,103 mg/kg

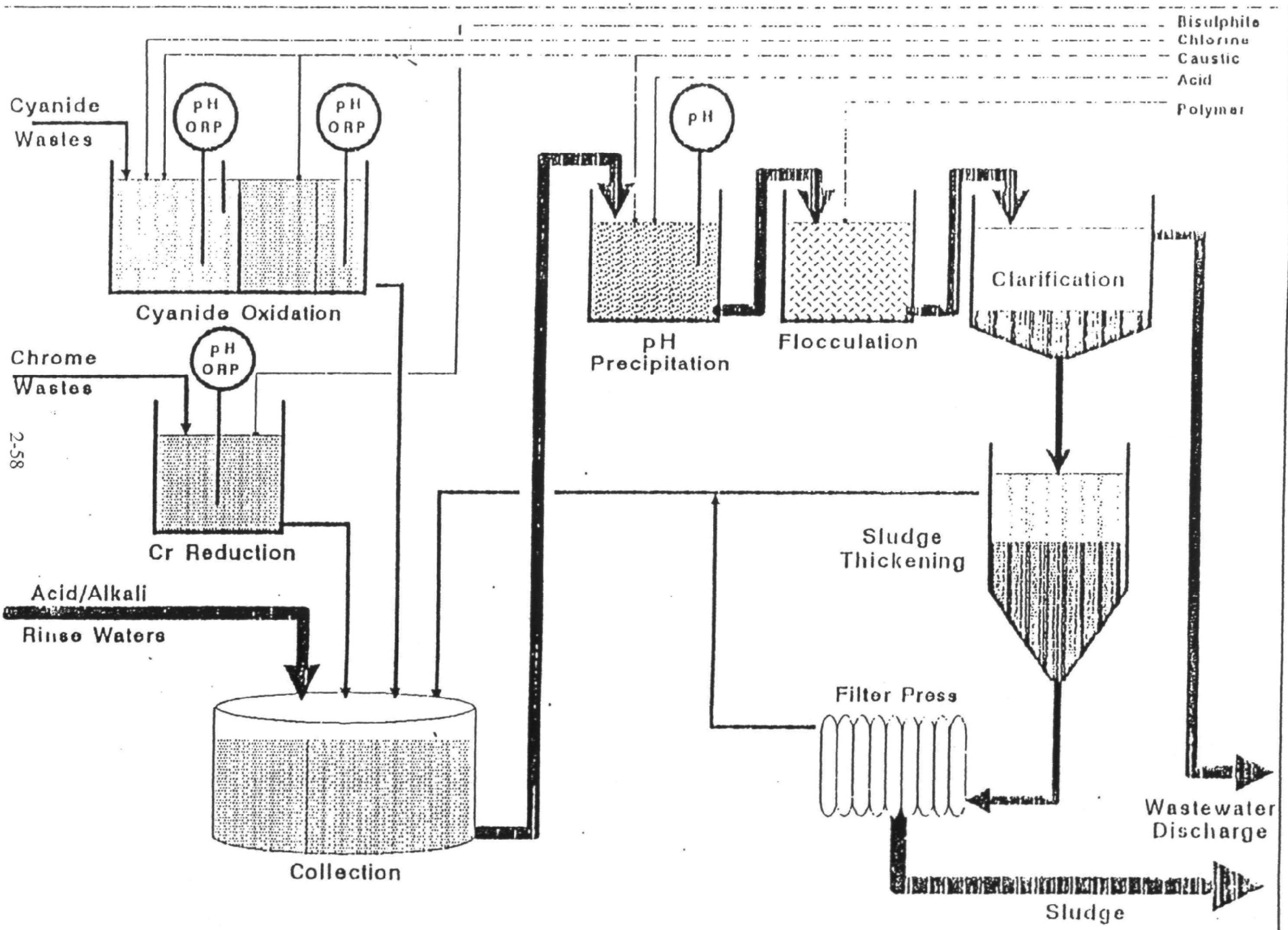


Exhibit 2-33. Conventional Waste Treatment

There are a variety of processes employed to thicken (concentrate) the sludge. These processes are described in the following text.

Coagulation is the process of mixing coagulants with wastewater and then creating large particles which will settle through the process of flocculation. Initially, coagulants are added to the wastewater to form small particles with the wastewater constituents. Coagulants are generally inorganic chemicals such as: alum, lime or ferrous sulfate.

Flocculation occurs through the growth of larger, more dense particles that have good settling characteristics. Floc builders are conventionally organic polyelectrolytes and are added after the neutralizing step ie: after precipitation. Gentle tank agitation is required.

2.7.2 Clarification

A clarifier is a settling chamber where the solids are separated from the waste stream solution. The resulting wastewater stream should only contain 5 - 50 mg/l solids, while the resulting sludge stream should be between 0.5 - 3.0 percent solids by weight. Three types of clarifiers utilized in the industry are described below:

2.7.2.1 Rectangular Clarifier - see Exhibit 2-34

Basic settling chambers are usually rectangular tanks. The wastewater stream is fed into one end of the tank and overflows at the other. The solids settle to the base of the unit and are raked to a sludge well at regular intervals by a travelling scraper bridge.

2.7.2.2 Circular Clarifiers - see Exhibit 2-35

In the circular clarifier, the incoming feed is mixed with a sludge blanket that is maintained within the chamber. The new solids join the sludge blanket and the clean effluent is removed from the tank.

2.7.2.3 Plate Settlers - see Exhibit 2-36

A plate settler consists of angled plates. As the solid particles settle due to gravity through the solution, they impinge on one of the angled plates and then slide down to the bottom of the tank. This accelerates the rate of settling. This unit is the smallest and hence most suited to applications where there is limited space available.

2.7.3 Sludge Dewatering

Sludge waste from plating operations is normally considered hazardous, due to the possibility of leaching metals. As such, it requires careful disposal. It is therefore desirable to reduce the volume in order to reduce disposal costs. Sludge dewatering can be carried out using different filter techniques is noted below.

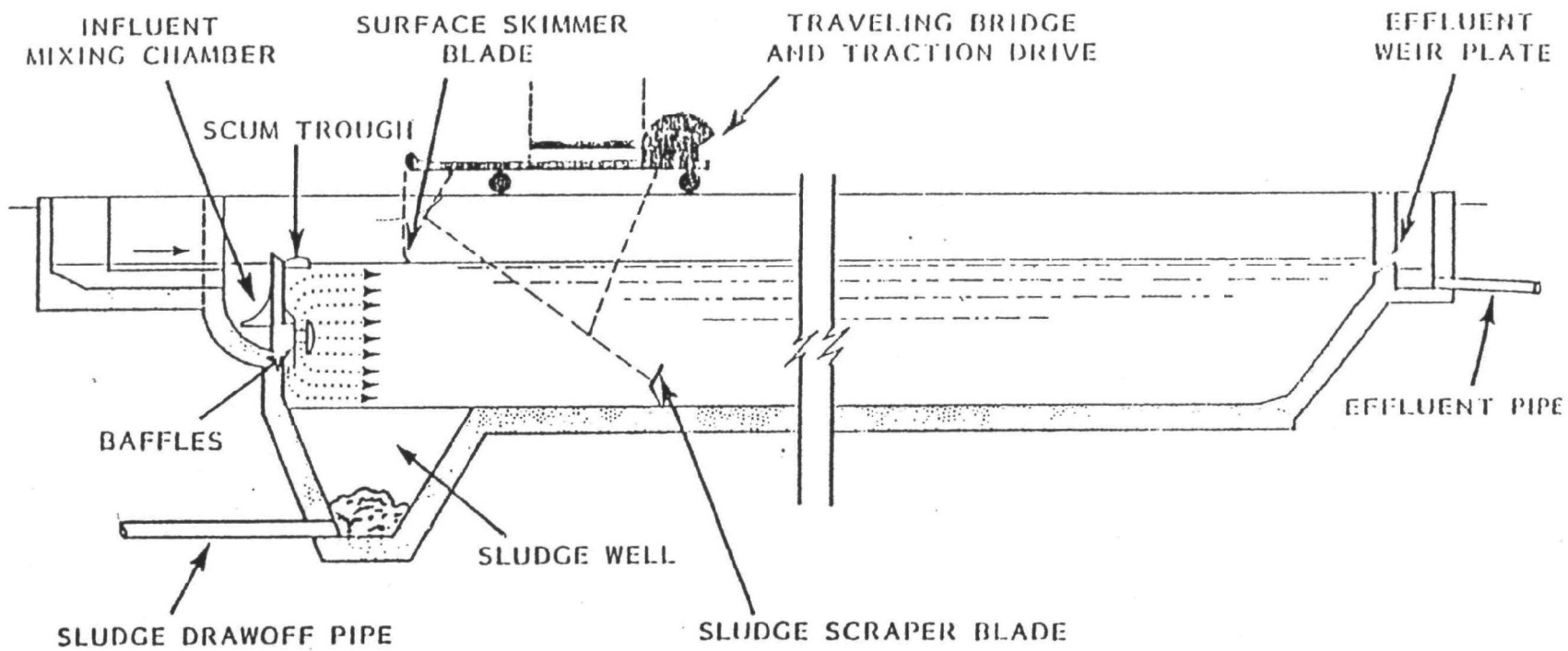


Exhibit 2-34. Rectangular Clarifier Basin

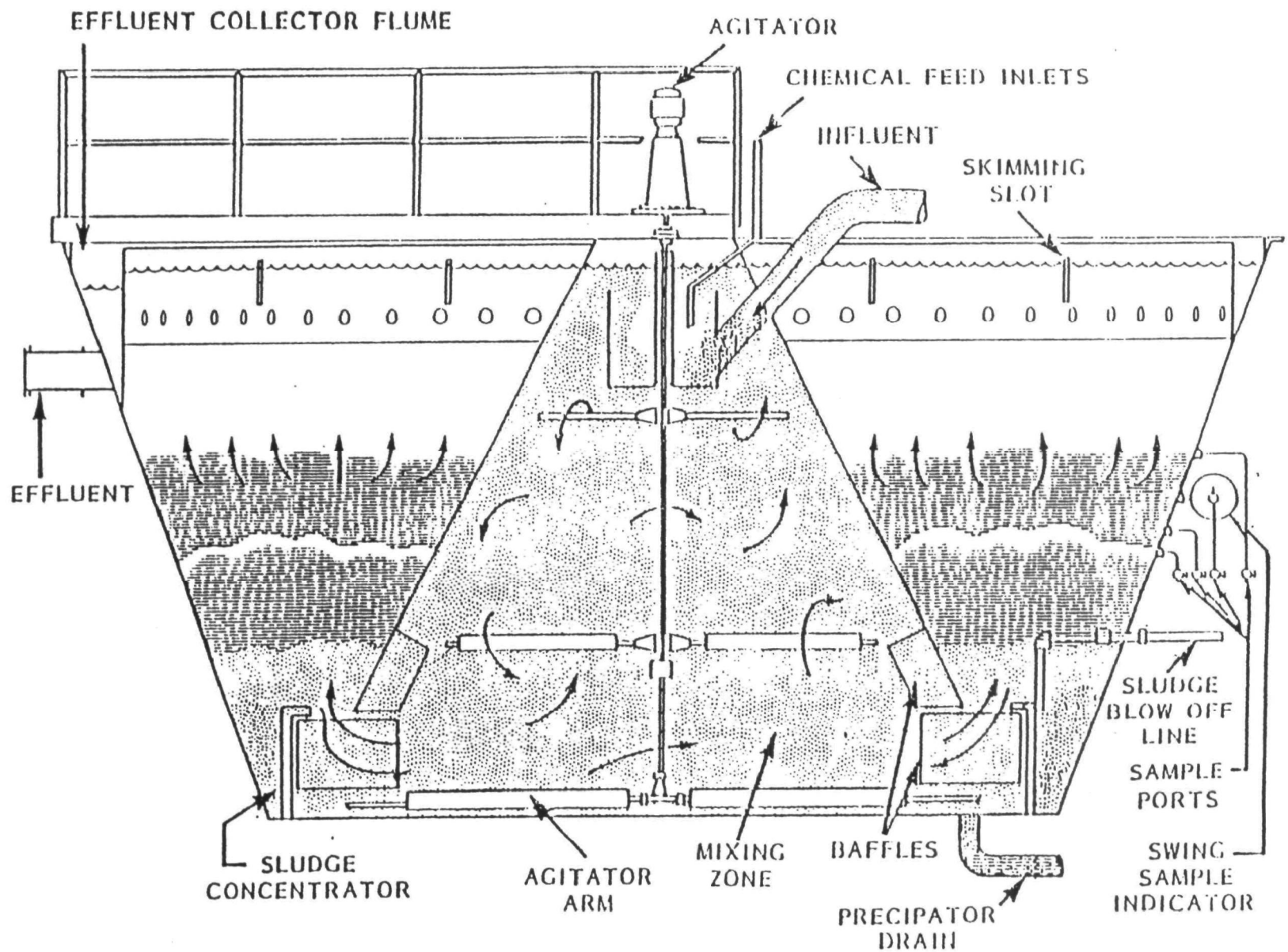


Exhibit 2-35. Solids Contact Clarifier with Sludge Blanket Filtration
(Courtesy of the Permutit Co.)

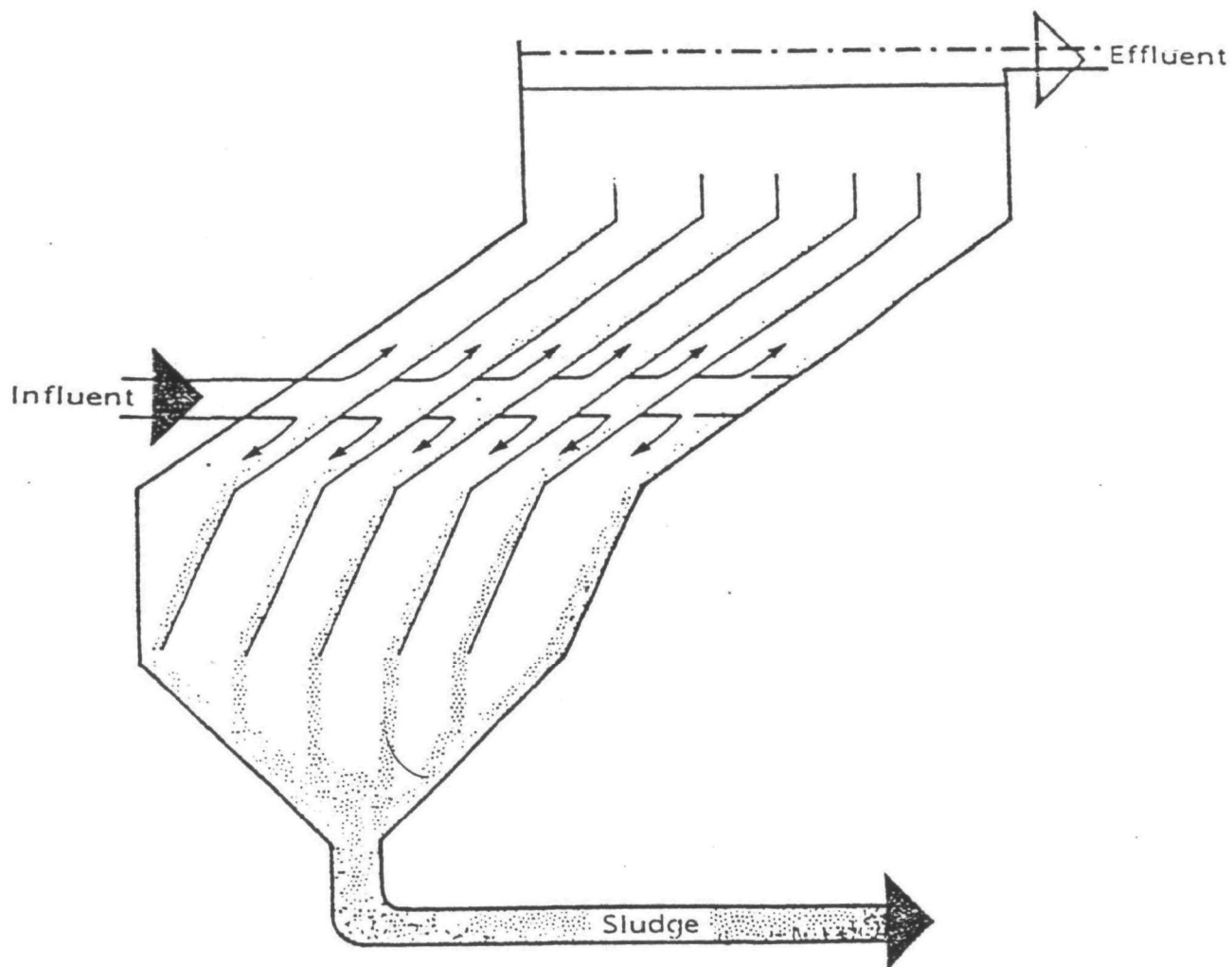


Exhibit 2-36. Inclined Plate Settler

2.7.3.1 *Filter Press* - see Exhibit 2-37

The filter process is generally a simple plate and frame construction. The sludge is fed into the cavities between the plates. When the cavities are full, the hydraulic ram applies pressure. The filtrate is forced out through the filter media and ports in the plate. When the filtrate starts to become concentrated with solids, the ram pressure is released. The dried cake falls onto a conveyor or directly into a hopper. The solids content ranges from 20 - 50 percent by weight.

2.7.3.2 *Vacuum Filters* - see Exhibit 2-38

The sludge slurry is placed in a basin which is placed on a rotary drum consisting of panels of filter material. A vacuum is applied to the panels and the sludge adheres to the panel surface. Water and air are drawn through the panel by the vacuum and are discharged to the filtrate outlet. The solids, adhering to the panel, are discharged in the discharge area by air blown through the panel. Efficiency can be improved by precoating the drum with diatomaceous earth, which acts as a filter medium. This technique is most suitable for dilute sludges. The resultant solids content of the sludge cake is 15 - 40 percent by weight.

2.7.3.3 *Basket Centrifuges* - see Exhibit 2-39

The sludge slurry enters the centrifuge and the heavier sludge is rejected to the inner wall while the clarified liquid is decanted from the top. When the basket is full, sludge solids begin to overflow from the top. At this stage, the centrifuge is decelerated and a rake pushes the sludge downwards off the inner walls. A solids content of 10 - 25 percent by weight can be expected.

2.7.3.4 *Pressure Belt Filter* - see Exhibit 2-40

This method is ideal for treating highly compressible polymer treated sludges. This type of sludge tends to collapse against the filter medium and block the transport of water. The belt filter is made up of a series of belts, each applying more compression to reduce the water content. The throughput can be accelerated by increasing the speed of the belts, but with subsequent degradation of solids content.

2.7.4 Ultrafiltration/Microfiltration

Ultrafiltration/Microfiltration is an alternative to clarification and is an effective means of removing suspended solid particles, oil, grease, large organic molecules and complexed heavy metals. The concentrate is passed over a porous structure until the desired concentration level is achieved. Turbulent flow is required to avoid build up of solids on the surface.

Ultrafilters have a pore size of 0.001 - 0.1 micrometers which is suitable for metal hydroxide precipitates.

Microfilters have a pore size of 1 - 5 micrometers.

Exhibit 2-37. Plate and Frame Filter Press

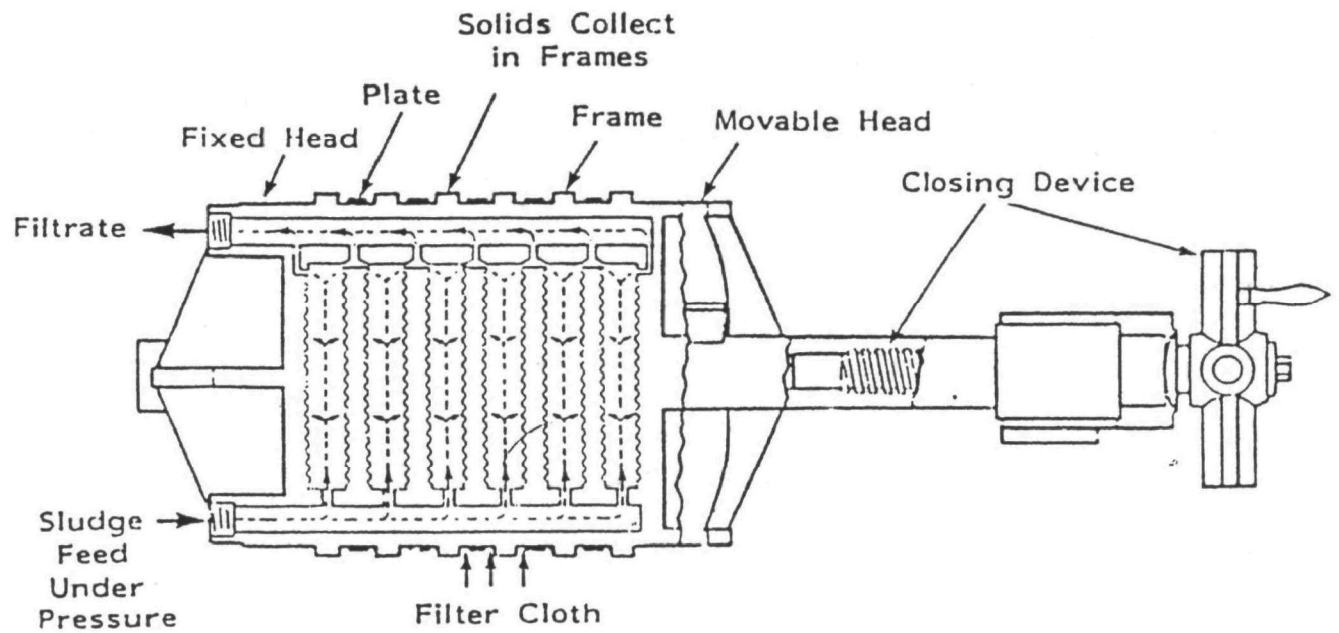


Exhibit 2-38. Rotary Vacuum Filter

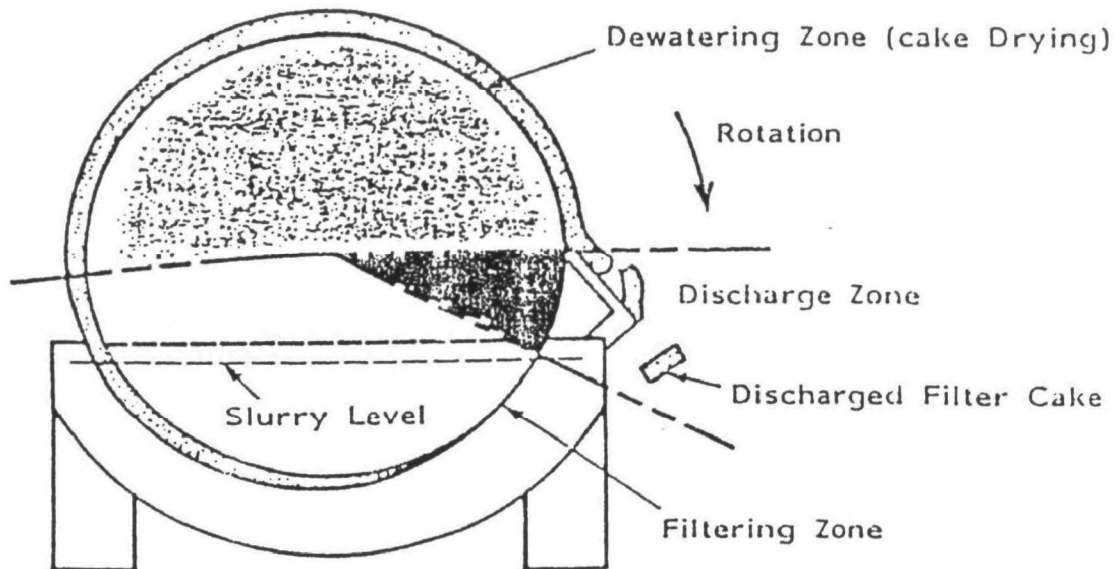


Exhibit 2-39. Basket Centrifuge

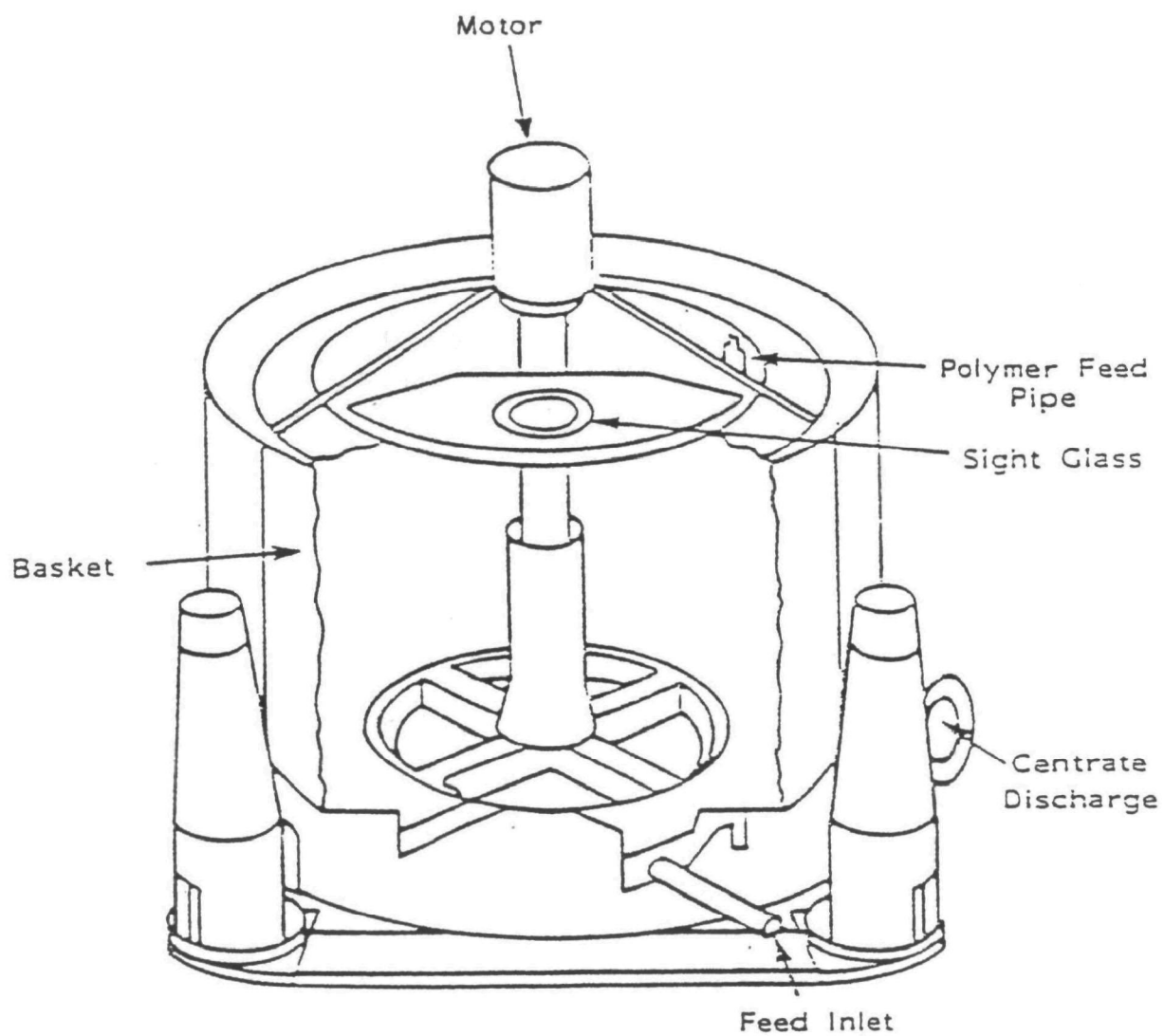
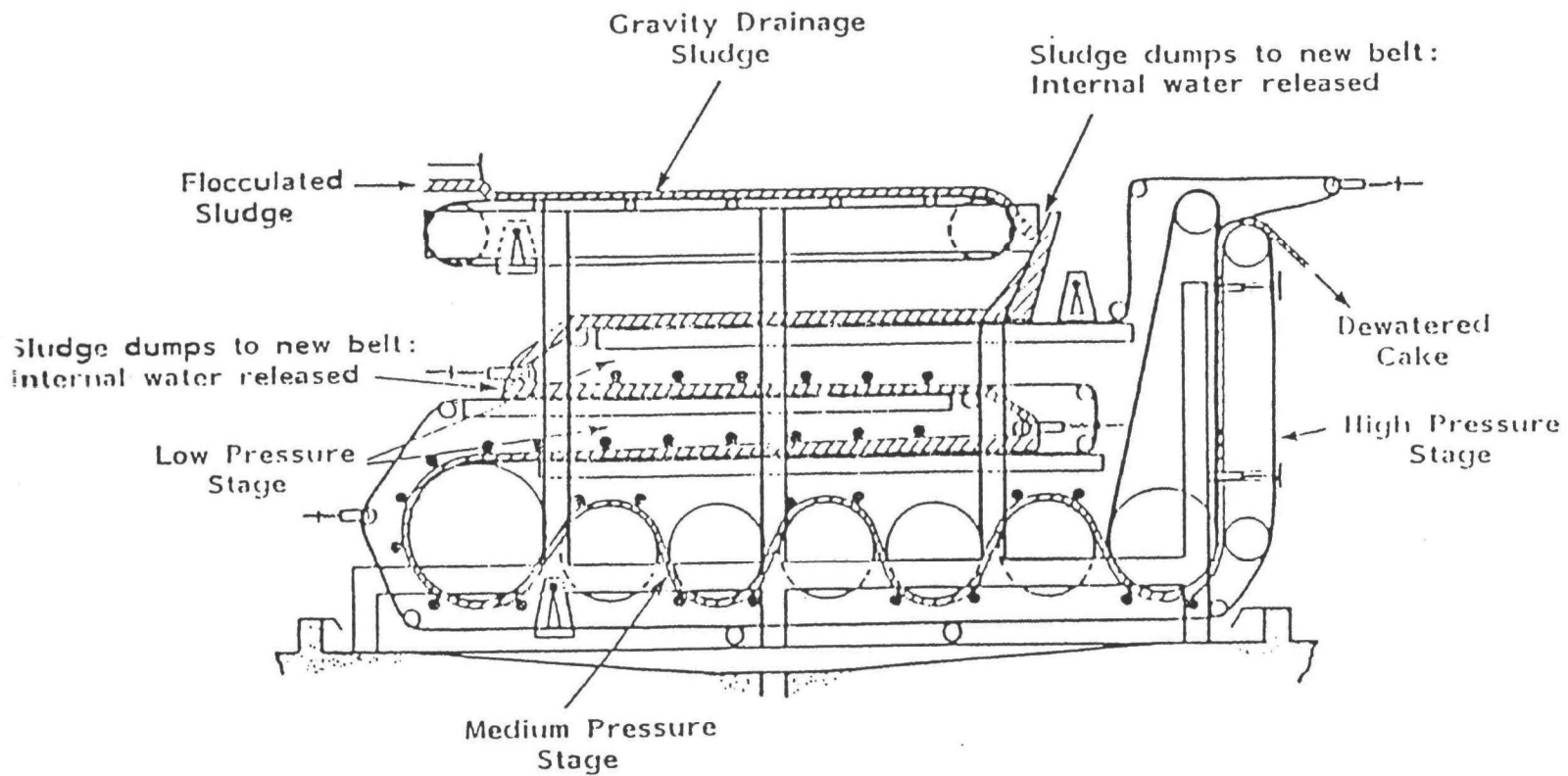


Exhibit 2-40. Pressure Belt Filter



2.7.5 Stabilization/Solidification - see Exhibit 2-41

The final sludge cake treated by any of the above processes, can be disposed of at a chemical landfill or can be further treated. One such method of further treatment is to stabilize or solidify the waste. A binder is used to form a concrete mix which is chemically stable and prevents leaching of contaminants, is able to withstand a great force and can resist crushing.

Stabilization is a chemical reaction which converts inorganic waste to the least soluble, most environmentally inert form. Solidification improves handling, decreases surface area and encapsulates the material in a monolithic solid of high structural integrity.

The waste is added to water and the binder (typical binders are cement, pozzolan, thermoplastic). The stream is mixed, cured at room temperature for over 48 hours and then cooled. It is important to determine the correct ratio of binder-water-waste at the start of each batch to ensure the integrity of the concrete mix.

2.7.6 Fixing Metals in Slags - see Exhibit 2-42

Metal oxides can be bonded to silica to form silicates (or glass). The components are fused into an homogenous liquid and then allowed to solidify. Other chemicals such as soda (sodium oxide), need to be added to achieve fusion at low temperatures. The residual slag can be crushed and sold as aggregate.

Further advantages of this technology are:

1. Hexavalent chromium can be dissolved in slags to about 6 percent and remains resistant to leaching.
2. Dried sludges with nickel and iron oxides can be recovered as ingots by addition of carbon which acts as a reducing agent.

example: 2450 g dried sludge + 1232 g additives
= 1079 g iron-nickel alloy ingots + 857 g slag

2.7.7 Resmelting of Metals

The waste sludge can be sent to a smelting facility in order to extract the metal content.

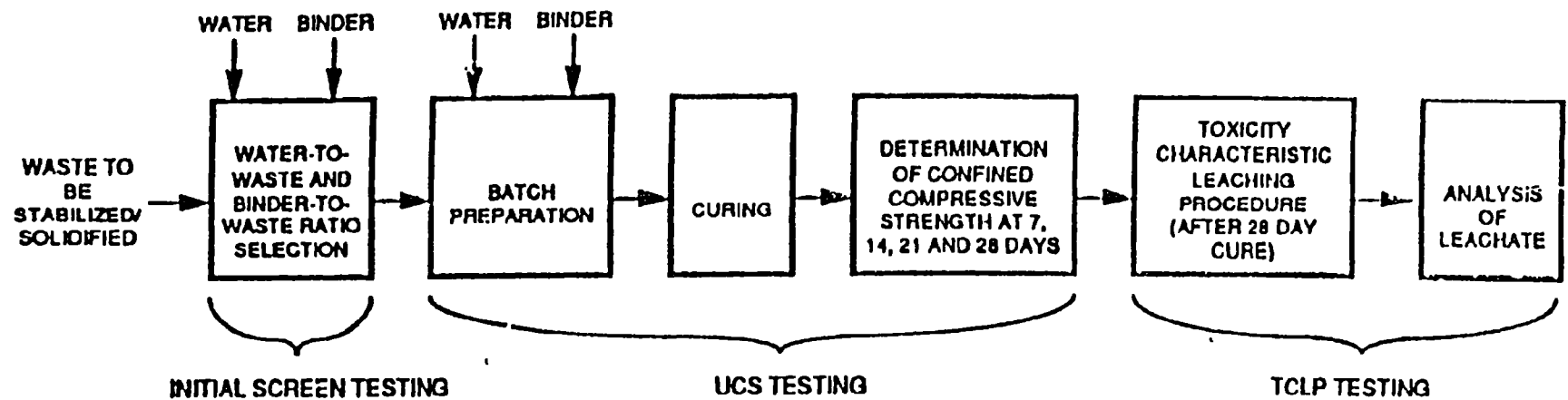


Exhibit 2-41. Flowchart for WES Stabilization/Solidification Processing

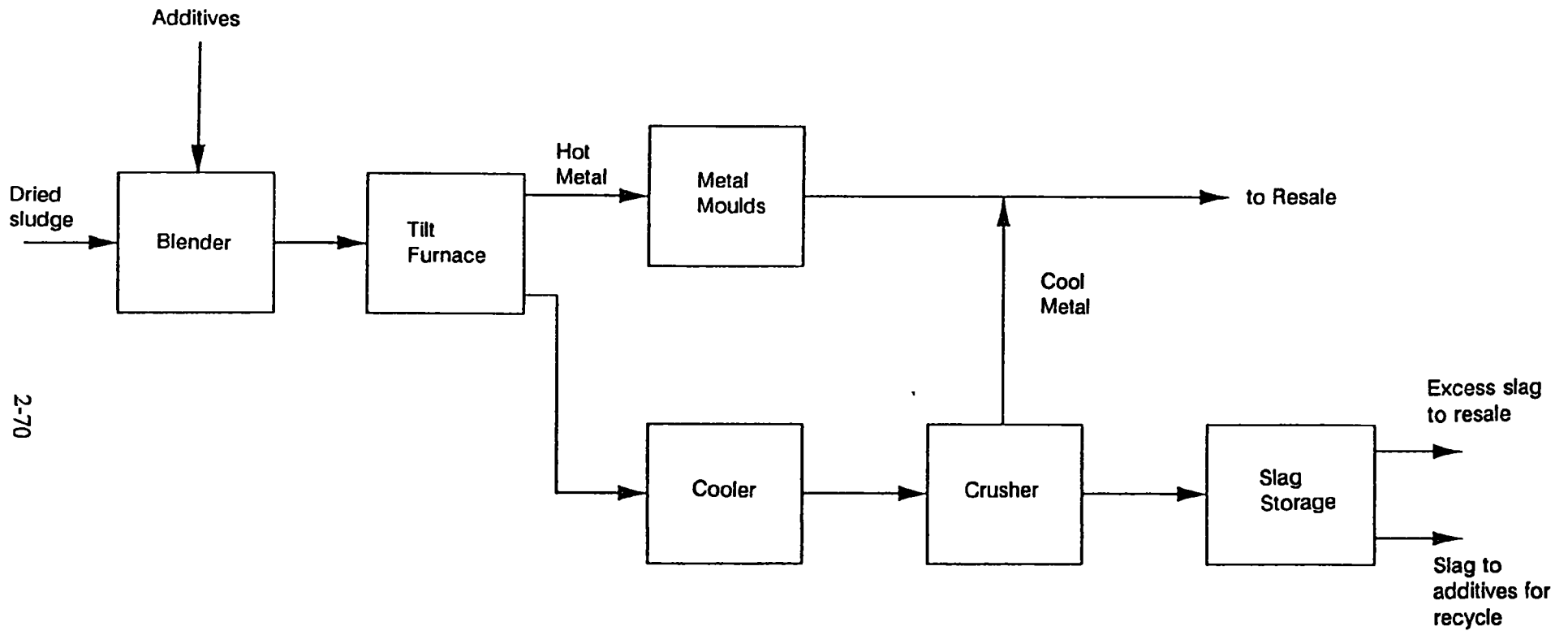


Exhibit 2-42. Metal Slag Recovery System

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Cal-tech management. Final Report

CHAPTER 3
PRINTED CIRCUIT BOARDS

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CHAPTER 3

PRINTED CIRCUIT BOARDS

3.1 INDUSTRY DESCRIPTION

Printed circuit boards are electronic circuits created by mounting electronic components on a non-conductive board, and creating conductive connections between them. The creation of circuit patterns is accomplished using both additive and subtractive methods. The conductive circuit is generally copper, although aluminum, nickel, chrome, and other metals are sometimes used. There are three basic types of printed circuit boards: single sided, double sided, and multi-layered. The manufacturing processes for each type are very similar, with multi-layered boards requiring the additional step of laminating.

3.2 PROCESS DESCRIPTION

There are two common methods of manufacturing printed circuit boards, additive and subtractive. The additive method uses a non-conductive board and deposits conductive material in a circuit pattern by electroless plating. The subtractive method uses a conductive copper-clad board and deposits additional conductive material in a circuit pattern using both electroless plating and electroplating. These two methods collectively are known as pattern plating. An alternative method known as panel plating is described briefly in Section 3.2.4. The additive method generally produces less metal waste, however it is a less common process than the subtractive method. The following discussion focuses on the subtractive method; however, the differences between the two methods are identified.

3.2.1 Raw Materials

The raw materials used in the manufacture of printed circuit boards include process chemicals as well as items that constitute the end product. The primary product materials are board materials, copper and other conductive metals, tin/lead, and electronic components.

Subsidiary processes which require additional raw materials include cleaning, electroless plating, printing of resists and sensitizer, electroplating, and etching. Exhibit 3-1 illustrates the raw materials used in the manufacture of printed circuit boards.

3.2.2 Basic Processes

There are five basic processes common to the manufacture of all printed circuit boards. They are cleaning and surface preparation, electroless plating, pattern printing, electroplating, and etching. These processes are completed in different sequences for the additive and subtractive methods. Exhibit 3-2 illustrates the sequence of operations for both the additive and subtractive manufacturing processes.

3.2.3 Subtractive Processing

3.2.3.1 Board Cleaning and Preparation

The subtractive process uses a copper clad board. The copper material is fixed to the non-conductive board with adhesive, screws, or pressure/heat bonding. These boards are sometimes baked to ensure complete curing of the lamination. The process of making a printed circuit board begins with the preparation of the circuit surface. The holes needed to mount the electronic components are drilled, deburred, and sanded, and the board is cleaned prior to the plating process. Cleaning is accomplished by immersing the boards in a bath of a mild etchant, such as a peroxide/sulfuric acid solution which cleans the copper and removes oxides.

3.2.3.2 Electroless Copper Plating

After cleaning, the boards are electroless plated with copper to provide a conductive layer through the drilled mounting holes. Electroless plating involves the catalytic reduction of a metallic ion in an aqueous solution containing a reducing agent, resulting in deposition

EXHIBIT 3-1. RAW MATERIALS USED IN THE MANUFACTURE OF PRINTED CIRCUIT BOARDS		
PROCESS	CATEGORY	MATERIALS
Cleaning and Prep	Board Materials	glass-epoxy, ceramics, plastic, phenolic paper, copper foil
	Cleaners	sulfuric acid, fluoroacetic acid, hydrofluoric acid, sodium hydroxide, potassium hydroxide, trichloroethylene, perchloroethylene, methylene chloride
Electroless Plating	Electroless Copper Bath	copper sulfate, sodium carbonate, sodium gluconate, Rochelle salts, sodium hydroxide, formaldehyde
	Catalysts	stannous chloride, palladium chloride
Pattern Printing and Masking	Screens	silk, polyester, stainless steel
	Screen Inks	composed of oil, cellulose, asphalt, vinyl or other resins
	Resists	polyvinyl cinnamate, allyl ester, resins, isoprenoid resins, methacrylate derivatives, polyolefin sulfones
	Sensitizers	Thiazoline compounds, azido compounds, nitro compounds, nitro aniline derivatives, anthones, quinones, diphenyls, azides, xanthone, benzil
Electroplating	Electroplating Baths	copper pyrophosphate solution, acid-copper sulfate solution, acid-copper fluoroborate solution, tin, lead, gold, and nickel plating solutions
Etching	Resist Solvents	ortho-xylene, meta-xylene, para-xylene, toluene, benzene, chlorobenzene, cellosolve and cellosolve acetate, butyl acetate, 1,1,1-trichloroethane, acetone, methyl ethyl ketone, methyl isobutyl ketone
	Etchants	Sulfuric and chromic acid, ammonium persulfate, hydrogen peroxide, cupric chloride, ferric chloride, alkaline ammonia

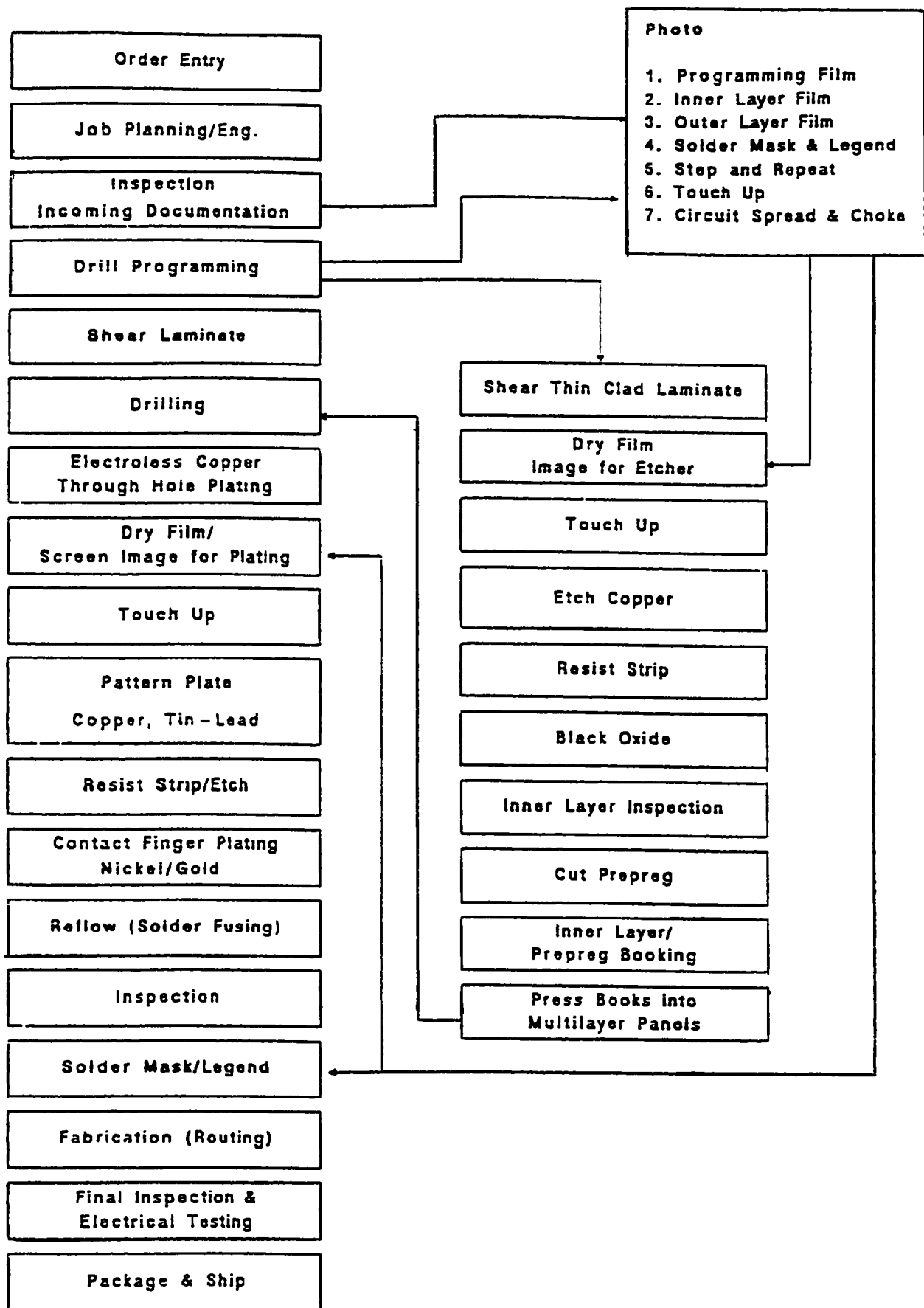
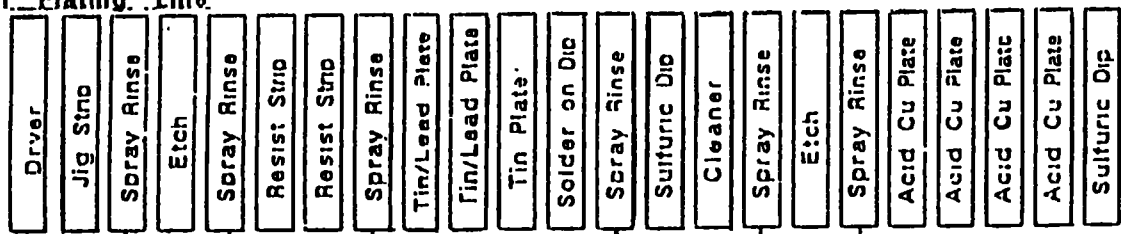
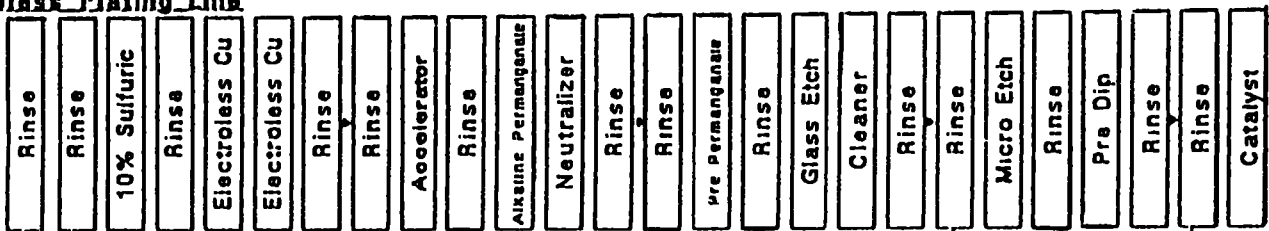


Exhibit 3-2. Printed Circuit Board PCB Manufacturing Process

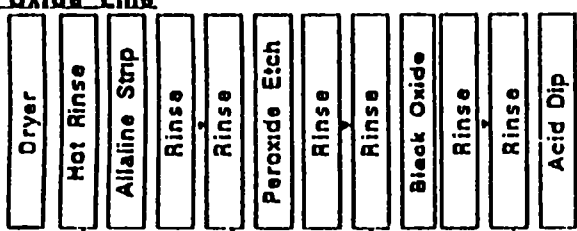
P
Pattern Plating Line



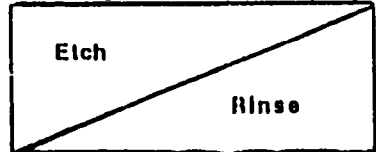
E
Electroless Plating Line



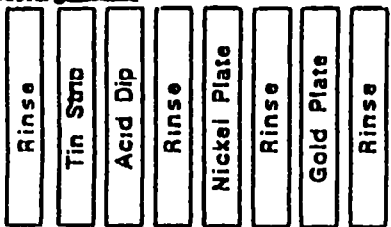
B
Brown Oxide Line



Etching Machine



ab
Plating Line



Machine Shop Effluent

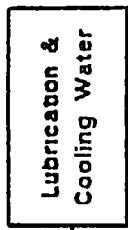
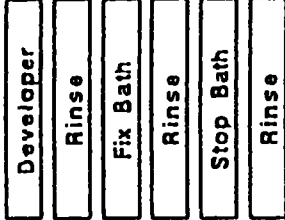


Photo Lab



Gold Recovery

Scrubber Water

Tin / Lead Sump

Unchelated Copper Sump

Chelated Copper Sump

Nickel Sump

Heavy Metal Free Sump

without the use of external electric energy. The deposited layer is very thin, covers the substrate uniformly, but is too thin to constitute a final circuit. To build the thickness and strength of the circuit, additional layers of conductive material must be applied to the board.

3.2.3.3 Pattern Printing and Masking

Building up the thickness of the individual circuit is done with a selective deposition of conductive material rather than the overall deposition practiced in the electroless setup. To add metal on just the circuit areas, a layer of plating resist is applied to the non-circuit area of the board, using screen printing or photolithography methods. This resist prevents the adherence of electroplated metal to the non-circuit areas of the board. The circuit areas then receive multiple layers of electroplated metals.

3.2.3.4 Electroplating of the Circuit Area

Electroplating is accomplished by immersing the board in a copper plating solution such as acid-copper sulfate along with a pure metal anode. The anode is then electrically charged, causing it to dissolve and be deposited on the board. The plating resist prevents the deposition of metal on the non circuit areas. Several layers are deposited in this manner, including a final layer of tin/lead to act as an etching resist.

3.2.3.5 Etching

Once the circuit has reached the desired thickness, the plating resist is stripped from the non-circuit area exposing the non-circuit areas. The boards are then run through an etching bath to remove the copper from the non-circuit areas. The circuit areas are protected from this etching process by the final layer of tin/lead deposited during electroplating. The resulting board has a strong electronic circuit, with conductive metal in the mounting holes and along the circuit path. The electronic components are subsequently mounted to complete the board.

3.2.4 Additive Processing

The additive process uses a plain board, so the baking step is not required. It also reverses the electroless plating/print resist steps. In the additive method the plating resist is printed on non-circuit areas, defined by pattern printing and masking, before the electroless plating. This prevents any copper from adhering to the non-circuit areas of the plain board and, most significantly, eliminates the need to etch copper away from the non-circuit areas. Finally, the circuit is built up to the desired thickness using electroless plating rather than electroplating.

3.2.5 Alternative Process

Both the additive and subtractive methods described above are pattern plating methods. In pattern plating copper or other conductive metals are deposited only on the circuit areas, and in the board's component mounting holes. An alternative method is panel plating. In this method, the entire board is electroplated with copper to the desired circuit thickness, and an etching resist is applied to the circuit areas. The board is then etched to remove copper from the non-circuit areas. This method results in the production of more metal waste than pattern plating, since a greater amount of copper is deposited on, and then removed from, the board.

3.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS AND WASTE STREAMS

Each of the five common processes associated with the manufacture of printed circuit boards results in specific emissions and waste streams. Air emissions customarily occur as part of the board preparation process. Although rinse water is not the primary waste stream of any one process, taken in total, it is the largest source of hazardous waste in the manufacture of printed circuit boards.

3.3.1 Air Emissions

The emissions of air pollutants from the manufacture of printed circuit boards are predominantly part of the board cleaning and preparation process while other emissions are generally of much less significance. The majority of the emissions are acid fumes and organic vapors from the cleaning processes. Some particulates are also emitted in the drilling and finishing of the boards. Proper ventilation and exhaust of all process baths, rinse operations, and mechanical operations is essential to managing the air emissions of a printed circuit board manufacturing operation and can also contribute to reduction in liquid and metal waste generation.

3.3.2 Waste Streams

Each manufacturing process may generate multiple waste streams. Rinse water and other rinse solutions are usually the largest streams by volume but are generally lower in concentration of hazardous chemicals than spent process baths. Exhibit 3-3 illustrates the origins of each waste stream in the manufacturing process. Exhibit 3-4 contains a detailed listing of the constituents of each waste stream. To put in perspective the rate of waste generation for the critical streams of waste water, acid copper wastes, and total sludge from metal bearing waste streams, Exhibit 3-5 has been developed to illustrate typical waste generation rates. Contamination of rinse streams can be minimized by strategies that reduce drag-out of process solutions. Treatment and reuse of rinse streams is also effective in reducing overall waste generation. Such strategies are summarized in Section 3.4. Detailed discussion of many of these strategies is found in the Electroplating chapter of this manual.

3.3.2.1 Cleaning and Preparation

Spent acid and alkaline solutions, fluoride, and spent halogenated solvents from the cleaning steps compose the primary wastes from this process. In addition, the wastewater stream from the rinsing operation can contain suspended metals and particulate board materials.

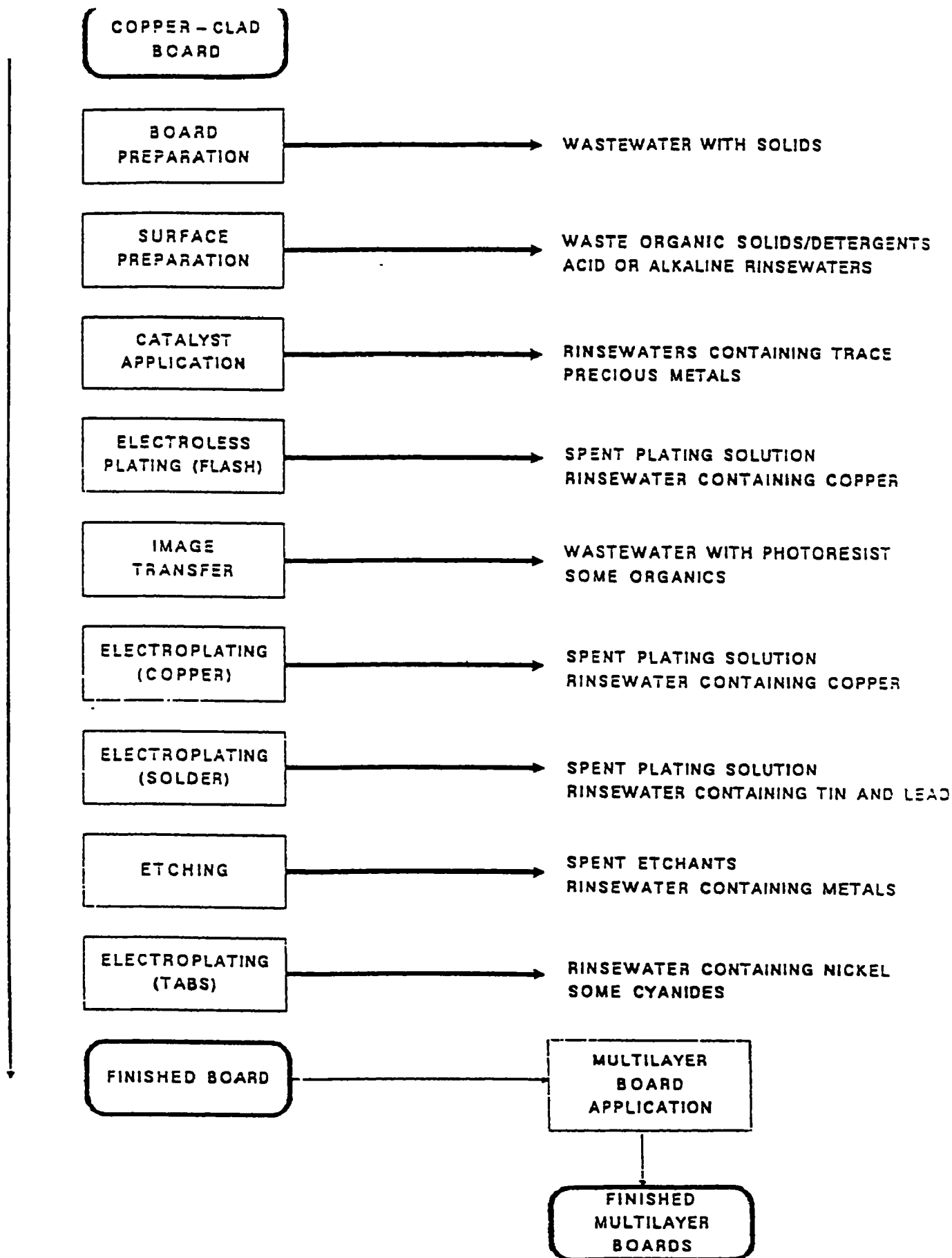


Exhibit 3-9. Printed Circuit Board Production Flowsheet and Waste Generation (15)

EXHIBIT 3-4. WASTE STREAMS FROM THE MANUFACTURE OF PRINTED CIRCUIT BOARDS		
WASTE SOURCE	WASTE STREAM DESCRIPTION	WASTE STREAM COMPOSITION
Cleaning/Surface Preparation	Spent acid/alkaline solution	metals, fluoride, acids, halogenated solvents, alkali, board materials, sanding materials
	Spent halogenated solvents	
	Waste rinse water	
Electroless Plating	Spent electroless copper bath	acids, stannic oxide, palladium, complexed metals, chelating agents, copper
	Spent catalyst solution	
	Spent acid solution	
	Waste rinse water	
Pattern Printing and Masking	Spent developing solution	vinyl polymers, chlorinated hydrocarbons, organic solvents, alkali
	Spent resist removal solution	
	Spent acid solution	
	Waste rinse water	
Electroplating	Spent plating bath	copper, nickel, tin, tin/lead, gold, fluoride, cyanide, sulfate
	Waste rinse water	
Etching	Spent etchant	ammonia, chromium, copper, iron, acids
	Waste rinse water	

EXHIBIT 3-5. ESTIMATED WASTE GENERATION LEVELS OF COPPER FOR TYPICAL PRINTED CIRCUIT BOARD MANUFACTURER		
	PRINTED CIRCUIT BOARD FACILITY	
OPERATION	SMALL	LARGE
PC Board Production Volume M ² /day (sq.ft./day)	23 (250)	371 (4,000)
Water Usage and Discharge litres/day (gal/day)	47,313 (12,500)	757,000 (200,000)
Acid Copper Plating Tank Volume of Drag-out ltr/day	3	48
Copper Metal Produced Kg/day	.08	1.2
Equivalent to Kg/year	18.75	300
Percentage of Total Acid Copper Wastes	10%	10%
Total Copper Sources Metal Produced Kg/day	.75	12
Metal Produced Kg/year	187	3,000
Total Copper in Untreated Waste mg/kg	15	15
Sludge Generation @ 3% Copper metric tons/year (tons/year)	5.44 (6)	907 (100)

3.3.2.2 Electroless Plating with Copper

The waste streams in this operation are spent catalyst solutions, spent electroless copper bath, spent acid cleaning solution, and waste rinse water. These streams contain acids, stannic oxide, palladium, complexed metals, and chelating agents, but the major component of waste is copper.

3.3.2.3 Pattern Printing and Masking

This process uses developing solution, resist removal solution, and acid cleaning solutions. The process' waste streams are comprised of these spent solutions, and waste rinse water. The streams contain vinyl polymers, chlorinated hydrocarbons, organic solvents, and alkali.

3.3.2.4 Electroplating and Electroless Plating

Spent plating bath (containing copper, nickel, tin, lead, and gold) is the major waste stream from this process. This waste stream can also contain fluoride, cyanide, and sulfate. Waste rinse water is a secondary waste stream (in terms of the concentration of hazardous waste) but is the highest volume stream and requires extensive treatment. Contamination of this rinse water is a direct result of drag-out, and can be greatly reduced by drag-out reduction strategies.

3.3.2.5 Etching

The majority of waste from this process is in the spent etchant, which contains ammonia, chromium, copper, iron, and acids. The quantity of waste rinse water is also an important factor in this process, and once again represents a high volume stream.

3.4 POLLUTION PREVENTION, WASTE TREATMENT, AND CONTROL SYSTEMS

The methods of controlling waste from the manufacture of printed circuit boards vary from proactive pollution prevention (waste minimization) techniques to reactive waste treatment. Each of the five subsidiary processes in board manufacture can be subjected to: 1. product substitution; 2. process modification including recycling and resource recovery; and 3. waste treatment strategies. While these technologies are discussed in detail in Chapter 2 - Electroplating, the significant features of the descriptions and process flow diagrams from that part of the manual are summarized below.

The industry has two significant production method substitutions available which can have a very positive effect on the volume of wastes produced in printed circuit board manufacturing. The first, the use of Surface Mounted Devices (SMD), can reduce the overall size of a printed circuit board by more than 50%, leading to lower raw material usage rates. The second, Injection Molding of substrate materials coupled with additive plating methods, can cut the generation of metal waste significantly. Each of these methods has defined drawbacks which must be carefully considered, especially the increased use of chloroflourocarbons in SMD technology.

The following discussion focuses on strategies appropriate to each of the subsidiary processes for substitution, recycling and waste treatment. Some relative advantages and disadvantages of the available options are also presented.

3.4.1 Cleaning and Board Preparation

This process includes the preparation and cleaning of boards and the cleaning and maintenance of manufacturing equipment such as electroplating racks. The primary sources of hazardous waste streams in this process are spent cleaning bath and waste rinse water. A number of proactive methods can be utilized to minimize these waste streams, and reactive waste treatment and recycling strategies can reduce their impact.

3.4.1.1 Material Substitutions

Reduction of wastes can be achieved by substituting abrasive or non-chelated cleaning agents for traditional aqueous cleaning methods. Non-hazardous abrasives can be used in blasting or vibratory cleaning techniques that generate less waste than chemical cleaning processes. The disadvantage is that they can only be used prior to the insertion of electronic components into the board. Non-chelated cleaning chemicals, such as alkaline cleaners, are less effective than chelated chemicals. However, if they provide adequate cleaning they eliminate the need for treatment chemicals that are required to counteract the effect of chelating compounds on the waste stream. Chelating compounds improve the solubility of metal ions, but they also inhibit precipitation of the ions in the waste stream. To counteract this effect, a reducing agent such as ferrous sulfate must be used to break down complex ions, resulting in a significant increase in iron precipitation in the waste stream. Non-chelated cleaners will reduce the overall volume of sludge by eliminating the presence of chelating compounds and treatment chemicals in the waste stream. Similar, although less dramatic, reductions can be obtained by using mild chelators that require lower concentrations of reducing treatment chemicals. One drawback to the use of non-chelated cleaners is the need for increased filtration to remove the solids that form in the bath.

3.4.1.2 Process Modifications

3.4.1.2.1 Extending Bath Life

The most important process modifications that can be introduced in the cleaning operations result in an extension of the cleaning bath life. Bath life can be extended by reducing impurities and reducing solvent loss due to drag-out. Several factors influence the drag-in of particle contamination in the cleaning operation. Impurities enter the bath from three sources: racks, drag-in, and water, chemical, or air quality.

Rack Design and Maintenance

Proper rack design and maintenance can minimize corrosion and salt buildup on racks that leads to contamination of the bath. Fluorocarbon coatings can also be applied to racks to prevent corrosion, with the added effect of reducing drag-out on the racks. Another process modification recommended for the reduction of cleaning bath contamination is the use of a multi-stage cascading rinse system to clean electroplating racks. These racks are generally cleaned with a nitric acid bath. This type of system circulates rinse solution through a series of tanks, counter to the flow of the work. In this arrangement, the work is first rinsed in the least clean tank, and then in successively cleaner baths. The spent solution from each bath is continuously moved forward to replenish the previous bath, with the effluent from the first bath used to replenish the process bath if possible. Such a system has the potential to reduce the generation of waste nitric acid by as much as 75% over a single tank system. The multi-tank arrangement will slow the degradation of the total volume of nitric acid used for rack cleaning. Furthermore, by having the effluent from each stage flow counter to the direction of travel of the racks, and serve as makeup for the previous stage, less bath makeup will be used. This type of rinsing system is described in detail in the Electroplating chapter section 2.5.2 of this manual.

Board Rinsing Between Operations

Efficient rinsing of boards between process steps will help reduce drag-in of particulate contaminants from the board drilling and finishing step. Rinse efficiency can be improved by increasing the turbulence between the board and the rinse water, increasing the contact time of the rinse water, and ensuring that sufficient volume of rinse water is used. A variety of methods for accomplishing these improvements are available. They include the use of: closed circuit rinses, supplementary spray rinsing, fog nozzles, increased agitation, multiple-stage counter current rinsing, and rinse water controls to manage flow in rinsing baths. Two very effective rinse control technologies are flow regulators, which maintain a predetermined optimal flow rate of rinse water, and conductivity probes, which can detect increased levels of dissolved solids in the rinse stream and trigger a greater rinse flow to compensate for the

increased solids levels. Immersion rinsing can be effectively combined with spray and fog methods to reduce overall rinse water usage, and reduce drag-in at subsequent operations. Counter flow systems such as the one described for rack cleaning can be very effective. Total rinse water used can be reduced by having the rinse flow counter to the work. This flow will concentrate the contamination of the rinse water in the early tanks. The effluent from the first rinse tank can be further concentrated by evaporation and used as influent for the bath. Exhibit 2- shows such a rinse system.

Water, Chemicals and Air Makeup

The use of deionized or distilled makeup water to compensate for evaporation will help reduce the introduction of minerals and other solids into the bath. Such contamination can lead to impurity buildup, requiring a change of the bath solution. Proper chemical storage can help reduce impurities as well, by avoiding unwanted chemical reactions that result in the generation of bath contaminants. All cleaning chemicals should be stored in non-reactive mixtures, or each chemical used in the cleaning baths should be stored separately. The introduction of airborne particulates into bath solutions can lead to premature exhaustion of the bath. Proper ventilation and exhaust of board preparation areas will help reduce this source of contamination.

Filtering

Reducing the introduction of contaminants into the bath provides dramatic improvement in bath life. Further increases can be gained through the use of effective filtering devices to remove contaminants that do find their way into the cleaning solution.

Active filtering can be accomplished by circulating the solution past a variety of available filtering devices, and passive filtering can be accomplished by removing settled particulates from the bath after prolonged shut down periods.

3.4.1.2.2 Reducing Chemical Drag-out

Once sources of bath contamination have been reduced as much as possible, additional bath life can be gained by reducing solvent loss from the effects of drag-out. Reducing drag-out has the double effect of prolonging cleaning bath life, and reducing the contamination of rinse water. Several factors lead to increased drag-out including large board size, high solution viscosity, high surface tension, and other factors affecting the drainage of fluid from the board, such as its withdrawal from the cleaning bath. Board size is a design issue, and frequently beyond the control of the manufacturer. Whenever possible, board size should be reduced to help minimize waste generation. The following discussion focuses on the methods more readily subjected to the manufacturer's control.

Chemical bath concentration

Drag-out can be reduced by controlling the bath chemical concentration. This technique can cut drag-out in two ways: 1. lowering the concentration of chemicals reduces the waste present in any drag-out that does occur; 2. reduced chemical concentrations will lower the viscosity of the bath solution, allowing the fluid to drain off the boards more rapidly upon withdrawal. Initial bath mixtures can be of lower concentration because of their freshness. Further chemicals can be added to the solution as the bath ages to maintain its level of effectiveness. Manufacturers should run experiments to determine the minimum effective chemical concentration for the bath, and the rate at which further chemicals should be added to compensate for chemical age and degradation. Minimum adequate concentrations are frequently lower than those recommended by the chemical manufacturer.

Operating the bath at higher temperatures

In addition to making changes in chemical concentration, viscosity can be further reduced by operating the bath at a higher temperature. The viability of this option must be carefully examined because of increased energy costs, increased rate of evaporation, and the need for additional air pollution controls.

Wetting agents

The use of wetting agents can reduce the surface tension of the bath solution, allowing greater drainage of the solution from the boards upon withdrawal from the bath. This option has some potential problems, particularly the tendency to cause foaming problems in the bath. It should be evaluated carefully, and if appropriate agents can be identified, the technique has the potential to yield drag-out reductions of up to 50%.

Board withdrawal and drainage

Proper withdrawal of the boards from the bath is very important to drag-out reduction. The boards should be withdrawn slowly, and should be allowed to drain sufficiently to minimize the amount of solution that adheres to their surface. Of the two requirements, slower withdrawal can have a more beneficial effect than increased drainage time, and will better avoid the possibility of adverse chemical oxidation effects on the board. The minimum recommended drainage time is 10 seconds.

3.4.1.3 Waste Treatment

A variety of treatment techniques, leading to neutralization or recycling of wastes, are available in the cleaning processes. Rinse water in particular is easily subjected to reuse and recycling strategies that can significantly reduce their volume and chemical concentration.

Recycling cleaning agents and recovering metal contaminants. Waste from the cleaning of boards can be treated to recover both the cleaning acid and the metal particles removed by the cleaning operation. Boards are cleaned using a peroxide/sulfuric acid solution, a mild etchant that removes oxides and cleans copper prior to plating. There are two methods that can be used to treat the spent acid bath. The spent cleaning bath can be brought off line and cooled, causing the suspended copper to crystalize as copper sulfate. These crystals can be dissolved into solution and treated with activated carbon to remove the organics. They can then be

used to top off the copper electroplating bath. The supernatant from the cooled spent cleaning bath can then also be returned to the bath. Alternatively, ion exchange can be used to regenerate the solution, or it can be returned to the tank and replenished with oxidizers.

Recycling rinse solutions. Rinse solutions can also be reused for a variety of purposes. One option is to use the effluent from a rinse that follows an acid cleaning bath as the influent for a rinse following an alkaline cleaning bath. If both systems require the same flow rate, 50% less rinse water would be used to operate them. This system can actually improve rinse efficiency for two reasons. First, the chemical diffusion process is accelerated by the reduced concentration of the alkaline material at the interface of the drag-out film and the surrounding water. Second, the neutralization reaction reduces the viscosity of the drag-out film. These methods have some potential problems. For example, unwanted precipitation of metal hydroxides onto the cleaned boards can occur. For this, and other reasons, careful investigation prior to combining acid and alkaline rinses is warranted.

Other recycling options include using acid cleaning rinse effluent as a rinse for pieces that have undergone a mild acid etch process. Rinses containing a high level of process chemicals can be concentrated through evaporation and returned to the process baths. As previously discussed, closed circuit rinsing can dramatically reduce the hazardous chemical content of the waste stream. Effluent from a critical or final rinse can be used for influent in rinses that do not require high efficiencies. This is the same principle that closed circuit, counter flow rinsing systems utilize, but can be applied in situations where such systems are not cost effective.

3.4.2 Pattern Printing and Masking

The techniques available to minimize waste in this process are very similar to those used in the photoprocessing industry. For general information on these methods, see the *Waste Minimization Opportunities Assessment Manual* (USEPA, 1988). The procedures discussed below have demonstrated high potential for improvement.

3.4.2.1 Material Substitutions

Aqueous resist formulas. Water based resists are currently being substituted for solvent based resists throughout the printed circuit board industry. The benefits of such a substitution include the elimination of toxic spent solvents from the processing and application of resists.

3.4.2.2 Process Modifications

Two significant process modifications, screen printing and use of dry resist, can be used in the pattern printing and masking process. Each of these opportunities is limited by the effectiveness of the technology in special, high-demand situations, but should be explored and implemented when feasible.

3.4.2.2.1 Screen-Printing

Transition of photolithography operations to screen-printing offers the opportunity to eliminate the use of developers in applying resist. Screen-printing technology has advanced sufficiently to overcome the major obstacle to this transition, resolution of the image. Screen-printing techniques resulting in 0.025 cm (.01 inch) resolution are now available, but were not previously achievable.

3.4.2.2.2 Dry Photoresist Removal

The Asher dry photoresist removal method can be used to eliminate the use of organic resist stripping solutions. This method is very common in the semiconductor industry, but has not gained widespread use in the printed circuit board industry as yet. This may be due to the greater thickness of resists used to manufacture printed circuit boards.

3.4.2.3 Waste Treatment

3.4.2.3.1 Recycle Photoresist Stripper

Photoresist stripper can be reused following a simple filtering operation. Photoresist is a polymer material that remains in the stripper tank in small flakes that slowly settle to the bottom. These flakes can be actively filtered out of the tank, or the resist stripper solution can be filtered into a clean tank and reused. Residue buildup will degrade stripper performance before chemical degradation in most cases. Multi-stage stripper tanks can also help reduce this problem. Flakes of polymer that adhere to the board in the first tank can be removed in the second tank, leaving less waste to enter the rinse water stream.

3.4.3 Electroplating and Electroless Plating

Source reduction efforts associated with the electroplating and electroless plating processes center on reducing the hazardous nature of the materials used, extending process bath life, improving rinse efficiency, and recovering/reusing spent materials. Many of the techniques are similar to those discussed for the cleaning and board preparation processes. There is potential to avoid the use of chemical plating operations altogether. Low volume manufacturers can use mechanical etching of copper clad boards for prototype and specialty boards. This method uses computer design of the circuit pattern and a stylus etching apparatus. It is not a viable process for high volume production, but should be considered for prototyping and low volume production.

3.4.3.1 Material Substitutions

Use of non-cyanide plating baths and stress relievers. Water soluble cyanide compounds of many metals are frequently added to electroless copper plating baths to relieve internal stress in the deposited layer. Polysiloxanes may be substituted for cyanides to reduce the hazardous nature of spent bath solutions.

Use of purer anode materials. During the plating process, impurities in the anode matrix are frequently left in the plating bath, contributing to the degradation of the solution. The use of purer anode materials will reduce this problem.

3.4.3.2 Process Modifications

Use of anode bags. Anode bags, wrapped around the anode, can be used to further reduce the contamination of the plating bath by trapping impurities. These bags will also prevent pieces of decomposed anode from falling into the plating bath.

Position the workpiece properly on the plating rack. When racks are removed from the plating bath, plating solution will adhere to the surface of each board on the rack. Boards should be placed to minimize this drag-out. Optimal placement should be determined experimentally, but the following guidelines may prove useful:

- Orient the plated surface as close to vertical as possible.
- Rack with the longer dimension of the board oriented horizontally.
- Rack with the lower edge tilted slightly from the horizontal so runoff will be from a corner rather than an edge.

Use computerized/automated control systems. Computerized process control systems can reduce the chance of unexpected decomposition of the plating bath. Board handling and bath monitoring systems are available but require significant capital outlays and improved worker training.

Recover drag-out from baths. Some drag-out will occur despite the best efforts to avoid it. The drag-out solution can be partially recovered by placing drainage boards, tilted towards the process bath, between plating operations and following rinses. The use of such drainage boards can capture and return solution that might otherwise fall to the floor and enter the waste water system on washdown.

Use of drag-out tanks. Another method for recovering drag-out is the use of static rinse tanks called drag-out tanks. Such tanks do not have a continuous inflow of rinse water, so the chemical concentration of the rinse solution increases as more work passes through it. Eventually the concentration reaches a level suitable for re-use in the process bath.

This is most advantageous for baths that are operated at an elevated temperature. Such baths suffer evaporative losses that can be restored by using the spent rinse water. Since these tanks do not have a continuous flow of water to create turbulence, air is sometimes used to create an agitation effect that improves rinsing although mechanical agitation may introduce fewer impurities. Manufacturers should carefully examine the potential for drag-out tanks before using them.

Maintain bath solution quality. In addition to the techniques used to extend bath life discussed in earlier sections, the quality of the solution in a process bath will have a distinct impact on its ability to perform, and thus to extend the effective life cycle of the bath. The methods to extend bath life outlined in Section 3.4.1.2 are applicable to the extension of plating baths. It is important to focus attention on maintaining optimum bath conditions. Many facilities use drag-out as a means of purging process baths of impurities that degrade their performance. From an environmental standpoint, this is a poor technique since it does not directly address the issue of impurity formation, results in a high loss of valuable process solutions, and moves the problem downstream to the treatment unit. By maintaining optimum bath conditions, the useful life of a bath can be extended. For example, frequent monitoring of the solution can lead to timely additions of reagents and stabilizers that will prolong bath life. Good bath temperature control can maximize bath performance and proper maintenance and cleaning of cooling/heating coils improves the heat transfer needed to maintain bath temperatures. Mechanical agitation rather than air agitation should be used when feasible. Air can introduce oil and carbon dioxide into process baths, shortening their life. Continuous filtering and treatment with activated carbon will prevent surface roughness on the plated boards. Since filters can seldom remove solids at the same rate as they are introduced into a bath, the filtering flow rate should be kept as high as possible, and the filter should be run

even when the bath is not in use. In general, any strategy that leads to the removal of impurities from the bath should be pursued. Innovative approaches, such as temporarily reducing the bath temperature to encourage the crystallization of metallic salts, and improve their removal by filtration, should be applied to all process baths.

Improve rinse efficiency. The discussion in Section 3.4.1.2 identifies a number of methods for improving rinse efficiency. These methods are equally applicable to the electroplating operation.

One additional issue which should be investigated to improve rinse efficiency is the design of rinsing systems. Many systems create excess rinse water because of poor design. Oversizing of pipes, the inability to turn systems off easily when not needed, lack of effective flow and pressure controls, and other design problems can lead to a significant increase in waste stream volume.

3.4.3.3 Waste Treatment

Segregate waste streams to promote recycling. In many printed circuit board manufacturing facilities rinse streams, and even process waste streams, are mixed and treated together. This approach places limits on the treatment strategies which can be employed, and on the types of reusable byproducts that can be obtained from treatment. The segregation of waste streams can alleviate this problem and promote efficient individualized treatment of specific waste streams.

3.4.3.3.1 Recover Metal Value From Bath Rinses

Historically, metal recovery has not been an economical option for manufacturers of printed circuit boards. However, new regulations governing effluent pretreatment have made recovery a more attractive approach. Increased regulatory requirements for sludge disposal have also led to renewed focus on recovery/reuse of the metal content of waste streams. As a

result, manufacturers may now find it advisable to recover copper, other metals, and metal salts lost due to drag-out of process chemicals. Chemical metal recovery costs are dependent on a variety of variables. Unit size, space available, production down time, and layout of equipment should all be considered before selecting and implementing a strategy.

Evaporation. Waste rinse water can be evaporated, using single or multiple effect evaporators, yielding a concentrated solution with a high metal content. Once the metal concentration is equal to that of the process bath, the solution can be used to top off the bath. Well designed evaporative systems can even recapture the water vapor, condense it, and reuse it as rinse water. Despite its relatively high energy requirements, this technique is simple and easy to use. A distinct disadvantage of this approach is the tendency of calcium and magnesium salts present in the original rinse water to contaminate the process bath, resulting in rapid deterioration of the bath quality. Deionization or softening of influent rinse water can alleviate this problem.

Reverse osmosis. Semipermeable membranes can be used to selectively filter rinse solutions, reconcentrating those constituents of the rinse stream that can pass through the membrane, and leaving a regenerated rinse solution behind. Such membranes cannot fully recover all process bath constituents, therefore the makeup concentrations achieved are not always equal to original bath concentrations. The membranes are also subject to wear from pH extremes and prolonged exposure to pressure. This approach has proven to be particularly effective for nickel plating baths and rinses.

Liquid membranes. Liquid membranes, composed of polymeric materials loaded with ion-carrying solution, can be used to remove chromium from rinse waters and spent etching baths. The solution drawn through the membrane forms a tertiary amine metal complex, which can be treated with sodium hydroxide solution.

Ion exchange. Ion exchange recovers metals from a dilute rinse stream by passing the solution through a bed containing a resin material. The resin replaces the organics in the solution with ions. The metals can then be recovered from the resin by cleaning it with an

acid or alkaline solution. This type of system is very complex and requires careful operation and maintenance, but may prove less delicate than reverse osmosis systems, and better for use on dilute rinse streams.

Electrolytic recovery. The metallic content in the rinse water can be collected in a solid slab by passing current between a submerged anode and cathode. As the current passes through the solution, metallic ions collect on the cathode forming a solid slab that can be reclaimed, or used as a plating anode.

This method has been successfully used to recover gold, silver, tin, copper, zinc, solder alloy, and cadmium. The process works best on solutions with a greater than 100 mg/l concentration of metal ions.

Electrodialysis. In this method, an electric current and selective membranes are used to separate the positive and negative ions from a solution into two streams. Feeding the solution through successive cation and anion membranes, charged with current, will segregate the streams, and concentrate salts or metal ions. This process has not been used as widely as other metal recovery techniques.

High surface area electrowinning/electrorefining. Using the same principle as electrolytic recovery, a metal containing solution can be passed through a carbon filter cathode. The metal will plate out on the cathode, which can be placed in an electrorefiner. The electrorefiner reverses the current, removing the metal fibers from the cathode and plating them on a stainless steel starter sheet.

3.4.4 Etching

3.4.4.1 Material Substitutions

Use differential plating instead of conventional electroless plating. The correct use of certain stabilizers in the electroless plating bath can cause copper to plate on the board's through

holes three to five times faster than on the surface. This differential plating leaves much less copper on the surface of the board that ultimately has to be etched away. Differential plating is not a fully developed technique, but has high potential for reducing the rate of metal contamination in etching baths.

Use non-chelated etchants. Non-chelate mild etchants such as sodium persulfate and hydrogen peroxide/sulfuric acid can be used to replace ammonium persulfate chelate etchant.

Use thinner copper foil to laminate board. Thinner foil reduces the amount of copper which must be etched away, and thus reduces the amount of waste generated. Many manufacturers are switching to thinner laminates on their boards.

Use non-chrome etchants. Ferric chloride or ammonium persulfate etchants are preferable to chromic-sulfuric etchants. Non-chromic etchants reduce the toxicity of spent etchant baths.

3.4.4.2 Process Modifications

Use pattern instead of panel plating. Panel plating requires plating of the entire board surface. Pattern plating, whether additive or subtractive, involves much less application of metal to the board. Some computer, microwave, and other applications requiring uniform cross section of circuitry may demand panel plating, however, most other applications can be satisfactorily manufactured using the pattern method.

Use additive instead of subtractive method. The additive method eliminates etching altogether. By printing the resist on a non-laminated board's non-circuit area prior to electroless plating the first layer of the circuit pattern, additive processing eliminates deposition of copper on the non-circuit area. While this technique does require the use of solvent based resists, it is gaining popularity because it creates less waste and results in lower manufacturing costs. Additive processing eliminates spent etchant waste and cuts down on the generation of metal hydroxide sludge.

3.4.4.3 Waste Treatment

Recycle spent etchant. Electrolytic diaphragm cells have been used to regenerate spent chromic acid from etching operations. The electrolytic cell oxidizes trivalent chromium to hexavalent chromium and removes contaminants. This can result in regenerated solution of equal or higher quality than fresh etchant.

Direct chlorination. Cupric chloride, a strong etchant used to produce patterns on board base material, can be regenerated through direct chlorination. The etchant becomes spent as copper reduces the cupric chloride (CuCl_2) to cuprous chloride (CuCl). The spent etchant can be oxidized, and reused.

3.4.5 General Wastewater and Sludge Treatment

In the processes described, wastewater treatment generates hazardous waste in the form of sludge. The volume of sludge generated is proportional to the level of contamination of spent rinse streams. These streams are contaminated through the drag-out of process chemicals. The major methods of reducing the waste found in sludge include waste stream segregation, use of alternative treatment chemicals, and alternative treatment technologies.

3.4.5.1 Waste Stream Segregation

Segregating waste streams can improve the efficiency of a waste treatment stream. The isolation of various waste streams creates a broader variety of treatment options. As an example, segregating streams containing chelating agents reduces the amount of ferrous sulfate that must be added to the stream to break down the chelators. This in turn minimizes the precipitation of iron in the sludge generated by the non-chelator streams.

Another volume reduction strategy is to isolate non-contact cooling streams from contaminated streams. Cooling streams can be redirected in a closed loop, without any

treatment, thereby reducing the total water discharge and the total volume of wastewater requiring treatment.

3.4.5.2 Use of Alternative Waste Treatment Chemicals

The selection of chemicals used in the treatment process can affect the volume of sludge generated. For example, lime and caustic soda are two common chemicals used for neutralization and precipitation. Although lime costs less per unit, it can generate as much as ten times more dry weight of sludge than caustic soda.

Alum and ferric chloride are coagulating agents used to improve floc formation, but they increase sludge generation by converting to hydroxides in use. Polyelectrolyte conditioners, which are more expensive, can be used without adding to sludge volume, and thus may be less expensive to use when the cost of sludge disposal is factored into the decision. These substitutions, and others, must be made after consideration of waste characteristics and removal efficiency in any given plant environment.

3.4.5.3 Alternative Treatment Technologies

Ion exchange can be used to treat the entire waste stream prior to discharge to the publicly owned treatment works. This treatment, coupled with an activated carbon filtering treatment system, can enable the recycling of rinse water, although process chemicals cannot be recovered after mixing of the various waste streams. Economic justifications for such a system must be developed if an ion exchange system is to be installed, but experience indicates payback can be achieved in three to four years.

3.4.5.4 Sludge Treatment

A full discussion of sludge dewatering and hazardous sludge disposal is presented in the Electroplating section. The methods detailed include filter pressing to dewater the sludge and final stabilization/solidification of the dried sludge cake.

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CHAPTER 4
WOOD PRESERVATION

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CHAPTER 4

WOOD PRESERVATION

4.1 INDUSTRY DESCRIPTION

The purpose of wood preservation is to improve the utility of wood by keeping it dry or by preventing its decay. By impregnating fibers with preservative, wood is made toxic to fungi, termites and other insects, marine borers, and bacteria which would use the wood as a food source.

Preservation techniques are used when the wood will come in contact with soil or water. Marine and land pilings, crossties, and telephone poles are only a few of the end-uses of treated wood. The preservation action is believed to begin with the movement of toxic material from the preserved timber to the surrounding environment. The movement of the preservative establishes a zone of defense against potential invading organisms. Over time, the preservative in the environment is leached away from the area and is replaced with more preservative from the treated wood. Although the goal of wood preservation is to achieve maximum fixation of the preservative within the wood, many factors influence this objective including the type of preservative used, the soil and moisture condition, and the microbial activity of the immediate ecosystem.

The cell structure of wood is important to the preservation process. Wood is composed of millions of hollow cells which are filled with air. These cells run both longitudinally from root to crown and radially from center to bark. Most of the cells in the center of a tree (i.e., the heartwood) are dead, their purpose being to provide support. The live, newly formed cells (i.e., the sapwood) located just inside the bark and cambium of the tree contain pits and a series of vertical flow channels through which nutrients flow. Some softwoods (e.g., pines, spruces, larches, and the Douglas fir) also contain resin canals which form another network within the tree. These natural passageways also serve as the transport method by which preservation chemicals are moved throughout the timber. The most common species of wood

used in preservation processes are the Southern Pine, the Ponderosa Pine and the Red Pine. Most other wood species do not readily accept chemical preservatives.

4.2 PROCESS DESCRIPTION

4.2.1 Seasoning

Because the most effective treating results are obtained with dry wood, wood is often subject to seasoning prior to treatment. Although air seasoning, or allowing the wood to air dry, is the easiest method of drying wood, it can also be very time consuming. Several of the commercial artificial seasoning methods include boultonizing, steam conditioning, and kiln drying. Boultonizing involves evaporating water from wood by heating the wood in a creosote or an oil-type preservative while simultaneously subjecting it to a vacuum. This method of conditioning varies in time from 6 to 40, hours depending on the type of wood being conditioned. Steam conditioning subjects wood to live steam at temperatures of 104° to 118°C (219° to 244°F) for periods of 1 to 20 hours. Immediately after steaming, a vacuum is applied to remove moisture. The kiln drying method involves placing wood in a drying kiln and evaporating the internal moisture.

4.2.2 Incising

After wood has been seasoned, it is often incised to obtain optimum treating results. Incising consists of making shallow slit-like holes in the surface of the material to be treated so that deeper and more uniform preservative penetration may be obtained.

4.2.3 Pressure Treating

Pressure treatment of wood with preservatives is the most effective method of protecting wood against attack by decay, insects, fire, and other wood-destroying agents. Pressure treatment allows deep, uniform, and controlled preservative penetration.

The pressure treating process involves two primary steps: loading and reloading a cylindrical retort with lumber while the preservation solution is prepared, and conducting the treatment cycle. The loading stage involves placing bundles of lumber on tram cars and rolling them into a retort which is normally 1.8 meters (6 feet) in diameter and 15.2 meters (50 feet) long. The retort cylinder is normally mounted on saddle blocks which allow for the slight expansion and contraction that occurs during processing at elevated temperatures. The cylinders are also frequently equipped with steam-heating coils to maintain the temperature of the preservative solution during the processing cycle. The cylinder is also equipped with an array of pipelines which transport preservative, water, air, and/or vacuum as necessary during the process.

A plant operator controls each treatment sequence according to the specific type of wood which is to be treated. The six stages of the treatment cycle, as illustrated in Exhibit 4-1, are initial vacuum, cylinder flood, pressure applied, initial drain, final vacuum, and final drain and unload. The entire pressure treating process may be completed in approximately one hour.

The initial vacuum removes air from the naturally occurring passageways within the lumber, allowing the subsequent penetration of preservative. The greater the quantity of air removed, the greater the percentage of treatment chemicals allowed to penetrate the lumber. The plant operator can control the time of vacuum and, therefore, the amount of preservative penetration. In most cases, 85 percent sapwood penetration is recommended. However, the penetration level does vary with the species and thickness of the wood. After the initial vacuum is complete, the retort is flooded with preservative and a secondary vacuum is applied at this time.

Pressure application begins after the preservative fills the retort. The preservative solution is pumped into the cylinder until the pressure reaches 150 psi. Once this pressure is reached, it is maintained for the time necessary to yield the required penetration. At the end of the pressure period, the pressure is released and the preservative is drained from the retort.

Some of the preservative solution remains trapped between the lumber in the packs of wood after the initial draining period. Another vacuum is applied to dry the lumber and to remove excess preservative solution.

The final drain serves to remove any excess preservative released as a result of the final vacuum. The preservative solution is drained from the retort and returned to a storage tank. Once the retort is drained, the treated lumber is unloaded.

4.2.4 Treatment Chemicals

4.2.4.1 Chromated Copper Arsenate (CCA)

One preservative commonly used in the pressure treating process is Chromated Copper Arsenate (CCA). As the name implies, this preservative consists of three active ingredients, each toxic to wood-destroying organisms, and each with its own function. Copper and arsenic prevent decay by a variety of fungi. The arsenic also prevents attack by insects and termites. Chrome ensures the safety of humans and animals that come into contact with the treated wood while still protecting against wood-destroying organisms by chemically fixing the copper and arsenic into the wood.

Although CCA is a waterborne preservative, it will not leach from wet wood. Copper, arsenic, and chrome begin reacting with the wood cells immediately after being forced into the lumber. The chromium salts react to form insoluble compounds, which subsequently render the CCA non-leachable.

4.2.4.2 Creosote, Coal-Tar, and Related Materials

The preservatives used in creosote treatment methods consist of creosote, coal-tar, and related materials. All of these preservatives are mixtures of organic materials resulting from the pyrolysis of natural organic materials and/or subsequent distillation of the resulting tars. The

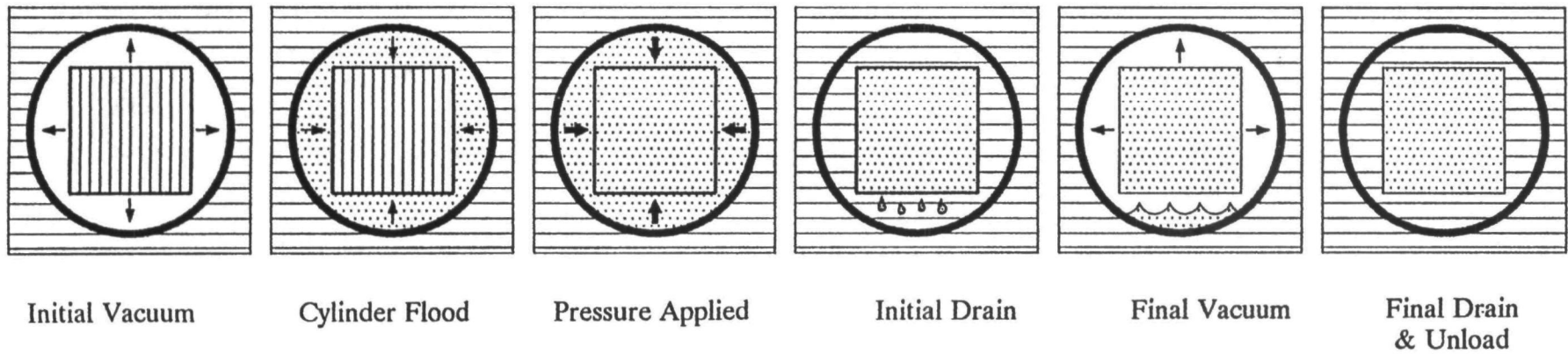


EXHIBIT 4-1. Stages in Pressure Treatment

primary preservatives in this class are coal-tar creosote and mixtures of creosote with crude coal-tar.

Coal-tar creosote is a residual product from the distillation and processing of coal-tar. It is a blend of naphthalene drain oil, wash oil, anthracene drain oil, and heavy distillate oil. These oils are blended to meet specifications as required by certain wood species. The resulting constituents of creosote coal-tar preservatives and their corresponding weight percentages are listed in Exhibit 4-2.

EXHIBIT 4-2. Principle Constituents of High-Temperature Creosote

Compound	Percent by Weight
Naphthalene	7-28
Phenanthrene	9-14
Acenaphthene	2-5
Fluoranthene	2-5
Fluorene	2-4
Methylnaphthalenes	1-4
Pyrene	2-3
Carbazole	1.8-2.7
Anthracene	1.2-1.8
Diphenylene oxide	0.5-1.0
9,10-Dihydroanthracene	0.1-0.3

Source. Nicholas, Darrel D., ed., *Wood Deterioration and Its Prevention by Preservative Treatments, Volume II: Preservatives and Preservative Systems*, Syracuse University Press, Syracuse, NY. 1973.

Creosotes and coal-tars are produced by the high-temperature carbonization of bituminous coal. The carbonization process takes place in a pusher-type oven with vertical flues. The coal is charged into the oven on the pusher side. The oven is heated by the combustion of coke-oven gas. The coal at the wall of the oven immediately softens and forms a plastic zone which moves toward the center of the oven as the coking continues. Coking is complete

when the two plastic zones meet in the center of the oven and the temperature has reached 900° to 1000°C (1,652° to 1,832°F). The molten liquid is then pushed from the oven in pieces three to six inches in cross section and about half of the oven width in length. A normal oven is 12.2 meters (40 feet) long, 4.3 meters (14 feet) high, and about 43 centimeters (17 inches) wide.

Almost 32.2 to 34 liters (8.5 to 9.0 gallons) of tar are recovered per ton of coal carbonized. Most of this is shipped to a distillation plant for further processing. Several of the fractions resulting from the distillation of coal-tar, including wash oil, anthracene oil, and heavy oil, are useful to the wood preserver. Upon cooling, the anthracene oils deposit crude anthracene crystals. The oil which is drained from this crystallization is used in blending creosote. These and other coal-tar fractions are listed in Exhibit 4-3.

EXHIBIT 4-3. Principle Fractions from a Typical Coke-Oven Tar

Compound	Percent	Boiling Point Range, °C (°F)
Benzol light oil	0.6	99-160 (210-320)
Naphtha light oil	2.9	168-196 (334-385)
Naphthalene oil	14.6	198-230 (388-446)
Wash oil	2.8	224-286 (435-547)
Anthracene oil	8.0	247-355 (477-671)
Heavy oil	9.5	323-372 (613-702)
Medium-soft pitch	56.6	---

Source: Nicholas, Darrel D., ed., *Wood Deterioration and Its Prevention by Preservative Treatments, Volume II: Preservatives and Preservative Systems*, Syracuse University Press, Syracuse, NY. 1973.

4.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS AND WASTE STREAMS

4.3.1 Seasoning

Steam conditioning is the most common method of seasoning and is a major source of water contamination. After steam conditioning, the excess preservative in the cylinder is returned to storage. A thin film of the preservative is left on the walls of the cylinder and is washed down by steam condensate during the succeeding steaming cycle. The steam condensate then leaves the cylinder through the steam trap. The condensates contain entrained oil, preservative, and other organic material such as sugar, which is extracted from the wood during the steaming operation.

4.3.2 Pressure Treating

The waste streams resulting from pressure treating operations are similar to those originating from steam conditioning. Between batch operations, the retort is rinsed, resulting in wastewater streams containing oil, preservatives, and sugars.

Other sources of wastewater resulting from the pressure treating process include cooling water, vacuum water, wash water, storm water, boiler blow-down water, and heating-coil condensate. The boiler blow-down water and condensate from heating coils may or may not contain contaminants, depending on the use and nature of the boiler water treating compounds and whether or not the heating coils contain leaks through which the preservative can enter.

Specific contaminants in the waste streams depend on the type of preservative used during the treatment process. Exhibits 4-4 and 4-5 relate effluent characteristics of facilities using CCA and creosote preservatives.

4.4 POLLUTION PREVENTION, WASTE TREATMENT, AND CONTROL SYSTEMS

4.4.1 Pollution Prevention

There are several in-plant process changes which can be made that will reduce the total flow and organic loading of wastewater streams. Several of these process modifications include closed steaming, modified-closed steaming, reduction in steam conditioning, reuse of cooling water, and recovery of free oils. Additional preventative maintenance measures can also be implemented which will reduce total water flow and water contamination.

4.4.1.1 Closed Steaming

Closed steaming aids in altering the characteristics of the wastewater streams and in reducing the volume of plant wastewater. The process consists of the following steps:

- Drawing water from a reservoir into the treating cylinder at the start of a steaming cycle to a depth sufficient to cover the heating coils
- Applying steam to the coils to generate more steam within the cylinder
- Returning the water to the reservoir for future use

The number of times that the water can be reused depends on the type and quality of the preservative and the characteristics of the water itself. In addition to reducing the volume of wastewater, closed steaming reduces the oxygen demand of the cylinder effluent by reducing the content of emulsified oils in the effluent. After the closed steaming cycle, the water in the cylinder is returned to the reservoir through a pipe sized to reduce agitation, thus preventing emulsification. The free oil can then be removed by gravity separation and skimming.

EXHIBIT 4-4. Analytical Data for Wastewaters from Creosote and Penta Treatments

Waste Characteristic	Concentration Range (mg/l - except pH)
Pentachlorophenol	40-100
Phenols	150-350
Chemical oxygen demand	3,000-60,000
Biochemical oxygen demand	1,500-25,000
Oil content	80-6,000
Total solids	2,000-20,000
pH	4.0-5.5
Total free sugars	1,800
Arabinose	460
Xylose	287
Glucose	213
Galactose	517
Mannose	403

Source. Nicholas, Darrel D., ed., *Wood Deterioration and Its Prevention by Preservative Treatments, Volume II. Preservatives and Preservative Systems*, Syracuse University Press, Syracuse, NY 1973.

Some of the advantages of closed steaming over conventional steaming include the following:

- Reducing the volume of wastewater that must be treated
- Improving the quality of steam-conditioning cylinder effluents by reducing oxygen demand
- Increasing oil recovery by eliminating the emulsion problem
- Reducing the cost of treating wastewater by reducing the total organic loading that must be removed by conventional wastewater treating methods

One of the difficulties associated with closed steaming is that the process adds approximately 30 minutes to steaming time.

EXHIBIT 4-5. Analytical Data for Wastewaters Containing CCA Salts

Waste Characteristic	Concentration Range (mg/l - except pH)
Chemical oxygen demand	1,700
Arsenic	300
Copper	170
Chromium (hexavalent)	375
Phenols	<1
pH	5.0

Source: Nicholas, Darrel D., ed., *Wood Deterioration and Its Prevention by Preservative Treatments, Volume II Preservatives and Preservative Systems*, Syracuse University Press, Syracuse, NY. 1973

4.4.1.2 Modified-Closed Steaming

Modified-closed steaming charges live steam to the cylinder as in open steaming, but retains the condensate in the cylinder. When the condensate reaches a depth slightly higher than the heating coils, open steaming is stopped and the remaining steam required for the process is generated within the cylinder using the heating coils. After the steaming cycle is complete, the oil is recovered and the water is discharged. Modified-closed steaming adds little or no time to the steaming cycle, which reduces boiler operating time and reduces fuel costs.

4.4.1.3 Reduction in Steam Conditioning

Much of the wastewater flow from a wood treatment plant comes from the steaming of green (not fully aged) stock. If the amount of wood to be steamed can be reduced, a significant reduction in wastewater flow will occur. One way to reduce the flow is to use kiln-drying rather than steaming.

4.4.1.4 Reuse of Cooling Water

Reusing cooling water will also reduce the total wastewater flow. Cooling water recirculation will require that a cooling pond or holding tank be constructed to act as a staging area prior to the water reentering the condensers.

4.4.1.5 Recovery of Free Oils

One difficulty in treating wastewater from wood treatment plants is handling the oils that often become entrained in wastewater from steaming condensate. Free oil can be recovered from wastewater by gravity separation. Creosote separation is normally accomplished in a sump equipped with a series of baffles to decrease turbulence and permit the heavier-than-water fractions to settle to the bottom of the sump. The lighter fractions then rise to the water's surface.

4.4.1.6 Preventative Maintenance

Cylinders, pipes, and sumps should be monitored, and repaired if necessary, on a regular basis to prevent preservative losses which can contaminate both process wastewater and stormwater. The preservative which is lost from treatment cylinders can be collected and returned to a preservative storage tank for future use.

4.4.2 Waste Treatment and Control Systems

The degree to which wastewater is treated depends on the outfall of the wastewater effluent and the permit requirements. More treatment is necessary for effluents terminating in receiving streams than for plant effluents which will be further treated by municipal treatment plants. Assuming complete on-site processing, both primary and secondary treatments are normally required to meet minimum treatment standards. Some of the secondary methods which may be used to treat wood preservation waste streams include biological treatments, chemical oxidation, and activated carbon filtration. The most effective method, or

combination of methods, will vary with the preservative mix, the flow rate, and the degree of automation.

4.4.2.1 Primary Treatments

Creosote waste streams often contain entrained oils which must be removed prior to secondary treatment methods. The methods used to capture the oils usually include flocculation and sedimentation. Flocculating agents include metallic hydroxides, alum, ferric chloride, and polyelectrolytes. Flocculation treatments normally generate a volume of sludge equal to five to ten percent of the volume of wastewater. The sludge often has a high water content and should be dewatered. The recovered water should then be sent to the secondary treatment operations.

The CCA salts, copper, chromium, and arsenic are not biodegradable and will stay in the environment for indefinite periods of time if not removed. Because they are toxic to the microorganisms found in biological treatment operations, the salts must be removed in primary operations. Many of the procedures used by the wood preservation industry for treating waters containing inorganic salts have been adapted from the electroplating industry. A detailed discussion of metal recovery options is found in Section 2.5.5 in the electroplating material. Information specific to reducing hexavalent chromium is located in Section 2.6.1. and Section 2.6.3 contains additional information concerning metal precipitation.

4.4.2.2 Secondary Treatments

The main purpose of secondary treatment is to remove dissolved organic material from wastewater. Biological processes are generally the most effective secondary treatment methods, but chemical oxidation and activated-carbon adsorption have also been successful. These processes are discussed in more detail in Section 2.7.

4.4.2.2.1 Biological Treatments

The four most commonly used methods of biological treatment are trickling filtration, activated sludge, and oxidation lagoons. Trickling filters consist of a cylindrical tower filled with crushed stone, slag, or plastic media. The media is covered with a layer of slime formed by aerobic bacteria. Wastewater is uniformly applied to the top of the cylinder by a rotating distributor arm equipped with nozzles. The wastewater trickles down through the media coming into contact with the slime layers. The contaminants in the water are then destroyed by the aerobic bacteria which form the slime.

Activated sludge units consist of an aeration basin and a settling tank. The wastewater enters the aeration basin at one end and leaves at the other. As the water moves through the basin, contaminants are destroyed by biologically active sludge. The water and some of the sludge is discharged into a settling tank or clarifier where the activated sludge is settled out and returned to inlets of the aeration basin. The treated water can then be discharged.

Oxidation ponds simulate the natural biological oxidation and sedimentation that occurs in lakes and streams. As with other biological treatment methods, the contaminants in the wastewater are destroyed by microorganisms, principally bacteria.

4.4.2.2.2 Chemical Oxidation

Creosote wastestreams contain phenol contaminants which can be successfully destroyed by chlorine and ozone. Chlorine gas and calcium or sodium hypochlorite are often used for chlorination treatments. The chlorine-containing materials may be added manually, as is often the case with the powdered calcium and sodium hypochlorite salts, or with a continuous-flow system for chlorine gas. In order to destroy the phenols, chlorine treatments must operate with the following restrictions:

- The proper amount of chlorine must be added to the wastewater

- The temperature of the wastewater must be maintained below 43°C (110°F) to prevent the formation of chlorates
- The pH must be adjusted to 7.0 or higher to prevent the formation of chlorophenols
- Sufficient reaction time must be allowed (1 to 2 hours) to ensure complete oxidation of phenols

4.4.2.2.3 Activated-Carbon Adsorption

Carbon has a strong affinity for nonpolar compounds such as phenol. As such, phenol and other organic materials in the wastewater are adsorbed to the carbon surface. Once spent, the carbon should be disposed of at a hazardous waste landfill. The process wastewater may be treated further or discharged.

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CHAPTER 5

ROCK CRUSHING AND CEMENT PRODUCTION

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CHAPTER 5

ROCK CRUSHING AND CEMENT PRODUCTION

5.1 INDUSTRY DESCRIPTION

5.1.1 Rock Crushing

Rock crushing, one of many non-metallic mineral processing industries, produces crushed rock in a wide range of quantities. The end uses of this rock are many and diverse. The minerals may be used in their natural state or processed into a variety of manufactured products. The construction and lime manufacturing industries use rock and crushed stones in their natural state. Major rock types processed by the crushed and broken stone industry include limestone, dolomite, granite, trap rock and sandstone, quartz and quartzite. Dolomite production constitutes the widest and most important end use of crushed and broken stone in the United States. Minor types include calcareous marl, marble, shell, and slate. Classifications used by the industry vary considerably and in many cases do not reflect actual geological definitions.

Non-metallic mineral processing, including rock and crushed stone, generally involves product unloading, conveying, crushing, screening, milling, size classifying, material handling, and storing. All of these processes can be significant sources of dust emissions if uncontrolled. Some mineral processing operations may also require washing, drying, calcining, or floating operations. The operations performed depend on the rock type and the desired product.

5.1.2 Cement Production

Most of the hydraulic cement produced in the United States is portland cement, a cementitious, crystalline compound composed of metallic oxides. Portland cement is used in the construction of many kinds of structures including buildings, bridges and highways, and in products such as concrete masonry, concrete piping, and many precast components for constructions such as

prestressed concrete. The primary process in portland cement manufacturing is the calcining or sintering of carefully ground and mixed raw materials in an inclined rotary kiln fired by fossil fuel. The raw materials are clay, sand, iron ore, limestone shale, feldspar, etc., which contain calcium carbonate, silica, alumina, ferric oxide, and other elements. The following five types of portland cement are manufactured in the United States. Each type differs in composition of raw materials and production methods.

- Type I is used for general concrete construction when the special properties of the other four types are not required.
- Type II is used in general concrete construction exposed to moderate sulfate action or where moderate heat of hydration is required.
- Type III is used when high early strength is required.
- Type IV is used when a low heat of hydration is required.
- Type V is used when high sulfate resistance is required.

Chemical reactions that occur during calcining result in the formation of a clinker. Pulverizing these clinkers with gypsum yields a powder called portland cement. Mixed with water, portland cement forms a slowly hardening paste. When sand and gravel are added to the mixture, it becomes concrete. Approximately 1.6 tons (1454 kg) of raw materials are required to produce 1 ton (909 kg) of cement.

5.2 PROCESS DESCRIPTION

5.2.1 Rock Crushing

Rock and crushed stone products are generally first loosened by drilling and blasting, then loaded by power shovel or front-end loader and transported by heavy earth-moving equipment. Techniques used for extraction vary with the nature and location of the deposit. A general process flow diagram for a typical crushed rock and stone processing plant is shown in Exhibit 5-1.

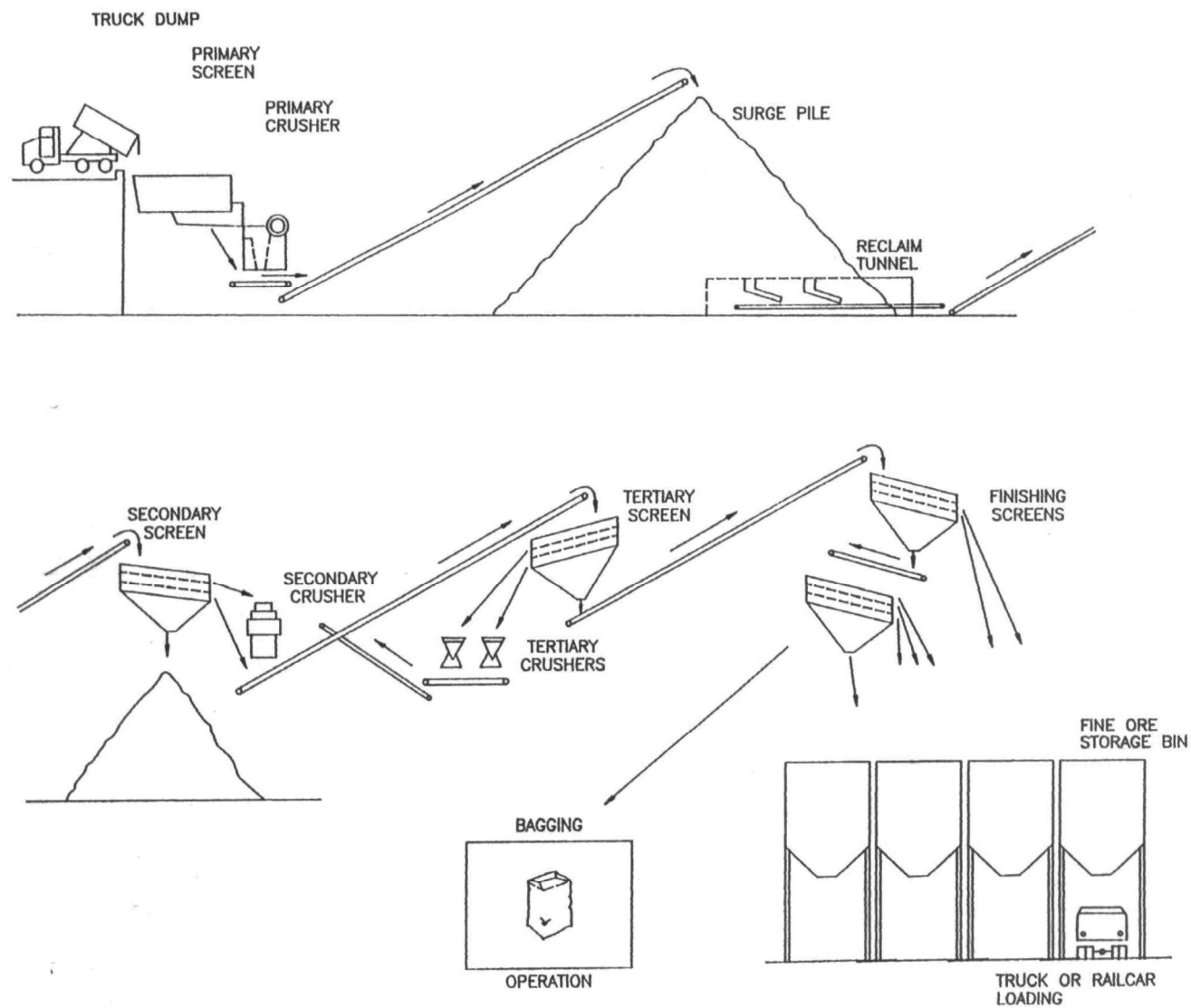


Exhibit 5-1. Flow Diagram of a Typical Crushing Plant

5.2.1.1 *Primary Crushing and Screening*

Quarried stones are normally delivered to the processing plant by truck and dumped into a hoppered feeder, usually a vibrating grizzly type, or onto screens. These screens separate or scalp larger boulders from finer rocks that do not require primary crushing, thus minimizing the load to the primary crusher. Crushing is the process by which coarse material is reduced by mechanical energy and attrition to a desired screening size. The mechanical stress applied to rock or stone fragments during crushing may be accomplished by either compression or impact. Compression crushers slowly squeeze the fragment and force a fracture, while an impact crusher applies an abrupt breaking force. Compression crushers produce relatively closely graded products with a small proportion of fines. Impact crushers produce a wide range of sizes and a high proportion of fines. Compression crushers, such as jaw or gyratory crushers, are usually used for initial production, although impact crushers are gaining favor for crushing low-abrasion rock, such as limestone and talc, and where high reduction ratios are desired. The crusher usually reduces the rock to between 3 and 12 inches (8 and 30 cm). The crusher product and the grizzly troughs (the undersize material) are discharged onto a belt conveyor and normally transported to either secondary screens and crushers, or to a surge pile or silo for temporary storage.

5.2.1.2 *Secondary Crushing and Screening*

The secondary screens generally separate the process flow into either two or three fractions (oversized, undersized, and troughs) prior to entering the secondary crusher. The oversized particles are discharged to the secondary crusher for further reduction. The undersized, which require no further reduction at this stage, normally by-pass the secondary crusher. The third fraction, the troughs, is separated when processing some minerals. Troughs contain unwanted fines that are usually removed from the process flow and stockpiled as crusher-run material. For secondary crushing, gyratory or cone crushers are most commonly used, although impact crushers are used at some installations.

5.2.1.3 *Tertiary Crushing and Screening*

The product from the secondary crushing stage, usually 1 inch (2 cm) or less in size, is transported to tertiary screens for further sizing. Sized material from this screen is either discharged directly to a tertiary crushing stage or conveyed to a fine-ore bin which supplies the milling stage. Cone crushers or hammermills are commonly used for tertiary crushing. Rod mills, ball mills, and hammermills are normally used in the milling stage. The product from the tertiary crusher or the mill is usually conveyed to a type of classifier such as a dry vibrating screen system, an air separator, or a wet rake or spiral system. Oversized materials are returned to the tertiary crusher or mill for further reduction. At this point, some mineral end products of the desired grade are conveyed directly to finished product bins or stockpiled in open areas by conveyors or trucks.

5.2.1.4 *Additional Crushed Rock Processing*

Most crushed rock and stones require additional processing depending on the rock type and product specifications. In certain cases, stone washing may be required to meet particular end product demands like concrete aggregate processing. Some minerals, especially light-weight aggregates, are washed and dried, sintered, or treated prior to primary crushing. Others are dried following secondary crushing. Crushed and broken stone normally are not milled and are screened and shipped to the consumer after secondary or tertiary crushing.

5.2.2 Cement Production

The portland cement production process involves three basic steps. First, raw materials are crushed and mixed. Second, the mixture is heated to high temperatures in a kiln where chemical reactions take place and a rock-like substance called clinker is formed. The clinker is then cooled in a clinker cooler. Finally, the cooled clinker is crushed, and ground gypsum or other materials are added to obtain the properties desired in the finished cement. The various steps are shown in Exhibit 5-2.

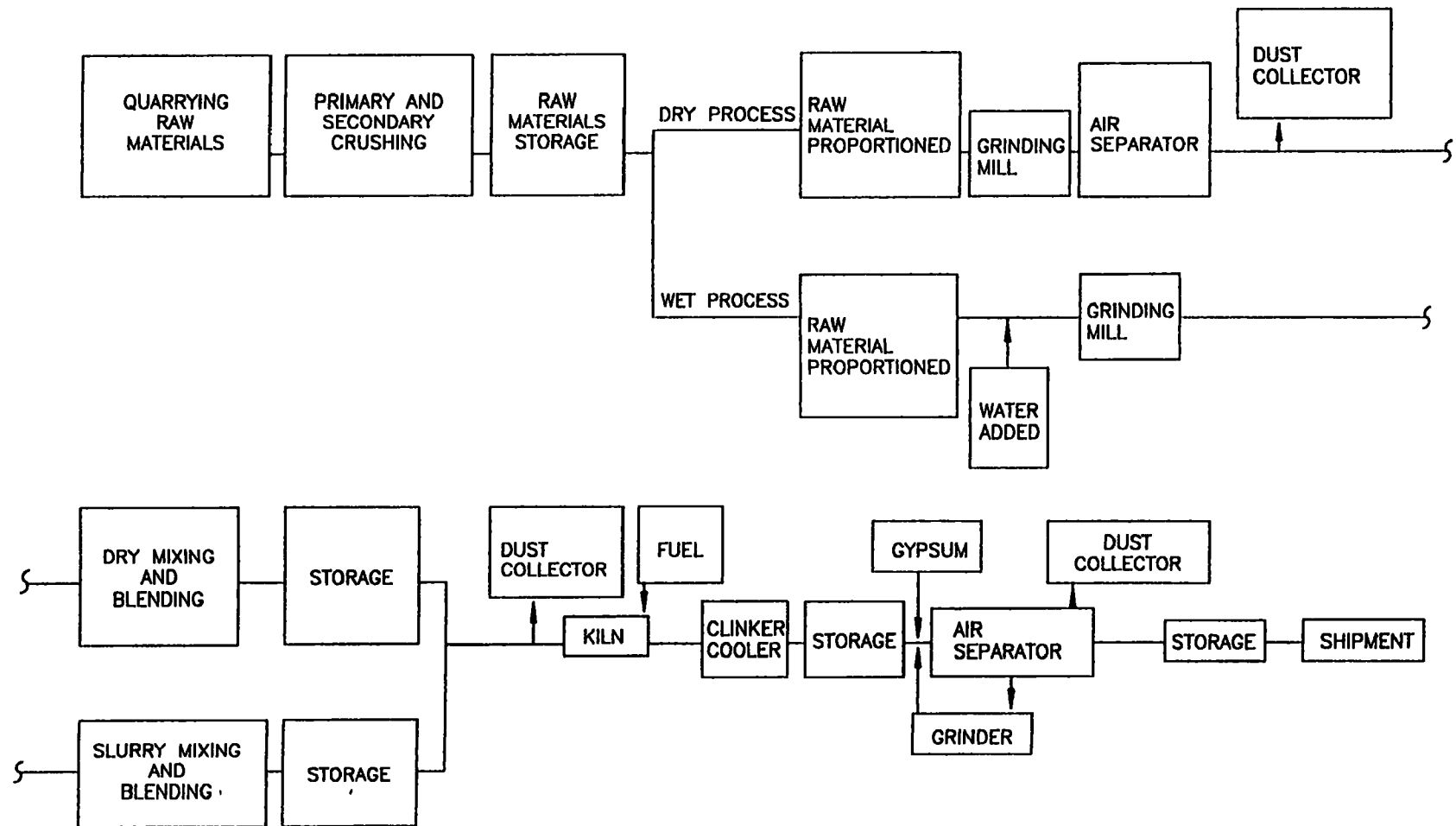


Exhibit 5-2. Portland Cement Process Flow Diagram

5.2.2.1 *Raw Material Handling*

The basic raw materials in portland cement manufacturing contain calcium carbonate, silicone oxide, and ferric oxides, with minor amounts of sulfate, alkali, and carbonaceous materials. Limestone is the most common source of calcium. Limestone can also have naturally high amounts of clay or shale, which contain aluminum silicates or free silica. Usually, raw materials such as clay, shale, or iron ore must be added to adjust the chemical composition of the clinker. Processing of these raw materials into kiln feed involves quarrying and crushing phases and mixing and grinding phases. Limestone is usually obtained from an open quarry located on or near the plant site. Raw materials not quarried at the site are typically brought to the plant by truck or rail and stored in stockpiles near the crushing machinery. The raw materials are crushed, screened, and ground to the appropriate size for mixing and blending before they are charged to the kiln. Crushing sometimes take place in two or three stages, as shown in Exhibit 5-3.

5.2.2.1.1 *Crushing and Screening*

Crushing reduces the size of rock obtained from the quarry. Crushing equipment typically consists of primary and secondary crushers, and occasionally uses tertiary crushers. Primary crushers may be of the gyratory, jaw, roll, or hammer type. Secondary crushers, often hammermills, crush the rock to smaller than 1 inch (2.5 cm) in diameter. Crushed raw materials are stored in silos or stockpiles.

Occasionally, a tertiary crusher is necessary, in which case the material is sent through a finer hammermill operation, which reduces it to about 5/16 inch (0.8 cm). After each crushing operation, the rock enters a screening operation. After the last crushing step, a bucket elevator transports each type of raw material to separate compartments for storage prior to fine grinding.

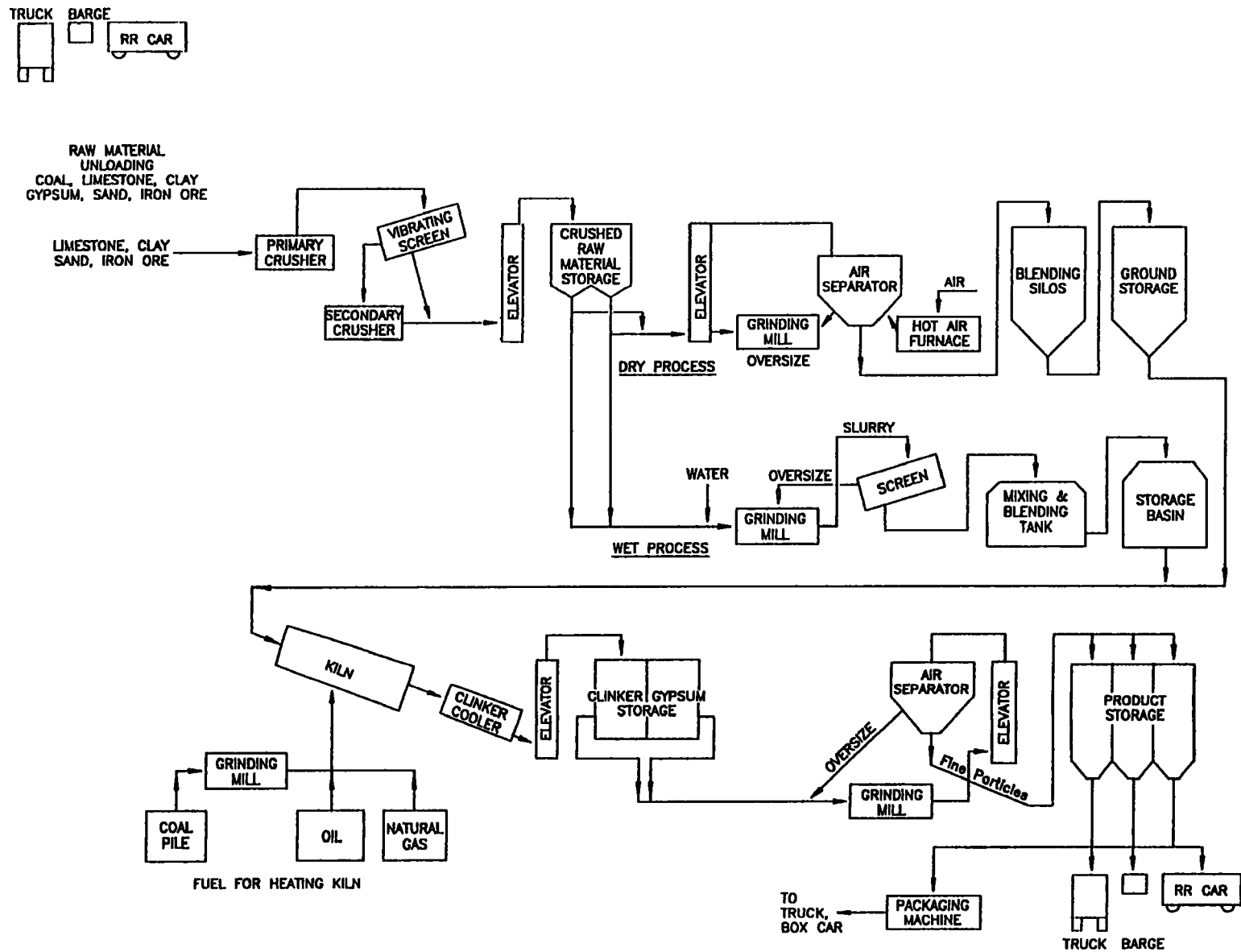


Exhibit 5-3. Crushing and Grinding Processes for Portland Cement Production

5.2.2.1.2 Fine Grinding, Mixing, and Blending

Raw materials are drawn from their separate storage compartments and proportioned to the proper composition before being charged to the kiln. Composition of the feed material depends on whether a "wet process" or a "dry process" is to be used. Exhibit 5-3 illustrates each of these techniques.

In the wet grinding process, ball mills or compartment mills (a ball mill combined with a tube mill) are used, and water is added to the mill with the crushed raw materials. The resulting slurry, which is about one-third water, is discharged from the mill and stored in open tanks where additional mixing takes place. From the tanks, the slurry may be fed directly to the kiln, may first be dewatered to form a cake containing about 30 percent moisture, or may be dried in a dryer heated by exhaust gases from the kiln or the clinker cooler.

In the dry grinding process, ball mills, roller mills, or compartment mills are also used, but the materials are ground without water. Crushed raw materials are dried in the mill itself or in a direct-contact rotary dryer until the free moisture content is less than one percent. Heat for the mill or dryer can be supplied by direct firing, although it is usually supplied by recirculation of hot exhaust gases from the kiln or clinker cooler. If a roller mill is used, all kiln exhaust gases can be directed through the mill for drying and preheating; if a ball mill is used, only a portion of the exhaust gases can be directed to the mill.

5.2.2.2 Clinker Production

The rotary kiln is the major potential source of atmospheric emissions at portland cement plants. Raw feed (wet slurry or dry feed) is fed into the upper end of an inclined rotary kiln and conveyed slowly toward the lower end of the kiln by gravity and rotation of the kiln cylinder. Kilns are fired from the lower end so that the hot gases pass countercurrent to the descending raw feed material. As it travels downward, the feed becomes exposed to increasing heat. First, the water is evaporated with the aid of various types of heat exchangers. As the temperature of the charge increases, organic compounds are volatilized, sulfates are decomposed, and chlorides

and alkali salts are partially volatilized. At about the mid-section of the kiln, calcium and magnesium carbonates are decomposed, and carbon dioxide is liberated. Calcium oxide and magnesium oxide are also formed. In the hot zone of the kiln (2700°F/1480°C), about 20 to 30 percent of the charge is converted to liquid. It is through this medium that the chemical reactions proceed.

5.2.2.2.1 Wet Process of Clinker Production

In the wet process of clinker production, feed material enters the kiln in a wet slurry form. Wet process kilns are either short kilns with cyclone preheaters or long kilns with internal chain preheaters. In the United States, rotary kilns are used, and most new plants use long kilns with chains or some other type of preheating system. The chains, which are suspended in the preheating zone of the kiln and arranged to help break up clumps of raw materials, aid in heat transfer and improve fuel consumption.

5.2.2.2.2 Dry Process of Clinker Production

Using a dry process kiln in the calcination process requires that less moisture be evaporated from the feed material than if a wet process kiln were used: this is the only difference between the wet process and dry process. Dry process kilns are short rotary units (either with or without preheaters), rotary kilns with a suspension preheater, or long rotary kilns with a built-in preheater. Dry process kilns can be 20 to 25 percent shorter than wet process kilns because little or no kiln residence time is needed to evaporate water from dry feed. Adding a preheater to a dry process kiln is more efficient, permitting use of a kiln one-half to two-third shorter than a dry kiln without a preheater. Also, because of the increased heat transfer efficiency, a preheater kiln system requires less energy than a wet kiln or a dry kiln without a preheater to achieve the same amount of calcination.

5.2.2.2.3 Clinker Cooling

Clinker is discharged from the kiln to a clinker cooler. The clinker cooler serves a dual purpose: it reduces the temperature of the clinker so that processing can continue; and it provides a means of recovering the heat from the clinker to preheat primary or secondary combustion air. Ambient air is passed through a moving bed of hot clinker, cooling the clinker from about 2700°F (1480°C) to about 150°F (66°C). Clinker coolers can be the planetary, (multicylinder), grate or vibrating type. The planetary cooler consists of a series of tubes located around the circumference of the discharge end of the kiln which rotates around the kiln. The material flows from the kiln into the tubes containing internal baffles that transfer the heat from the material to the cooling air being pulled in. This heated air is returned to the kiln as preheated combustion air. In a grate cooler, the hot clinker is cooled by passing air upward through the moving bed of clinkers on a perforated grate. The exhaust gases from a grate-type cooler can either be routed to an emission control device or recycled to the kiln or preheater.

Cooled clinker can be stored in silos, storage halls, or outdoor stockpiles. Clinker cooler exhaust gases can be ducted to emission control equipment or can be recycled to the kiln, the preheater, the raw mill, or a raw feed dryer.

5.2.2.3 Cement Manufacture and Shipment

Exhibit 5-4 is an illustration of finished cement grinding and shipping. The process consists of grinding the clinker with about 5 percent gypsum to regulate the setting time of the cement. The finishing mills are sometimes sprayed with water to keep them sufficiently cool and to minimize dehydration of the gypsum. Depending on the type of cement being made, other additives such as water proofing and air-entraining agents may be mixed at this time. The finish mill can be an open circuit, where the material passes through the mill regardless of particle size, or a closed circuit, where air classifiers send over-sized clinker back through the mill for further grinding. The finished cement is packaged in bags or bulk loaded and delivered by rail, truck, or ship. The uncontrolled finish grinding operation can contribute substantial amounts of particulate emissions. If control devices are used, the collected dust, which represents about 15 percent of

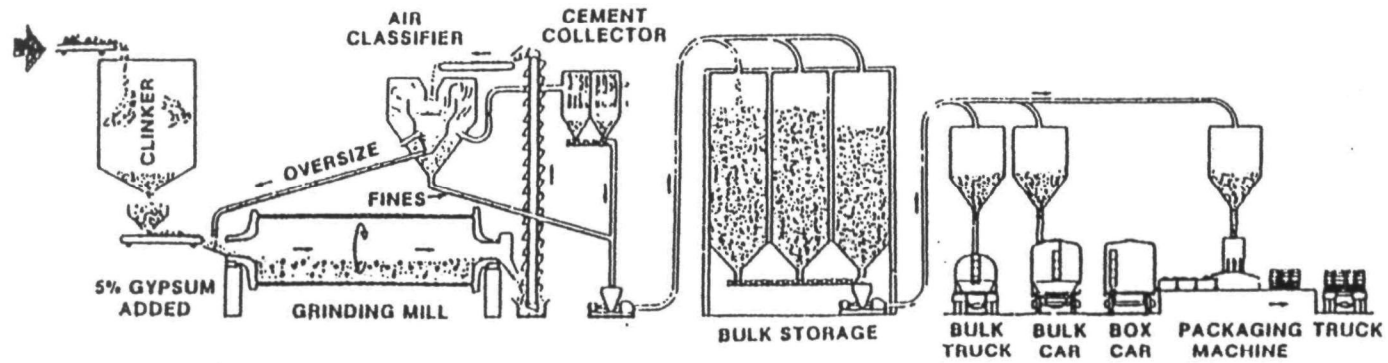


Exhibit 5-4. Finish Mill Grinding and Shipping

the feed, is usable product. Transfer of the material after grinding can also generate fugitive emissions.

5.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS

5.3.1 Rock Crushing

Essentially, all mineral processing operations are potential sources of particulate emissions. Emissions may be categorized as either process fugitive emissions or open fugitive dust emissions. Process fugitive emission sources include those sources for which emissions are amenable to capture and subsequent control. Sources of process fugitive emissions include crushing, screening, grinding, loading, and conveying. Open fugitive dust sources are not amenable to control using conventional control systems and would require strategies that prevent entrainment of settled dust by wind or machine movement. Fugitive dust sources include hauling, haul roads, stockpiles, and plant yards. Some fugitive dust sources, like emissions from silos, can be effectively controlled by conventional control strategies such as baghouses.

Dust emissions occur from many operations in rock and stone quarrying and processing. A substantial portion of these emissions consists of heavy particles that may settle within the plant. Factors affecting emissions from either source category (process fugitive source and fugitive dust source) include the type of ore (rock), quantity and surface moisture content of the ore processed; topographical and climatic factors; and the type of equipment and operating practices employed. Available emission factors for uncontrolled emissions from process fugitive and fugitive dust sources are provided in Exhibits 5-5 and 5-6, respectively.

The type of ore processed is important. Soft rocks produce a higher percentage of fine-grained material than do hard rocks because of their greater friability and lower resistance to fracture. Thus, the processing of soft rocks results in a greater potential for uncontrolled emissions than the processing of hard rock. Major rock types arranged in order of increasing hardness are talc,

**Exhibit 5-5. Emission Factors for Uncontrolled Particulate Emissions
from Crushing Operations at Rock Crushing Facilities**

Type of crushing ^b	Particulate ≤ 30 µm	Particulate ≤ 10 µm	Emission factor rating
	kg/Mg (lb/ton)	kg/Mg (lb/ton)	
Primary or secondary			
Dry material	0.14 (0.28)	0.0085 (0.017)	D
Wet material ^c	0.009 (0.018)	-	D
Tertiary dry material ^d	0.93 (1.85)	-	E

^aBased on actual feed rate of raw material entering the particular operation. Emissions will vary by rock type, but insufficient data are available to characterize these phenomena. Dash = no data.

^bTypical control efficiencies for cyclone, 70 - 80%; fabric filter, 99%; wet spray system, 70 - 90%.

^cRefers to crushing of rock either naturally wet or moistened to 1.5 - 4 weight % with wet suppression technique.

^dRange of values used to calculate emission factor is 0.0008 - 1.38 kg/Mg.

**Exhibit 5-6. Emission Factors for Uncontrolled Particulate Emissions
from Fugitive Dust Sources at Rock Crushing Plants**

Operation	Dust Sources	Emission Factor	
		g/Mg	lb/ton
Wet quarry drilling	Unfractured stone	4×10^{-2}	1×10^{-4}
Batch drop			
Truck unloading	Fractured stone	8×10^{-3}	2×10^{-5}
Truck loading			
Conveyor	Crushed stone	5×10^{-2}	1×10^{-4}
Front end loader	Crushed stone	NA ^b	NA
Conveying			
Tunnel belt	Crushed stone	1.1×10^{-1}	2×10^{-4}

^aExpressed as g/Mg (lb/ton) of material through primary crusher, except for front end loading, which is g/Mg (lb/ton) of material transferred.

^bNA = Not available.

clay, gypsum, barite, limestone and dolomite, feldspar, and quartz. Thus, talc could be expected to exhibit the highest uncontrolled emissions and quartz the least.

The moisture content of the material processed can have a significant effect on uncontrolled emissions. This is especially evident during quarrying, initial material handling, and initial plant process operations such as primary crushing. Surface wetness causes fine particles to adhere to the faces of larger stones, with a resulting dust suppression effect. However, as new fine particles are created by crushing and attrition, and as the moisture content is reduced by evaporation, this suppression diminishes and may disappear. Since moisture content is usually expressed as a basis of overall weight percent, the actual moisture amount per unit area will vary with the size of the rock being handled. On a constant mass fraction basis, the per-unit-area moisture content varies inversely with the diameter of the rock. Therefore, the suppressive effect of the moisture depends on both the water content (mass) and the size of the rock product. Typically, a wet material contains 1.5 to 4 percent water.

The primary geographic and seasonal factors affecting uncontrolled particulate emissions are wind and material moisture content. Wind parameters vary with geographical location, season and weather. It can be expected that the level of emissions from unenclosed sources (principally fugitive dust sources) will be greater during periods of high winds. The material moisture content also varies with geographic locations, season and weather. Therefore, uncontrolled emissions from both process emission sources and fugitive dust sources generally will be greater in arid regions than in temperate ones and greater during the summer months because of a higher evaporation rate.

A large number of material, equipment, and operating factors influence emissions from processing plants. Principal processing facilities include crushers, screens, and material handling and transfer equipment. All these units are potential sources of particulate emissions. Emissions are generally emitted from process equipment at feed and discharge points and from material handling equipment at transfer points.

5.3.1.1 Crushing Operations

Generating particulate emissions is inherent in the crushing process. The most important element influencing emissions from crushing equipment is the type and moisture content of the rock being crushed. The crushing mechanism employed also has a substantial impact on the size reduction that a machine can achieve. The crushers used in the rock crushing industry are jaw, gyratory, roll, and impact crushers. Jaw crushers are principally applied for primary crushing. There are three types of gyratory crushers: pivoted spindle, fixed spindle, and cone crushers. The fixed and pivoted spindle gyratories are used for primary and secondary crushing, and cone crushers for secondary and tertiary crushing. Roll crushers are utilized primarily at intermediate or final reduction stages and are often used at portable plants. Crushing units using impact rather than compression generally produce a larger proportion of fines. In addition to generating more fines, impact crushers generate larger quantities of uncontrolled particulate emissions per ton/kilogram of material processed than any other crusher type.

The level of uncontrolled emissions from jaw, gyratory, cone and roll crushers closely parallels the reduction stage to which they are applied, with emissions increasing progressively from primary to secondary to tertiary crushing.

Insufficient data are available to present a matrix of rock crushing emission factors detailing the different rock types and variables discussed above. Available data for preparing emission factors also vary considerably for extractive testing and plume profiling. Emission factors from extractive testing are generally higher than those based on plume profiling tests, but they have a greater degree of reliability. Some test data for primary crushing indicate higher emissions than from secondary crushing, although factors affecting emission rates and visual observations suggest that the secondary crushing emission factor, on a throughput basis, should be higher. Exhibit 5-5 shows single factors for either primary or secondary crushing which were derived from a combined data base. An emission factor for tertiary crushing is also given, but it is based on extremely limited data. All factors are rated low because of the limited and highly variable data base.

5.3.1.2 Screening Operations

Screening is the process by which a mixture of stones is separated according to size. Screening surfaces may be constructed of metal bars, perforated or slotted metal plates, or woven wire cloth. Screening equipment commonly used in the non-metallic minerals processing industry includes grizzlies, shaking screens, and vibrating screens. Grizzlies are used to remove fines prior to primary crushing, thus reducing the load on the primary crusher. Shaking screens are generally used for screening coarse material, one-half inch (1.3 cm) or larger. Vibrating screens are by far the most commonly used screen type in the rock crushing industry. Where large capacity and high efficiency are desired, the vibrating screen can be used in place of all other screen types.

Dust is emitted from screening operations as a result of the agitation of dry material. The level of uncontrolled emissions depends on the quantity of fine particles contained in the material, the moisture content of the material, and the type of screening equipment. Generally, the screening of fines produces higher emissions than the screening of coarse materials. Also, screens agitated at large amplitudes and high frequency emit more dust than those operated at small amplitudes and low frequencies.

Screening emission factors are not available for crushed rock and stone processing however, screening emission factors for sand and gravel processing (0.16 lb/ton [0.08 kg/Mg] for TSP and 0.12 lb/ton [0.06 kg/Mg] for PM-10) should be similar to those expected from screening of crushed stones.

5.3.1.3 Conveying Operations

Material handling devices are used to convey materials from one point to another. The most common devices include feeders, belt conveyors, bucket elevators, and screw conveyors. Feeders are used to receive material and deliver it to process units, especially crushers. Belt conveyors are the most widely used means of transporting, elevating, and handling materials in the non-metallic minerals processing industry. Elevators are utilized where substantial elevation is

required within a limited space. Screw conveyors are usually used with wet classification, thus preventing significant emissions.

As with screening, the level of uncontrolled emissions from conveying operations depends on the material being handled, its size, moisture content, and the degree of agitation. Perhaps the largest emissions occur at conveyor belt transfer points. Depending on the conveyor belt speed and the free fall distance between transfer points, substantial emissions may be generated. Emission factors for transfer operations are included in Exhibit 5-6.

5.3.1.4 Grinding Operation

Grinding further reduces material to particle sizes smaller than those attainable by crushers. Grinding mills generally utilize impact rather than the compression mechanism. The principal types of mills used are hammer, roller, rod, and fluid energy. Hammermills are used for nonabrasive materials and can accomplish a size reduction up to 12:1. Roller mills can produce material ranging from 20 mesh to 325 mesh or finer. Rod mills are principally used for handling a maximum feed size of 1 to 2 inches (2.5 to 5 cm) and grinding to a maximum of 65 mesh. Fluid energy mills are used when the desired material size is in the range of 1 to 20 μm .

Grinding mills usually produce a larger proportion of fines. Particulate emissions are generated from grinding mills at the grinder's inlet and outlet. Gravity-type grinding mills accept feed from a conveyor and discharge product into a screen or classifier or onto a conveyor. These transfer points are sources of particulate emissions. The outlet has the highest emissions potential because of the finer material. Air-swept mills include an air conveying system and/or an air separator. The air separators are generally cyclone collectors. In some systems, the air merely conveys the material to a separator for deposit into a storage bin, with the conveying air escaping through the cyclone vent. In other grinding systems, the air is continuously recirculated. Maintaining this circulating air system under suction keeps the operating mill dustless, and any surplus air drawn into the system due to the suction created by the fan is released through a vent. In both cases, the vent gases will contain a certain amount of particulate matter.

5.3.1.5 Bagging and Bulk Loading Operations

In the nonmetallic minerals industry, the valve-type paper bag is widely used for shipping fine materials. The valve bag is "factory closed," that is, the top and bottom are closed either by sewing or by pasting, and a single small opening is left in one corner. Materials are discharged into the bag through the valve. The valve closes automatically due to internal pressure as soon as it is filled. Bagging operations are a source of particulate emissions. Dust is emitted during the final stages of filling when dust-laden air is forced out of the bag. The process fugitive emissions due to bagging operations are generally localized in the area of the bagging machine.

Fine product materials that are not bagged for shipment are either bulk-loaded in tank trucks or enclosed in railroad cars. The usual method of loading is gravity feeding through plastic or fabric sleeves. Bulk loading of the fine material is a source of particulate emissions because dust-laden air is forced out of the truck or railroad car during the loading operation.

5.3.2 Cement Production

The potential sources of emissions from portland cement plants are illustrated in Exhibit 5-7. Particulate, NO_x, SO₂, CO and CO₂ are the primary emissions in the manufacture of portland cement, and emissions may also include minute particles from the fuel and raw materials. Many of the emission areas are at the ends of material conveying devices, called "transfer points." Uncontrolled emissions at transfer points are reduced by lightly spraying the feed with water or an aqueous chemical solution.

Exhaust gases from kilns, clinker coolers and dry milling systems constitute the larger emission sources. In the wet process plants, raw materials are not dried but are ground with water to form a slurry; therefore, the only dust is liberated from the transfer point at which rock is fed into the grinding mill.

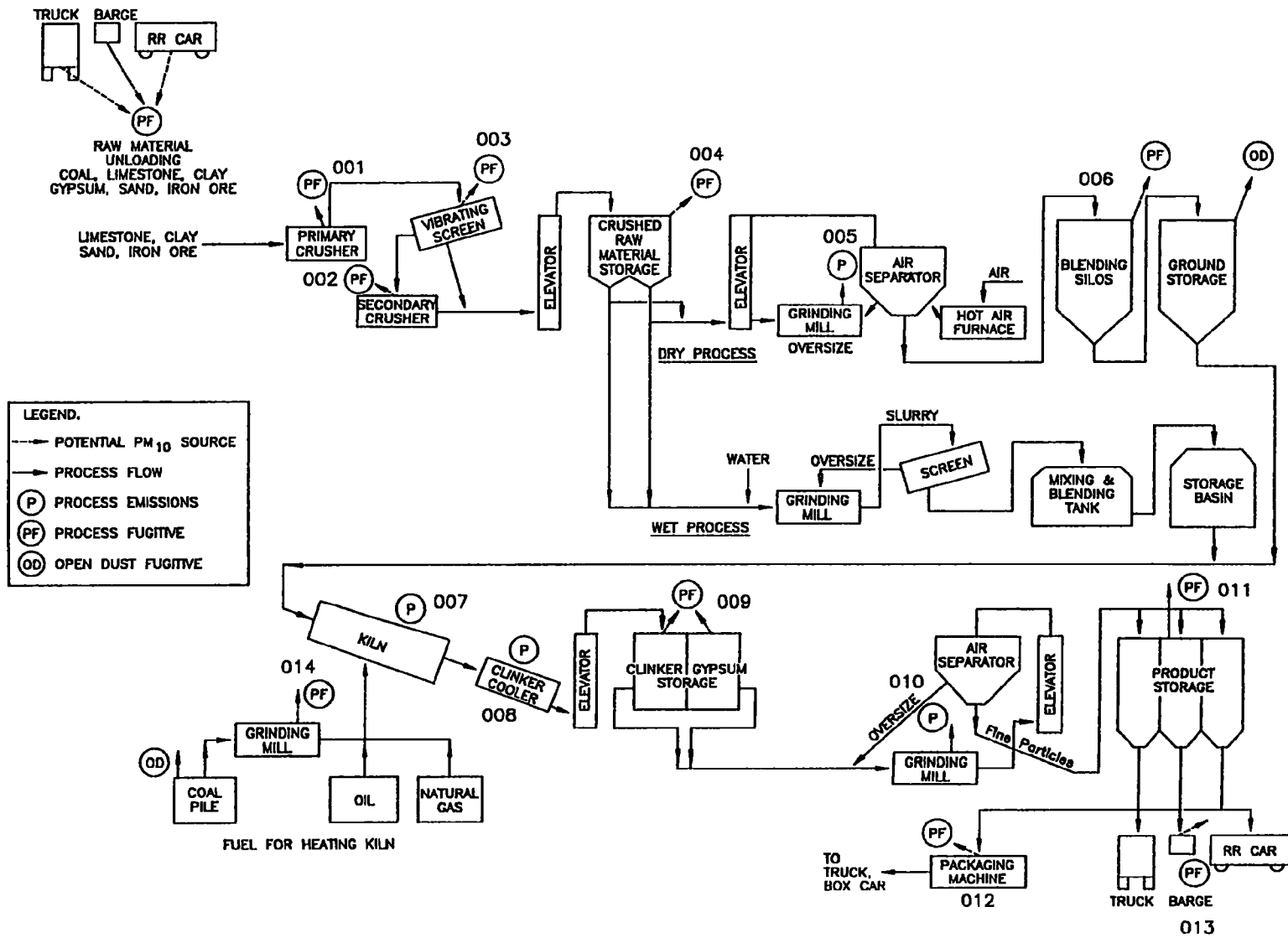


Exhibit 5-7. Potential Emission Sources from Portland Cement Plants

5.3.2.1 *Particulate Emissions*

Particulate matter is the primary pollutant from the manufacture of portland cement. The most significant sources of particulate emissions at a cement plant are the kiln and clinker cooler. Kilns controlled by a cyclone dust collector for product recovery purposes can emit as much as 45 lbs (20 kg) of particulate matter per ton (900 kg) of raw material, and clinker coolers controlled by a cyclone dust collector can emit as much as 30 lb/ton (15 kg/Mg) of raw material.

Approximately 50 percent of the particles in exhaust gases from a dry process kiln with a preheater are smaller than 1.5 to 3.5 micrometers in diameter (*i.e.*, the mass median diameter [MMD] is 1.5 to 3.5 micrometers), and 85 to 99 percent of the particles are smaller than 10 micrometers. Similarly, for wet process kiln exhaust gases, the MMD is 7 to 40 micrometers, and 20 to 60 percent of the entrained particulate matter is smaller than 10 micrometers in diameter. However, the clinker cooler exhaust gas particles are larger; the MMD is from 30 to over 100 micrometers, and less than 20 percent of the clinker cooler dust is smaller than 10 micrometer. Exhibit 5-8 presents size-specific emission factors for wet, dry, and uncontrolled cement kiln operations. Exhibit 5-9 presents emission factors for uncontrolled and controlled clinker coolers.

Quarrying, raw material storage, grinding and blending (in the dry process only), finish grinding, and packaging operations can be vented to the atmosphere, and all are potential sources of particulate emissions. The emission rate depends on the kind of raw material and its moisture content, characteristics of the crusher, the kind of control equipment, and its operation and condition. Particulate emissions also result from the open transporting of the crushed material and from the crushing and screening operations that are vented to the atmosphere.

5.3.2.2 *Gaseous Emissions*

The exhaust streams from cement kilns and clinker coolers contain a number of gaseous species in addition to the particulate matter. The following paragraphs discuss those emissions of carbon monoxide, sulfur oxides and nitrogen oxides which remain in a gaseous state and therefore

Exhibit 5-8. Size-Specific Particulate Emission Factors for Cement Kilns

Particle size (µm)	Cumulative mass % < stated size ^b				
	Uncontrolled			Baghouse	
	Wet process kiln	Dry process kiln	Wet process kiln with ESP	Wet process kiln	Dry process kiln
2.5	7.0	18	64	NA	45
5.0	20	NA	83	NA	77
10.0	24	42	85	NA	84

^aESP = electrostatic precipitator. NA = not available.

^bAerodynamic diameter. Percentages rounded to two significant figures.

Exhibit 5-9. Size-Specific Emission Factors for Clinker Coolers

Particle size ^a (µm)	Cumulative mass % < stated size ^b		Cumulative emission factor < stated size ^c			
	Uncontrolled	Gravel bed filter	Uncontrolled		Gravel bed filter	
			kg/Mg	lb/ton	kg/Mg	lb/ton
2.5	0.54	40	0.025	0.050	0.064	0.13
5.0	1.5	64	0.067	0.13	0.10	0.20
10.0	8.6	76	0.40	0.80	0.12	0.24
15.0	21	84	0.99	2.0	0.13	0.26
20.0	34	89	1.6	3.2	0.14	0.28

^aAerodynamic diameter

^bRounded to two significant figures.

^cUnit weight of pollutant/unit weight of clinker produced. Rounded to two significant figures.

uncontrolled. Fluorides, hydrocarbons and hydrogen sulfide may also be emitted.

5.3.2.2.1 Carbon Monoxide

Carbon monoxide emissions are generally negligible due to the excess air present in the kiln. A typical analysis of the kiln exhaust gas would have zero to two volume percent carbon monoxide.

5.3.2.2.2 Sulfur Oxides

Emissions of sulfur oxides from portland cement kilns are caused by fuel combustion and clinker formation. Sulfur oxide emissions are almost solely in the form of sulfur dioxide (SO_2), although small quantities of sulfuric acid (H_2SO_4) and SO_3 may exist in kiln exhaust gases.

The SO_2 emissions result from both sulfur in the fuel and sulfur in the raw materials. Direct correlation of these factors with SO_2 emissions is difficult because of the complex chemistry of sulfur in the kiln. Sulfur can be absorbed into the clinker, raw feed, or dust collected in a control device or emitted as a gas. In addition, the amount of sulfur found in the fuel and the feed can vary significantly from plant to plant. Wet process kilns tend to emit larger quantities of SO_2 than dry process kilns because they require more heat per Mg of clinker produced than do dry process plants.

Emissions of SO_2 from the kiln are reduced significantly by the production process because the SO_2 is absorbed into the clinker. About 75 percent of the SO_2 formed in the kiln reportedly is absorbed into the clinker. Data on reduction of SO_2 emissions in the production process vary widely because of differences in process parameters and in sulfur content of raw feed material and fuel.

5.3.2.2.3 Nitrogen Oxides

Parameters that affect emissions of NO_x from cement kilns include the nitrogen content in the fuel and raw materials, the flame and kiln temperature, the residence time that combustion gases remain at this temperature, the rate of cooling of these gases, and the quantity of excess air in the flame. As flame temperature increases, the amount of thermally generated NO_x increases, and the amount of NO_x generated from fuel increases with the quantity of nitrogen in the fuel. NO_x can form in portland cement kilns at temperatures of 2600° to 3000°F (1427° to 1649°C). Because clinkering occurs at about 2700°F (1482°C), temperatures favorable for NO_x formation are reached in routine kiln operation.

5.3.2.2.4 Fluorine

Fluorine can be released in the kiln from the raw materials and fuel during the formation of clinker. Tests performed on the cleaned gas from 11 cement kilns in the United States found no gaseous fluorides. This is expected since calcium fluoride is produced in the presence of excess calcium oxide and can be removed by fabric filters or electrostatic precipitators.

5.3.2.2.5 Hydrocarbons

Hydrocarbons, principally aldehydes, can result from the discharge of the products of incomplete fuel combustion. This would ordinarily only occur during start-up or malfunction.

5.3.2.2.6 Hydrogen Sulfide

Hydrogen sulfide and other odiferous sulfides can be emitted from a cement plant if certain raw materials such as marl, clay, shale, and marine shells are used in a wet process kiln. Establishing excess air conditions by reducing the fuel supply and increasing the air supply will control this.

5.4 EMISSION REDUCTION METHODS

5.4.1 Rock Crushing

5.4.1.1 Available Particulate Control Technology

The diversity of the particulate emissions sources involved in mining and processing non-metallic minerals requires use of a variety of control methods and techniques. Dust suppression techniques designed to prevent particulate matter from becoming airborne are applicable to both process fugitive and fugitive dust sources. Where particulate emissions can be contained and captured, particulate collection systems are used. Emission sources and applicable control options are listed in Exhibit 5-10.

Methods used to reduce emissions include wet dust suppression and/or dry collection. In a wet dust suppression system, dust emissions are controlled by applying moisture in the form of water or water plus a wetting agent sprayed at critical dust-producing points in the process flow. This causes fine particulate matter to be confined and remain with the material flow rather than becoming airborne. Dry collection involves hooding and enclosing dust-producing points and exhausting emissions to a collection device. Combination systems utilize both methods at different stages throughout the processing plant. In addition to these control techniques, the use of enclosed structures to house process equipment may also be effective in preventing emissions to the atmosphere.

5.4.1.1.1 Wet Dust Suppression

In a wet dust suppression system, dust emissions are controlled by applying moisture in the form of water or water plus a wetting agent sprayed at critical dust-producing points in the process flow. This causes dust particles to adhere to larger mineral pieces or to form agglomerates too heavy to become or remain airborne. Thus, the objective of wet dust suppression is not to fog an emission source with a fine mist to capture and remove particulates emitted, but rather to prevent emissions by keeping the material moist at all process stages. However, no actual

**Exhibit 5-10. Control Options for Particulate Emission Sources
in the Non-Metallic Minerals Industry**

Operation or Source	Control Option
Hauling	<ol style="list-style-type: none"> 1) Water wetting of haulage roads 2) Treatment of haulage roads with surface agents 3) Soil stabilization 4) Paving 5) Traffic control
Crushing	<ol style="list-style-type: none"> 1) Wet dust suppression systems 2) Capturing and venting emissions to a control device
Screening	<ol style="list-style-type: none"> 1) Wet dust suppression systems 2) Capturing and venting emissions to a control device
Conveying (Transfer points)	<ol style="list-style-type: none"> 1) Wet dust suppression systems 2) Capturing and venting emissions to a control device
Stockpiling	<ol style="list-style-type: none"> 1) Stone ladders 2) Stacker conveyors 3) Water sprays at conveyor discharge 4) Pugmill
Grinding	<ol style="list-style-type: none"> 1) Wet dust suppression systems 2) Capturing and venting emissions to a control device
Storage Bins	<ol style="list-style-type: none"> 1) Capturing and venting emissions to a control device
Conveying (other than transfer points)	<ol style="list-style-type: none"> 1) Covering 2) Wet dust suppression systems
Windblown dust from stockpiles	<ol style="list-style-type: none"> 1) Water wetting 2) Surface active agents 3) Covering (i.e., silos, bins) 4) Windbreaks
Bagging	<ol style="list-style-type: none"> 1) Capturing and venting emissions to a control device
Loading (product into rail cars, trucks, ships)	<ol style="list-style-type: none"> 1) Water wetting 2) Capturing and venting emissions to a control device

particulate emission measurements have been made to estimate the attainable control efficiency of wet dust suppression systems at rock crushing plants.

The wet dust suppression method has been used on a wide variety of stones including limestone, granite, shale, dolomite, sand, and gravel. It can generally be considered to have a universal application to stone handled through a normal crushing and screening operation. In some cases, however, water sprays cannot be used since the moisture may interfere with further processing such as crushing, screening, or grinding, where blinding problems may occur. In addition, the capacity of the dryers used in some of the processing steps limits the amount of water that can be sprayed onto the raw materials. Once the materials have passed through the drying operations, water cannot be added and other means of dust control must be utilized.

In order to enhance the effectiveness of the wet suppression technique, wetting agents are added to the water to lower its surface tension and consequently improve its wetting efficiency. The dilution of such an agent in minute quantities in water (1 part wetting agent in 1,000 parts water) is reported to make dust control practical throughout an entire crushing plant. In a crushed stone plant, this may amount to as little as 1/2 to 1 percent total moisture per ton (900 kg) of stone processed.

A typical wet dust suppression system is illustrated in Exhibit 5-11. Exhibit 5-11 shows the basic components and features of the wet dust suppression system including a dust control agent, proportioning equipment, a distribution system, and control actuators. A proportioner is necessary to proportion the wetting agent and water at the desired ratio and to provide moisture in sufficient quantity and at adequate pressure to meet the demands of the overall system. Distribution is accomplished by spray headers fitted with pressure spray nozzles. One or more headers are used to apply the dust suppressant mixture at each treatment point at the rate and spray configuration required to effect dust control. A variety of nozzle types may be used depending on the spray pattern desired. Exhibit 5-12 shows a typical arrangement for the control of dust emissions at a crusher discharge. As for spray actuation, it is important to prevent waste and undesirable muddy conditions, especially when the material flow is intermittent. Spray headers at each application point are normally equipped with an on-off controller which is

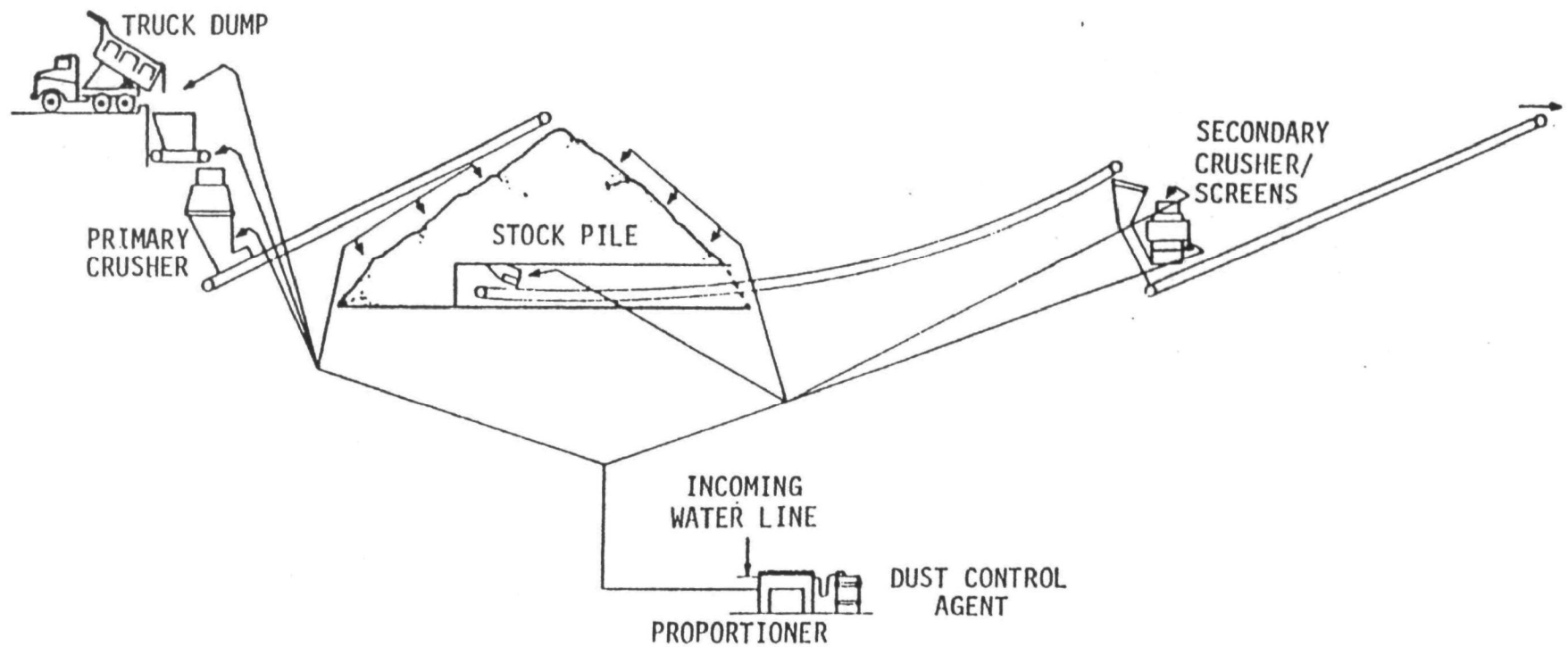


Exhibit 5-11. Wet Dust Suppression System

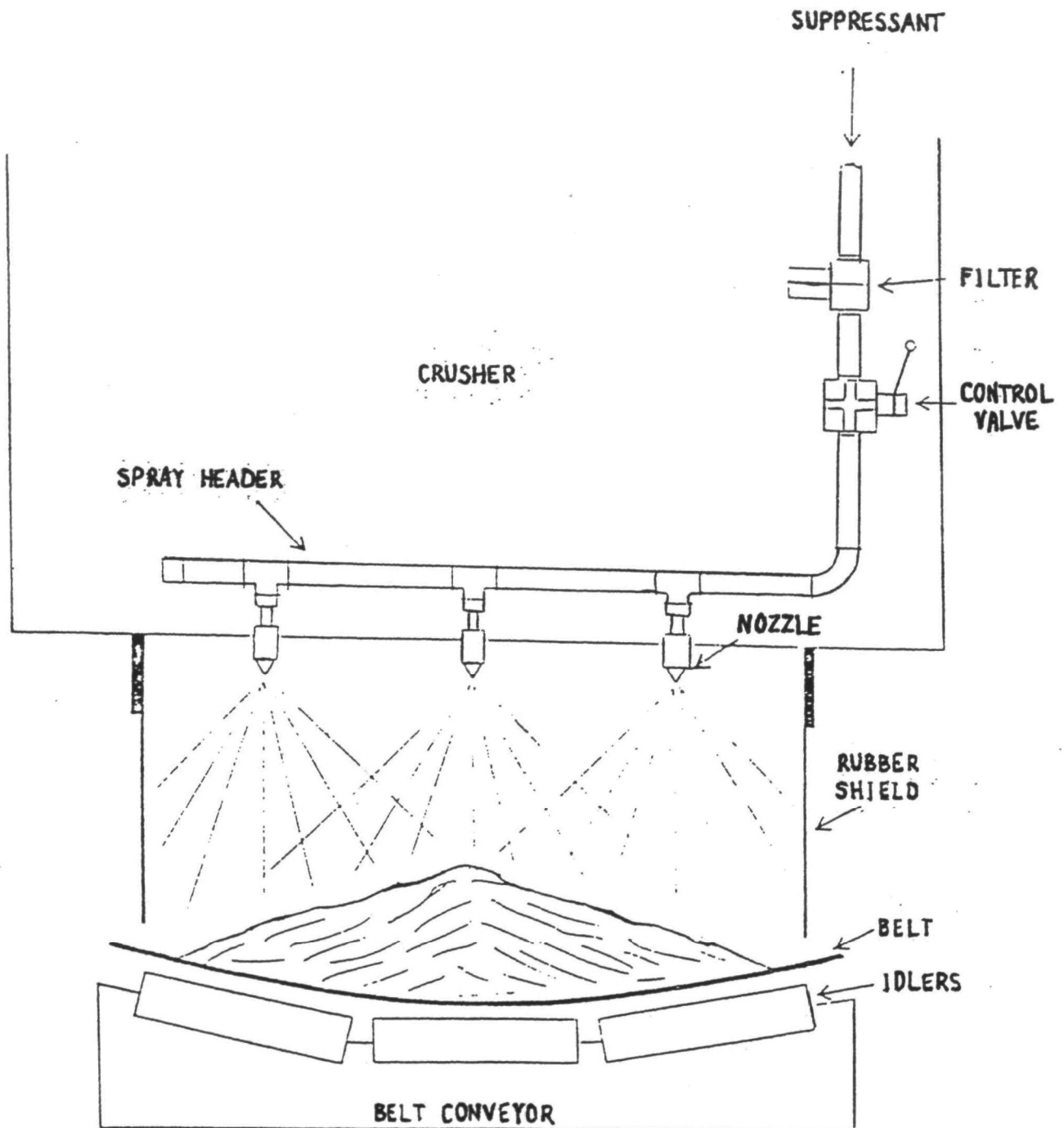


Exhibit 5-12. Dust Suppression Application at Crusher Discharge

interlocked with a sensing mechanism so that sprays will be operative only when there is material actually flowing.

In adding moisture to the process material, several application points are normally required. The initial application point is commonly made at the primary crusher truck dump. Applications are also made at the discharge of the primary crusher and at all secondary and tertiary crushers where new dry surfaces and dust are generated by the fracturing of stone. In addition, treatment may also be required at feeders located under surge or reclaim piles if this temporary storage results in sufficient evaporation. The amount of moisture required at each application point is dependent on a number of factors including the wetting agent used, its dilution ratio in water, the type and size of process equipment, and the characteristics of the material processed (type, size distribution, feed rate and moisture content).

5.4.1.1.2 Dry Collection Systems

Particulate emissions generated at plant process operations (crushers, screens, grinders, conveyor transfer points, fine product loading operations and bagging operations) may be controlled by capturing and exhausting potential emissions to a collection device. Depending on the physical layout of the plant, emission sources may be manifolded to a single centrally located collector or ducted to a number of individual control units. Collection systems consist of an exhaust system utilizing hoods and enclosures to capture and confine emissions, dusting and fans to convey the captured emissions to a collection device, and a collection device for particulate removal prior to exhausting the air stream to the atmosphere.

Exhaust Systems and Ducting. If a collection system is to effectively prevent particulate emissions from being discharged to the atmosphere, local exhaust systems including hooding and ducting must be properly designed. Process equipment should be enclosed as completely as practicable, allowing for access for operation, routine maintenance and inspection requirements. For crushing facilities, recommended hood capture velocities range from 61 to 150 meters per minute. A well designed enclosure can be defined as a housing which minimizes open areas between the operation and the hood and contains all dust dispersion action. Good duct design

dictates that adequate conveying velocities be maintained so that the transported dust particles will not settle in the ducts along the way to the collection device. Based on information for crushed stone, recommended conveying velocities range from 1,100 to 1,400 meters per minute.

Collection Devices. The most efficient collection device used in the non-metallic mineral processing industry is the fabric filter or baghouse. Fabric filters will be discussed in detail in Section 5.4.2.1. Other collection devices include wet capture. The principle of collection in wet capture devices involves contacting dust particles with liquid droplets and then having the wetted and unwetted particles impinge upon a collecting surface where they can be flushed away with water. The major types of wet collectors are cyclone, mechanical, mechanical-centrifugal, and Venturi scrubbers.

Wet cyclones impart a centrifugal force to the incoming gas stream causing it to increase in velocity. Atomized liquids are introduced to contact and carry away dust particles. The dust impinges upon the collector walls, with clean air remaining in the central area of the device. Efficiencies in this type of equipment average in the vicinity of 98 percent.

Mechanical scrubbers have a water spray created by a rotating disc or drum contacting the dust particles. Extreme turbulence is created which insures this required contact. Efficiencies are about the same as cyclone wet scrubbers.

Mechanical centrifugal capture devices with water sprays are similar to their dry counterparts with the exception that a water spray is located at the gas inlet so that the particulate matter is moistened before it reaches the blades. The water droplets containing particulate are impinged on the blades while the clean air is exhausted. In this case, the spray not only keeps the blades wet causing dust to impinge upon them, but it also serves as a medium to carry away particles.

Venturi scrubbers rely on an impaction mechanism and extreme turbulence for dust collection. The extreme turbulence causes excellent contact of water and particulate. The wetted particles travel through the Venture tube to a cyclone spray collector. Efficiencies are very high, averaging 99.9 percent. These high efficiencies are also evidenced in the low particle size ranges

collected (less than 1 micrometer in diameter). This design is best suited to applications involving removal of 0.5 to 5 micron size.

5.4.1.1.3 Combination Systems

Wet dust suppression and dry collection techniques are often used in combination to control particulate emissions from crushing plant facilities. Wet dust suppression techniques are generally used to prevent emissions at the primary crushing stage and at subsequent screens, transfer points and crusher inlets. Dry collection is generally used to control emissions at the discharge of the secondary and tertiary crushers, where new dry surfaces and fine particulates are formed. In addition to controlling emissions, dry collection results in the removal of a large portion of the particulates generated with the resultant effect of making subsequent dust suppression applications more effective with a minimum of added moisture. Depending on the product specifications, dry collection may also be necessary at the finishing screens.

5.4.2 Cement Production

5.4.2.1 Available Particulate Control Technology

Typical methods used for control of particulate emissions from potential sources at portland cement manufacturing facilities are listed in Exhibits 5-13 and 5-14. The kiln and clinker cooler are the first and second largest sources, respectively, of particulate emissions at a cement plant. Particulate emissions also occur during material handling, transfer, and storage. Particulate emissions from kilns are controlled by fabric filters, electrostatic precipitators (ESP), or cyclones. Particulate emissions from clinker coolers and other facilities (mills, storage facilities, and transfer facilities) are typically controlled by fabric filters.

Exhibit 5-15 includes controlled particulate emission factors for the different processes in cement manufacturing. The types of controls listed in Exhibit 5-15 are discussed below.

**Exhibit 5-13. Potential Sources of Particulate Emissions
and Typical Control Technologies**

Operation or Source	Control Option
Raw material system (including crushing and grinding)	1) Fabric filter
Raw material dryer	1) Fabric filter
Crushed raw material storage (except coal piles)	1) Fabric filter 2) Capturing and venting emissions to a control device
Raw blending	1) Fabric filter 2) Capturing and venting emissions to a control device
Kiln (including preheater/ precalciner systems)	1) Fabric filter 2) Electrostatic precipitator
Clinker cooler	1) Fabric filter 2) Electrostatic precipitator 3) Gravel bed filter
Clinker storage	1) Capturing and venting emissions to a control device 2) Fabric filter 3) Enclosure 4) Cover 5) Wind breaks
Finish mill system	1) Fabric filter 2) Electrostatic precipitator
Finished product storage	1) Fabric filter
Conveyor transfer points (e.g., to primary crusher, secondary crusher, elevators, materials storage, grinding mill)	1) Fabric filter 2) Capture to control device 3) Wet suppression 4) Work practice
Packaging (i.e., bagging)	1) Fabric filter

Exhibit 5-14. Application of Emission Control Devices to Portland Cement Processes

Process	Effectiveness of Emission control device ^a			
	Cyclone separator	ESP	Fabric filter	Gravel bed filter
Raw material crushing and grinding	Unsatisfactory	Impractical	Successful	Impractical
Calcining	Successful ^b	Successful	Successful	Impractical
Clinker cooling	Successful	Successful	Successful	Impractical
Product storage packaging and loadout	Unsatisfactory	Impractical	Successful	Impractical
General housekeeping and fugitive controls	Impractical	Impractical	Successful	Impractical

^aWet collectors are generally not used for portland cement processes.

^bPreliminary cleaning only; used with ESP or fabric filter.

**Exhibit 5-15. Controlled Particulate Emission Factors for
Cement Manufacturing**

Type of source	Control	Particulate		Emission Factor Rating
		kg/Mg clinker	lb/ton clinker	
Wet process kiln	Baghouse ESP	0.57	1.1	C
		0.39	0.78	C
Dry process kiln	Multiclone	130 ^b	260 ^b	D
	Multicyclone + ESP	0.34	0.68	C
	Baghouse	0.16	0.32	B
Clinker cooler	Gravel bed filter	0.16	0.32	C
	ESP	0.048	0.096	D
	Baghouse	0.010	0.020	C
Primary limestone crusher ^c	Baghouse	0.00051	0.0010	D
Primary limestone screen ^c	Baghouse	0.00011	0.00022	D
Secondary limestone screen and crusher ^c	Baghouse	0.00016	0.00032	D
Conveyor transfer ^c				
	Baghouse	0.000020	0.000040	D
Raw mill system ^{c,d}				
	Baghouse	0.034	0.068	D
Finish mill system ^e				
	Baghouse	0.017	0.034	C

^aFactors are for kg particulate/Mg (lb particulate/ton) of clinker produced, except as noted.

ESP = electrostatic precipitator.

^bBased on a single test of a dry process kiln fired with a combination of coke and natural gas.

Not generally applicable to a broad cross section of the cement industry.

^cExpressed as mass of pollutant/mass of raw material processed.

^dIncludes mill, air separator and weight feeder.

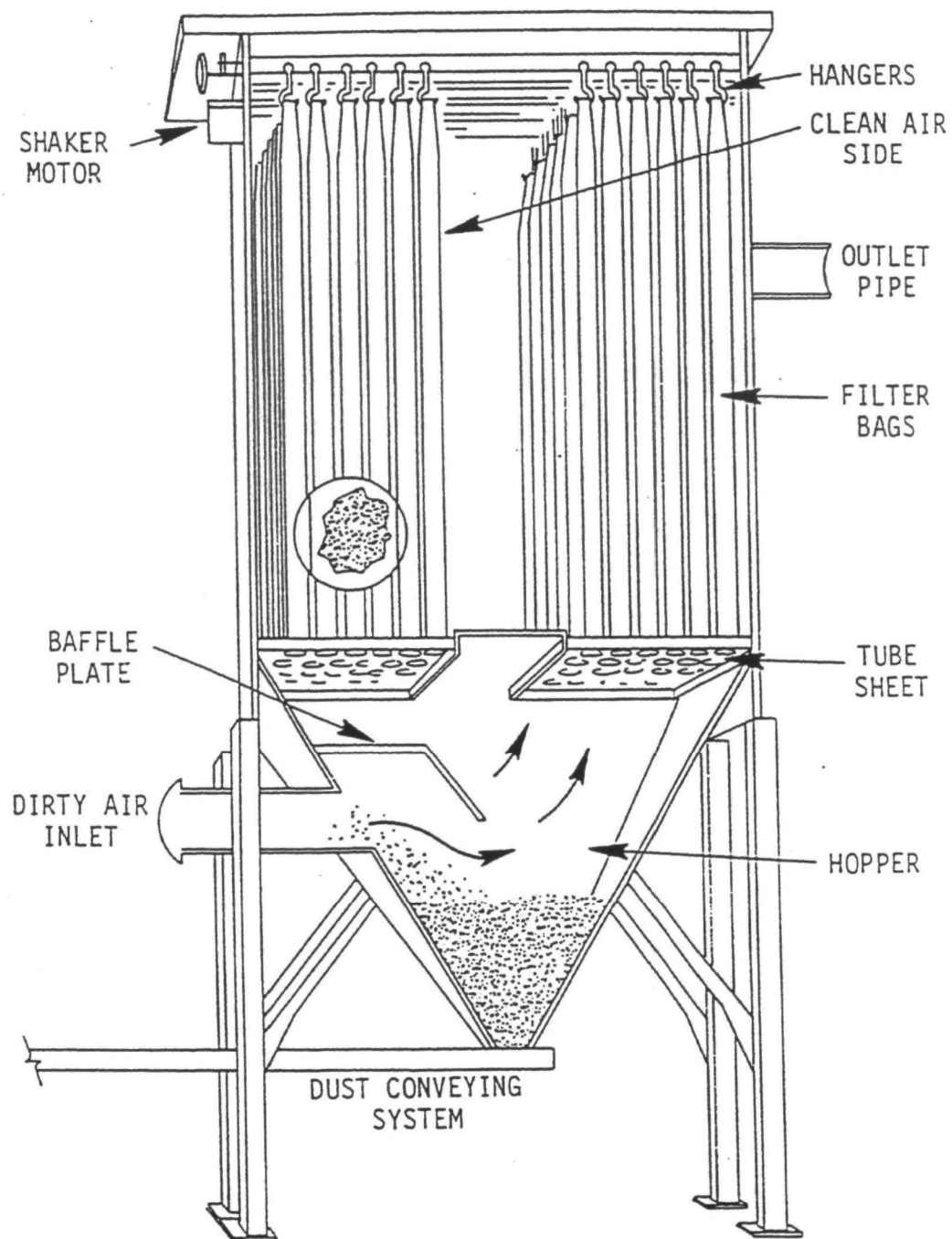
^eExpressed as units of cement produced. Includes mill, air separator(s) and one or more material transfer operations.

5.4.2.1.1 Kiln

Fabric Filters. A fabric filter system consists of a woven textile material, usually in the shape of a cylindrical bag, housed in a metal enclosure having inlet and outlet gas connections, a dust discharge hopper, and a means for periodic cleaning of the fabric. Exhibit 5-16 illustrates a fabric filter system. The particulate-laden gas enters the filter through the inlet gas connection and passes through the filtering medium, where the particulate matter is retained. The gas then leaves the filter via the outlet gas connection. The efficiency of a fabric filter is directly proportional to the fabric area. Design efficiencies of greater than 99.9 percent are typical. The filter is sized in terms of cloth area as a function of the amount of gas handled and the method of filter cleaning. The area is determined from the air-to-cloth ratio, which is arrived at by dividing total air flow by the cloth area. The air-to-cloth ratio of fabric filters ranges from about 1.3:1 to 2:1 for kilns and alkali bypass systems. The bags are typically made of fiberglass and cleaned by reverse air. Bag life is affected by the abrasiveness of the particulate matter in the exhaust gases, temperature of the gases, and maintenance practices.

Advantages of fabric filters include high efficiencies, simplicity in operation, reliability, and the ability to isolate compartments for repairs. Disadvantages of fabric filters include the need for a high pressure drop (necessitating high energy consumption), a low resistance to temperatures above 600°F (316°C), and the potential for blinding of the bags at temperatures below the dew point.

Electrostatic Precipitators. Electrostatic precipitators can operate economically and at high control efficiencies on exhaust gas streams with high-volume flow rates ($> 2,000$ cfm/ > 56.6 m³/min) and temperatures in the 300° to 600°F (149° to 315°C) range. In the portland cement industry, ESP are mainly used to control particulates in the exhaust gas flow streams from cement kilns. Cleaning of exhaust gases using electrostatic precipitators involves three steps: (1) passing the suspended particles through a direct-current corona to charge them electrically; (2) collecting the charged particles on a grounded plate; and (3) removing the collected particulate from the plate by a mechanical process. Design efficiencies greater than 99.9 percent are typical of ESP.



**Exhibit 5-16. Typical Fabric Filter Arrangement With Shaker
for Dust Removal
(Courtesy of Wheelabrator-Frye Corporation)**

The high resistivity of particles in cement kiln exhaust gases requires that the gases be conditioned prior to entering the ESP. Resistivity is about a factor of 10 lower for wet process kilns than for dry process kilns because of the moisture in the gases; however, the resistivity of exhaust gases from the dry process kilns can be lowered by spray cooling. Exhaust gases from dry process kilns with preheaters have higher resistivity than those from dry process kilns without preheaters. ESP can operate at high temperatures and at temperatures below the dew point.

Cyclones. Use of cyclone separators has been limited in the portland cement industry. Cyclone collection systems consist of one or more conically shaped vessels in which the gas stream follows a circular motion prior to outlet (typically at the bottom of the cone). As shown in Exhibit 5-17, the dust-laden gas enters the upper cylindrical section tangentially, which produces a centrifugal force that preferentially throws the larger, heavier particles outward to the walls of the cylinder. The gas spirals downward into the conical section, where the gas velocity increases and greater centrifugal force is generated. The particulate matter collected at the walls is swept to the bottom of the cone section, where it is discharged into a collection hopper or drum. The cleaned gas exits from the unit through an outlet at the top center of the cylindrical section. Cyclones are easy to operate but cannot readily achieve high efficiencies in the removal of small particles. Collection efficiency is a function of (a) size of particles in the gas stream, (b) particle density, (c) inlet gas velocity, (d) dimensions of the cyclone, and (e) smoothness of the cyclone wall. In the cement industry, cyclone-type collection systems are used for product recovery. Cyclones are typically used as precollection systems in combination with fabric filters and ESP.

5.4.2.1.2 Clinker Cooler

Fabric Filters. Most of the fabric filters used for control of clinker cooler emissions are the negative-pressure type. The bags in fabric filters controlling clinker coolers are typically cleaned by a pulse jet cleaning mechanism and have air-to-cloth ratios ranging from about 4:1 to 9:1. The bags may be made of fiberglass. Clinker cooler exhaust gas temperatures range from about 200° to 450°F (93° to 232°C).

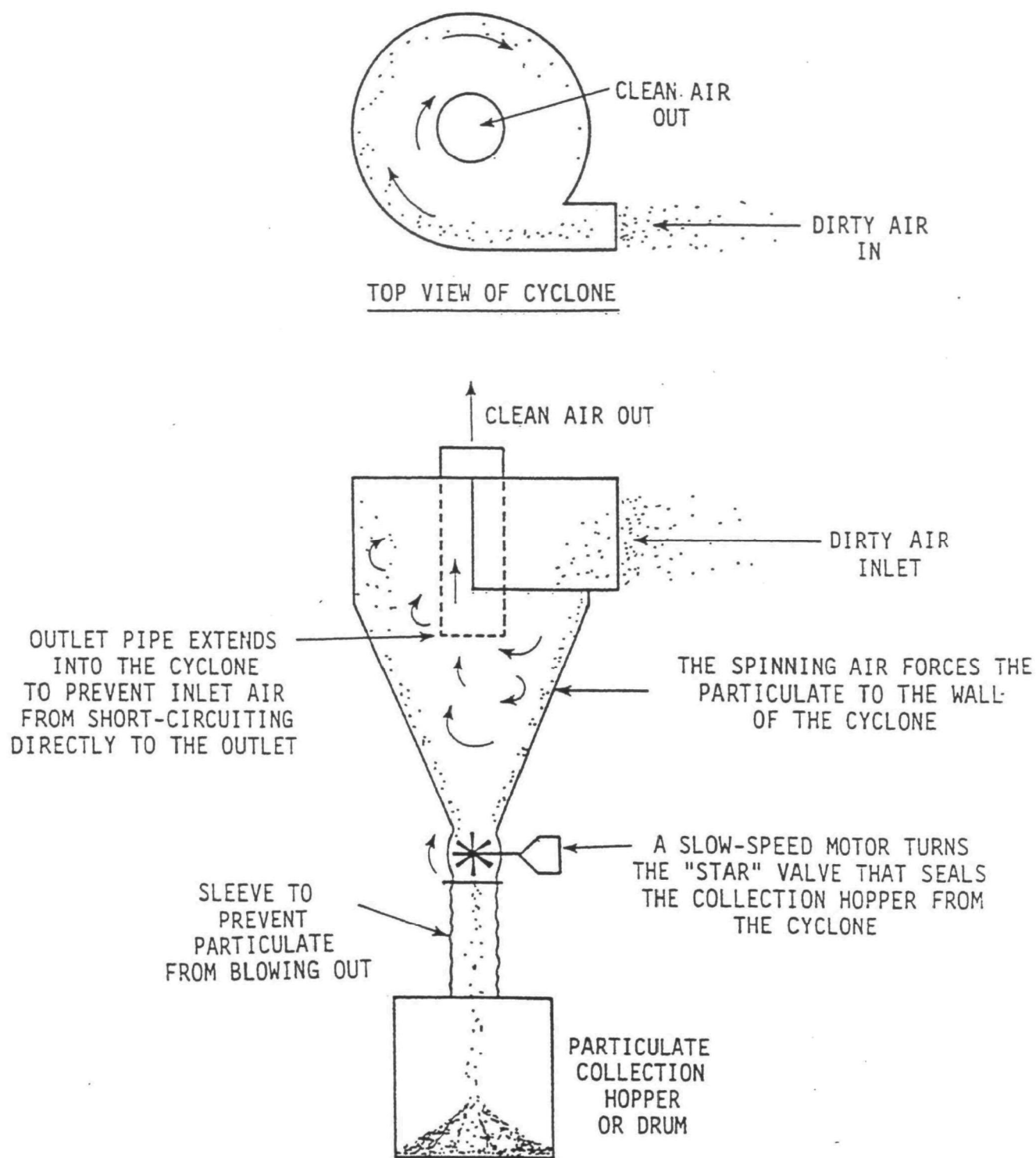


Exhibit 5-17. Flow Diagram of a Dry Cyclone Collector

Electrostatic Precipitators. In the portland cement industry in North America, ESP are rarely used to control particulates in the exhaust gas streams from clinker coolers. If exhaust gas streams contain a large amount of moisture, care must be taken to maintain the gas temperature well above the dew point to prevent condensation in the precipitator.

Advantages of ESP include the ability to handle large volumes of gas with very little pressure drop, the relatively lower power requirements (as compared to fabric filters) due to the low pressure drop, and the ability to handle high temperature gases and corrosives. However, ESP have disadvantages: sulfur oxides in the exhaust gas corrode the metal parts causing reduced efficiency, sulfur acids can diffuse into concrete casings and eventually destroy them, and alkalies can coat high-voltage components and cause short circuits.

Gravel Bed Filter. Gravel-bed filters have been used successfully in the portland cement industry for many years, although their application is limited. A gravel-bed filter control system consists of 6 to 20 modules, each of which may contain from 1 to 3 gravel beds.

The gravel-bed filter applies the principles of centrifugal force and impingement to the removal of particulates from an exhaust gas stream. As shown in Exhibit 5-18, as the particulate-laden gas enters the filter, it is subjected to centrifugal forces which move the larger particulates outward to the walls, from which they eventually fall to the bottom for removal via an air lock. The partially cleaned gas first flows up through a riser to one or more filter chambers located above and then passes down through gravel beds supported on wire mesh screens. The particulate in the gas impinges upon the gravel surface and is captured by deposition. The cleaned gas stream from the beds is exhausted through a clean-gas chamber into an exhaust duct that conveys it to a stack for discharging to the atmosphere. Modules must be removed from service at regular intervals and subjected to cleaning by backflushing them with air.

The one process point in a portland cement plant where the gravel-bed filter has been widely used is the clinker cooler. The cooler is frequently subjected to process upsets that cause high-temperature-gas excursions, a condition that is easily accommodated by the gravel-bed filter. The filter does an excellent job of removing the abrasive particulate from the cooling exhaust gases.

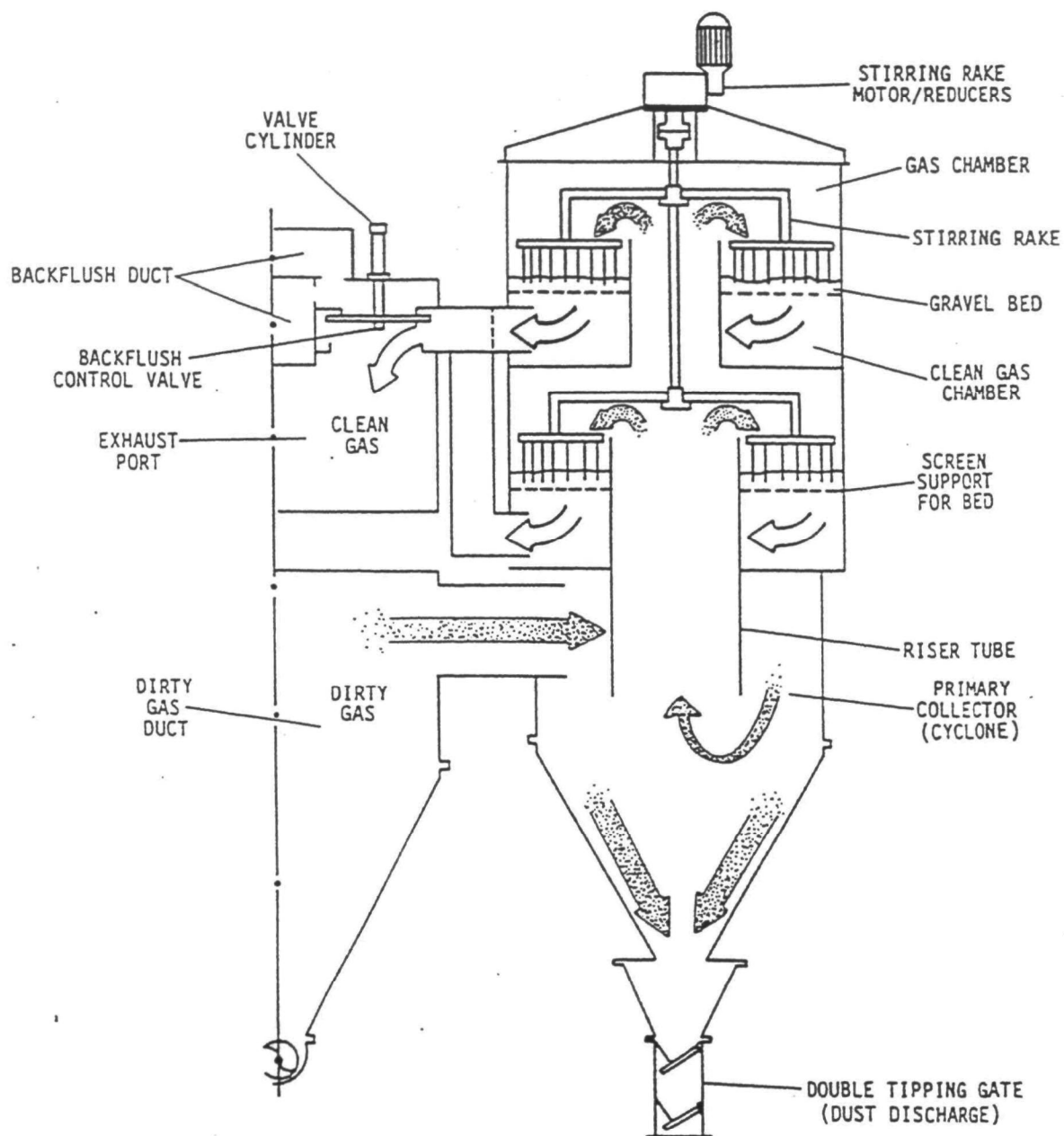


Exhibit 5-18. Gas Flow Diagram for a Gravel-bed Filter
(Courtesy of Rexnord Corporation)

Stack tests show that the gravel-bed filter has particulate removal efficiencies averaging 99.85 percent. Because of the inherent ability of the gravel-bed to withstand temperatures in excess of 1,000°F (538°C), inlet gas streams require no cooling. The gravel-bed is also resistant to attrition and therefore can be used to filter abrasive particulate materials.

5.4.2.1.3 Other Facilities

Affected facilities other than the kiln and clinker cooler include feeding, transfer, and discharge operations; raw material, clinker, and finished product storage; loading and unloading of raw and final products; and disposal of material collected by the control devices. Because of the volume of material processed, these sources have the potential of contributing significant amounts of emissions. Containment and dust suppression practices prevent these sources from generating excessive emissions, however.

Feeding, transfer, and discharge operations are all sources of emissions problems, and spilled product and wind are responsible for entrainment of the dust. Most of the entrained dust results from spillage and agitation of material at the transfer points. Such emissions are contained by either enclosing (totally or partially) or hooding these transfer points with exhaust gases directed to fabric filters. The air-to-cloth ratios of fabric filters controlling these facilities range from 4:1 to 8:1. The bags are less heat resistant than those used to control kilns or clinker coolers.

Loading and unloading operations of both raw materials and final product create an emission problem because of the mechanical agitation of the material as it strikes the sides and bottom of the receiving vessel and because of displaced air during loading and unloading. Various containment practices are used in combination. Such practices include enclosing the operation, choke-feeding or using a telescoping chute to limit the free-fall distance of the material, and using movable hoods ducted back into the unloading vessel.

Dust emissions from storage piles occur when the material is dumped onto the pile and when wind blows across the pile. Containment methods are enclosure of the storage area or the application of dust suppressants to the material. Wet suppression methods include the application

of water, chemicals, and foam. The point of application is most commonly at the conveyor feed and discharge points, but some applications are at conveyor transfer points and equipment intakes. A wet suppression system is shown in Exhibit 5-19. The type of material stored determines which containment method should be used (*e.g.*, the application of water is not a suitable containment method for stored finished cement). The use of telescoping chutes is also an effective containment practice during the dumping of material onto storage piles.

Finally, the disposal of material collected by the control devices also can be a source of emissions. The disposal process consists of loading, unloading, and transporting of the waste. Containment methods for loading include enclosing the loading area and reducing the free-fall distance into the disposal vehicle. Containment in transport can be accomplished by the use of an enclosed vehicle. Containment during the unloading of the waste at the disposal site can be accomplished by reducing the free-fall distance and covering or chemically stabilizing the material at the site to prevent wind erosion. Exhibit 5-19 summarizes the various containment practices.

5.4.2.2 *Available Gaseous Emissions Control Technology*

5.4.2.2.1 *Carbon Monoxide*

Currently, there are no methods available for reducing CO or CO₂ except process control for CO and reduced production for CO₂.

5.4.2.2.2 *Sulfur Oxides*

Sulfur dioxide may be generated both from the sulfur compounds in the raw materials and from sulfur in the fuel. The alkaline nature of the cement, however, provides for direct absorption of SO₂ into the product. Using a baghouse that allows the SO₂ to come into contact with the cement dust provides inherent reduction of 75 percent or more of the raw material and fuel sulfur

Exhibit 5-19. Dust Suppression Practices

Operation	Enclosing	Hooding	Telescoping or choke-feeding	Chemical or water spray
Transfer and conveying	X	X		
Loading and unloading	X	X	X	
Paved and unpaved roadways				X
Storage piles	X		X	X
Disposal	X		X	X

content. The percent reduction will vary with the alkali and sulfur content of the raw material and fuel.

5.4.2.2.3 Nitrogen Oxides

Currently, there are data to support only two types of NO_x reduction in the cement industry in the United States. First, for conventional wet and dry process kilns, NO_x emissions are reduced by fuel conversion, with coal producing the least NO_x. For new construction, the data are not yet clear. Some preheater/precalciner systems have low emissions and others have high emissions.

There are at least ten different preheater/precalciner systems used in the cement industry in the United States and each appears to have unique emission properties. However, it is evident that for a single system, burning oil in the calciner produces less NO_x than coal. The NO_x emissions from preheater/precalciner appear to relate to design. Some have very low emissions and others have emissions in a mid range of some conventional or wet processes.

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CHAPTER 6
PLASTIC INJECTION MOLDING

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CHAPTER 6.0

PLASTIC INJECTION MOLDING

6.1 INDUSTRY DESCRIPTION

The plastics industry is one of the world's largest and fastest growing manufacturing enterprises whose products are used worldwide. The plastics industry processes raw materials into finished goods by several methods, the most common being injection molding and extrusion. These two methods comprise more than 64 percent of the total plastics production. This discussion will concentrate on injection molding, which accounts for 23 percent of plastics production.

A large number of items used in daily life are produced through injection molding. Typical product categories include housewares, toys, automotive parts, building supplies and household furnishings. Plastic molding facilities range from small plants with a single process and a few employees to large plants with several hundred employees.

Injection molding is used to produce intricate plastic parts with excellent dimensional accuracy. Injection molding has the advantage that molded parts can be manufactured with little or no need for finishing operations such as polishing or other surface treatments. The products of injection molding adopt the surface characteristics of the mold in which they were formed (i.e. smooth or textured). Injection molding involves the plasticizing of pelletized or granular plastic with heat and the subsequent injection of the melt into a mold cavity. Most mold cavities are comprised of multiple cavities, allowing for very high production rates. The high production rates make injection molding a very economical method for producing plastic products.

Plastic is a generic term for a group of synthetic or natural organic materials composed of high molecular weight, long chain molecules. The molecular composition, in combination with the pattern and amount of branching in the molecule and the degree of crosslinking between chains, determines the characteristics of the material. Plastic materials include many types of resins, resinoids, organic polymers, cellulose derivatives, casein derivatives, and proteins. Except for

some specialty applications, the majority of plastic materials used in consumer and industrial products is made of synthetically produced organic polymers and copolymers.

Plastic materials are generally classified into two basic groups: thermoplastics and thermosets. Thermoplastics become soft when exposed to specific amounts of heat and harden when cooled. The heating and cooling process can be repeated several times. Thermoplastic materials can be processed by a large number of forming processes, the most common being injection molding and extrusion. Some common thermoplastic materials include: acrylonitrile-butadiene-styrene (ABS), high and low density polyethylenes (HDPE and LDPE), polypropylene, polystyrene, and polyvinyl chloride (PVC).

Thermosetting plastics are set into permanent forms by applying heat and pressure during molding or forming. Unlike thermoplastics, thermoset products cannot be softened or reformed after they are set into a shape. Thermoset plastic products are usually formed by processes such as compression molding, transfer molding and casting. However, some thermosets are also used by injection molders. Thermoset plastic materials include alkyd resins, nylons, epoxy resins, phenolic resins, and silicon.

Exhibit 6-1 lists a variety of the thermoplastic and thermoset resins used in injection molding. Formulation criteria and typical end uses are also included.

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS

Polymer	Formulation	Products
Acrylic Resins	Usually requires desiccant drying	Thin wall, complex parts for household, optical, and technical applications
	Antistatics Colorants Flame Retardants Lubricants UV Stabilizers	<i>Automotive lenses</i> Decorative escutcheons Nameplates Lighting louvers Lighting lenses Video disk products Medallions Typewriter buttons and bars Pump parts Piano keys
Acrylonitrile-Butadiene-Styrene (ABS)	Resin must be dried 2-4 hours at 82-93°C (180-200°F) in a dehumidifying air hopper drier	Appliance housing Bobbins and spools Bores, containers, carry cases, tackle boxes
	Antioxidants Antistatics Blowing Agents Colorants Flame Retardants Lubricants Reinforcers Stabilizers UV Stabilizers	Flashlight housings Football helmets Furniture parts Household items Machine housings Pipe fittings Radio cabinets Suitcases <i>Automotive components for instrument panels, consoles, ducts, door post covers, door locks, knobs, radiator grills, and headlight housings</i> Toys Sporting goods Hobby kits Canoe parts

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(Continued)

Polymer	Formulation	Products
Fluoroplastics		
Ethylene-Tetrafluoroethylene Copolymer ETFE (Teflon@)	Pelletized Resins	Pump components
	Fillers	Process equipment parts Tower packings
Fluorinated Ethylene Propylene Copolymer FEP (Tefzel@)	Pelletized Resins	Process equipment parts
	Reinforcers	Electrical insulators Valve fittings
Polyvinylidene Fluoride PVDF (Kynar@)	Pelletized Resins	Pumps for corrosive fluids
	Activators	Bearing seals and rings
	Blowing Agents	Valves
	Colorants	Pumps
	Crosslinking Agents	Impellers
	Curing Agents	Seals
	Fillers	Gaskets
	Plasticizers	Electrical Connectors
	Processing Aids	
	Reinforcers	

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Nylon 6 and Nylon 6/6	Polymer must be dried 4-10 hours at 110°C (230°F) Antioxidants Antistatics Blowing Agents Colorants Fillers Lubricants Plasticizers Reinforcers UV Stabilizers	Medical items
		Precision moldings
		Shoe heels
		Military items
		Cases
		Cookware
		Valve caps
		<i>Automotive parts for fuel vapor recovery, canisters, emissions control components, fan blades, distributor parts, cable ties, dome light covers, and speedometer gears</i>
		Electrical components for connectors, housings, battery boxes, small motor casings, relay covers, wire ties, switch housings, fuse holders, terminal boxes, grommets, and clips
		Machine parts for small gasoline engine parts, starter gears, air silencers, carburetors, cams, roller bearings, small gears, sprockets, pulleys, bushings, bearings, and impellers
		Fasteners
		Drapery hardware
		Plumbing hardware
		Furniture
		Fixtures
		Door hardware
		Tool parts
		Shower heads
		Irrigation devices
		Suspension mechanism for file cabinets
		Valves for aerosol cans
		Marine deck fittings
		Golf club parts
		Gun stocks
		Cigarette lighter
		Spatulas bodies

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Phenolics	Colorants Fillers Lubricants Reinforcement	Bearings
Polyacetal	Antioxidants Colorants Reinforcers UV Stabilizers	Conveyors Gears Office supplies Ballcocks Pushbuttons for telephones Pens Tape cartridges Toys Zippers Aerosol valves Turn signals for autos Specialty electrical parts Molds
Polycarbonate	Resin must be dried 2-4 hours at 127°C (260°F) in a dehumidifying hopper drier Antioxidants Blowing Agents Colorants Flame Retardants Lubricants Mold Release Agents Reinforcers UV Stabilizers	<i>Automotive parts</i> Battery cases Electrical parts Household items Petri dishes Printed circuit boards Safety shields Templates and slide rules Lenses
Polyester		
Polybutylene Terephthalate (PBT)	Resin must be dried 2-4 hours at 121°C (250°F) Reinforcers	Electrical parts <i>Automotive parts</i> Housewares
Polyethylene Terephthalate (PET)	Crystalline resin must be dried 2-4 hours at 150-180°C (302-350°F) Antioxidants Antistatics Colorants Flame Retardants Reinforcers	Containers

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Polyethylene		
Low Density Polyethylene (LDPE)	Antiblocking Agent Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Impact Modifiers Reinforcers UV Stabilizers	Bobbins Containers Packaging Lids for coffee cans, margarine tubs, shortening, nuts, and pipe tobacco Toys Novelties Housewares
High Density Polyethylene (HDPE)	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Flame Retardants Impact Modifiers Reinforcers Stabilizers UV Stabilizers	Ice cream containers Pails Paint cans Seating components Tote boxes Toys Catsup and mustard containers Ice cube trays Canisters Butter dishes Hard hats Furniture
Ethylene Vinyl Acetate (EVA)	Antioxidants Antistatics Colorants Corrosion Inhibitors Crosslinking Agents Fillers Flame Retardants Mold Release Agents Reinforcers Thermal Conductors	Plates and sheets Blocks Rods and tubes
Polyphenylene Oxide		TV parts Filter stacks Filter discs Valve seats Surgical instruments Food trays Small appliance housings <i>Dashboard electrical connectors</i> <i>Knobs and handles</i> Cases Pumps Shower heads

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Polyphenylene Sulfide	Colorants Mineral Fillers Reinforcers	Bearings and cams Electronic parts Hair dryer parts Small cooking appliances Range components Valves
Polypropylene	Antiblocking Agents Antioxidants Antistatic Agents Blowing Agents Colorants Fillers Flame Retardants Lubricants Plasticizers Reinforcers Stabilizers UV Stabilizers	Battery cases Closures, lids, caps, and containers Luggage and carry cases Packaging Tables Toys and novelties Washing machine agitators Clothes drier filter housings Dishwasher pump components, silverware baskets, detergent dispensers, inlets and drains Refrigerator ice maker components Room air conditioner air deflectors, condensate pans, filter frames and impellers Television set parts Butter dishes Light shield Ice cube trays Tupperware® Seats Furniture frames Sports equipment Syringes Labware Medical tubing and connectors <i>Automotive door panels, fender aprons, glove compartments, interior trim</i>

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Polystyrene	Antioxidants	Appliance parts
	Antistatics	Cups, lids, dishes, and cutlery
	Blowing Agents	Containers, boxes, vials, jars, and tubs
	Colorants	Housewares
	Fillers	Refrigerator trays and covers
	Flame Retardants	Toys and hobby kits
	Lubricants	Produce trays
	UV Stabilizers	Cocktail glasses
		Sporting goods
		Soap dishes
		Handles for kitchen utensils
		Salt and pepper shakers
		Coffee servers
		Watering cans
		Room dividers
		Picture frames
		Letter trays
		Calendar bases
		Toilet seats
		Architectural trim moldings
		Calculators
		Tape reels, reel covers, and cassettes
		furniture
		Combs
Polyvinyl Chloride (PVC)	Antiblocking Agents	Boots
	Antioxidants	Building and construction supplies
	Antistatic Agents	<i>Bumper parts</i>
	Blowing Agents	Business machines and appliance parts
	Colorants	Footwear, sandals, heels, and soles
	Fillers	Hospital and health care supplies
	Flame Retardants	Pipe fittings
	Fungicides	Plugs and connectors
	Impact Modifiers	Refrigerator gaskets
	Lubricants	Toys
	Plasticizers	Filler strips
	Heat Stabilizers	Rear view mirror housings
	UV Stabilizers	Window winder knobs
		Bicycle grips

(continued)

EXHIBIT 6-1. INJECTION MOLDING INPUT MATERIALS AND PRODUCTS
(continued)

Polymer	Formulation	Products
Styrene-Acrylonitrile (SAN)	Resin must be dried for a minimum of 2 hours at 71- 82°C (160-180°F)	Appliance parts <i>Automotive parts</i> Cosmetic containers Tumblers
	Fillers Lubricants Reinforcers	<i>Automotive instrument lenses</i> Blender jars and covers Dishes and trays in appliances Medical instruments and utensils Tape reels Picnic ware
Vinylidene Chloride	Antioxidants Heat Stabilizers UV Stabilizers	Gasoline Filters Valves Pipe fittings Containers
		Chemical process equipment parts

6.2 PROCESS DESCRIPTION

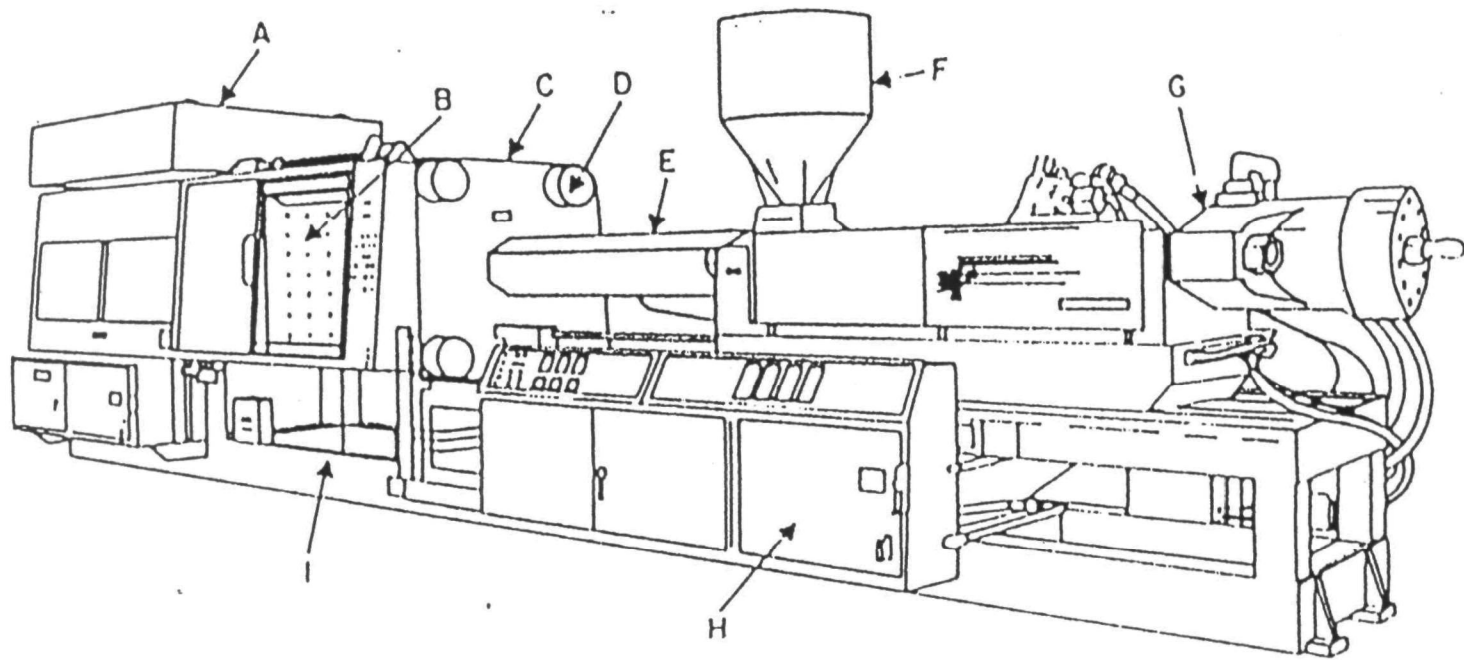
Injection molding is a cyclical process in which granular plastic feed is melted and injected into a mold. After cooling, the product is ejected from the mold and finished. Injection molding units consist of three principal parts, the heating/injection system, the clamp unit, and the removable mold. There are several types of heating/injection units which are described in Section 6.2.1. The clamp unit has two platens, one movable and one fixed, which support the mold as well as absorbing some of the pressure applied to the injected plastic during the injection stage of the molding cycle. The movable platen allows the two halves of the mold to be separated and the product removed. Molds typically have two halves, although some special-purpose molds have more parts. Exhibit 6-2 illustrates a typical injection molding machine. A detailed description of the injection molding process is provided in Section 6.2.2.

6.2.1 Heating/Injection Systems

An injection machine can mold parts weighing from a few ounces to many pounds. The majority of machines mold parts weighing from an ounce to a pound.² The rate at which the plastics are injected into the mold can vary. Generally, faster rates permit reducing cycle times but require molding thinner parts. For example combs may be produced in a mold containing 12 comb cavities. The mold may receive two shots per minute, resulting in a total production rate of 24 combs per minute. Typical injection rate specifications are presented in Exhibit 6-3.²

The four basic types of heating/injection systems used for commercial injection molding include:

- Conventional injection molding machines
- Piston-type preplasticizing machines
- Screw-type preplasticizing machines
- Reciprocating-screw injection machines



- | | | |
|--------------------------|------------------------------|---------------------------|
| <i>A. Oil reservoir</i> | <i>D. Tie rod</i> | <i>G. Hydraulic drive</i> |
| <i>B. Movable platen</i> | <i>E. Injection cylinder</i> | <i>H. Control cabinet</i> |
| <i>C. Fixed platen</i> | <i>F. Hopper</i> | <i>I. Base with pumps</i> |

Exhibit 6-2. A typical injection-molding machine, with its major elements identified.¹

(reprinted with permission from Weir, Glifford, *Introduction to Injection Molding*, Society of Plastics Engineers, Inc., Greenwich, Connecticut, 1975.)

EXHIBIT 6-3. TYPICAL INJECTION RATES

Machine Size (ton)	Injection Rate (in ³ /sec)	Shot Capacity (ounces)
150	8 - 16	6 - 12
500	25 - 45	48 - 76
1000	70 - 90	160 - 180

Two of the injection molding machines, the piston-type and the screw-type preplasticizers, have an auxiliary heating cylinder, known as the preplasticizer. This cylinder is used to melt the plastic feedstock and then transfer the melt to the injecting cylinder from which it is injected into the mold.

Conventional Injection Molding. The plastic granules or pellets are poured into the machine hopper and feed into the chamber of the heating cylinder, which is heated by conduction and convection from the electrically heated walls. A plunger compresses the material, forcing it through progressively hotter zones of the heating cylinder. Because there is little mixing within the cylinder, a torpedo-shaped spreader is usually located in the heating cylinder to force the polymer to flow against the heated metal surface of the cylinder. The presence of a spreader makes the molten resin more uniform. The material flows from the heating cylinder through a nozzle into the mold. This type of molding machine will produce mottled-colored molded parts since colorants are not thoroughly mixed with the plastic material in the heated cylinder unless pre-colored polymers are used as feed. Exhibit 6-4a illustrates a conventional injection molding machine.

Piston-Type Preplasticizing. In a piston-type preplasticizing machine the plasticizing is performed in a separate unit. An auxiliary chamber is used to heat the plastic material by conduction. A plunger pushes the melted plastic material into a second stage injection unit. This injection unit serves as a combination holding, measuring, and injection chamber. During the

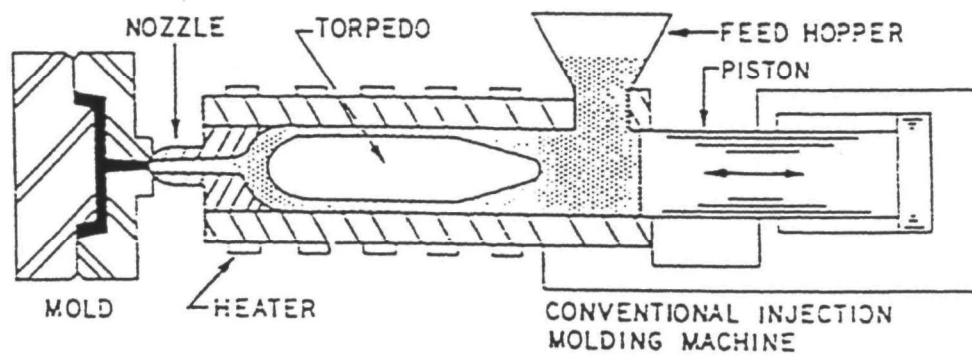


Exhibit 6-4a. Conventional injection molding machine.

injection cycle the shooting plunger forces the plastic melt from the injection chamber through the nozzle and into the mold cavity. This machine produces pieces faster than a conventional machine because the holding chamber can be filled to the proper volume (called a "shot") while a part is cooling in the mold. This process is used to produce large molded parts (*e.g.*, flower parts, garbage pails, and automobile fenders and body parts), but is not in wide commercial use.¹ Exhibit 6-4b illustrates a piston-type preplasticizing injection molding machine.

Screw-Type Preplasticizing. Screw-type preplasticizing systems use an extruder to plasticize the plastic feedstock. A rotating screw feeds the pellets forward to the heated interior surface of the extruder barrel (auxiliary heating chamber). The molten plastic is then driven from the extruder into the injecting chamber and is forced into the mold by an injection plunger. The extruder screw rotates backwards to begin the next cycle, while the screw in the shooting cylinder injects the plastic melt into the mold. The use of a screw in the heating cylinder allows the following advantages over other types of injection equipment:

- Better mixing and shear action of the plastic melt
- Better color blending
- Less stress in the molded part

Exhibit 6-4c illustrates a screw-type preplasticizing injection molding machine.

Reciprocating-Screw Injecting. This type of injection molding uses a horizontal, rotating screw in place of the piston used in the heating chamber of conventional injection molding machines. The rotating screw moves the plastic material forward under pressure to the front of the injection cylinder, while the screw itself is pushed backwards by the accumulating melt. The shearing action of the screw on the resin is the principal source of the melt heating. Back pressure inside the heating cylinder is adjustable, thereby varying the amount of internal heat transmitted to the melt. Increased back pressure raises the melt temperature without requiring an increase in heating cylinder temperatures by external electrical heating. As the molten plastic material moves forward, the screw backs up until it reaches a limit switch which indicates that the

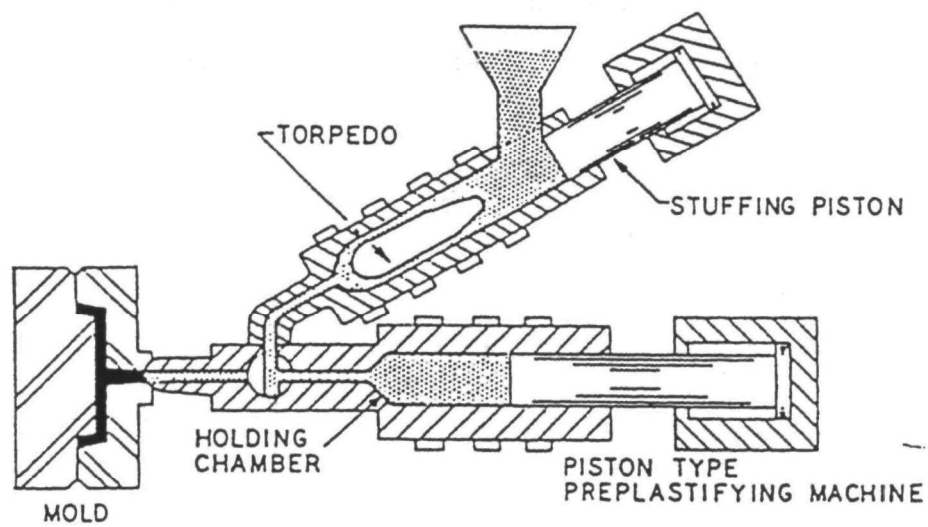


Exhibit 6-4b. Piston type preplastifying machine.

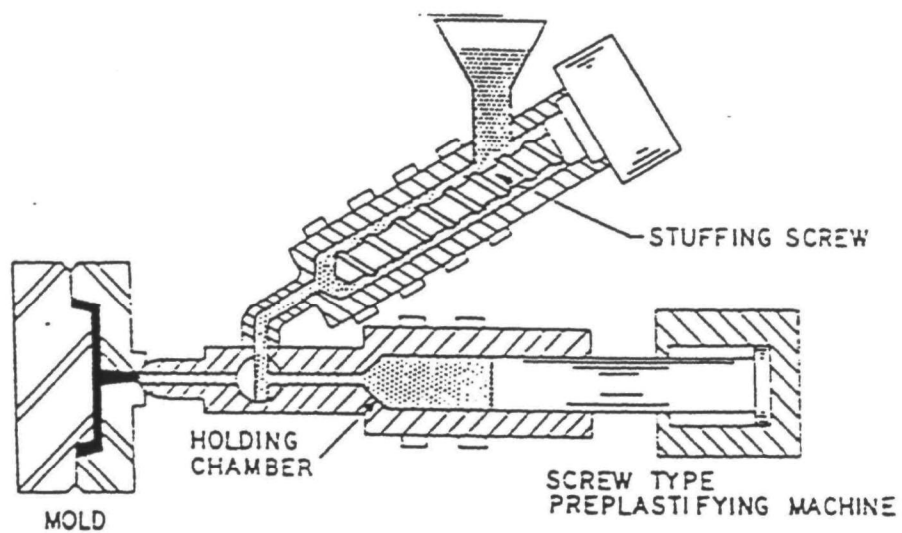


Exhibit 6-4c. Screw type preplastifying machine.

cylinder contains enough melt. Once the limit has been reached, the screw stops turning and moves forward, injecting the plastic material through the injection nozzle into the mold cavity. The advantages of the reciprocating-screw injection system include:

- More efficient plasticizing of heat sensitive materials
- Rapid color blending
- Lower heat requirements

The reciprocating-screw injection machine is the most common machine for modern plastics processing due to its fast cycles, low melting temperature requirements, and efficient mixing. Exhibit 6-4d illustrates the typical reciprocating screw injection molding machine.

6.2.2 The Injection Molding Process

The basic operations of the cyclical injection molding process encompass the following step:²

- Drying
- Blending
- Plasticizing the feed
- Injecting the melt into the mold
- Molding - solidification of the melt
- Ejecting the finished part
- Finishing processes

These operations are the primary determinants of the productivity of the process and are discussed in greater detail in the remainder of this section. Manufacturing speed will depend on the rate at which the plastic can be heated to the molding temperature, the time required to inject the melted plastic, and the cooling period before the product can be ejected from the mold. Exhibits 6-5 and 6-6 show the cyclical injection molding processes for thermosets and thermoplastics. The time required for an injection molding cycle varies according to the design of the product and the polymer formulation being utilized. Typical injection molding cycles

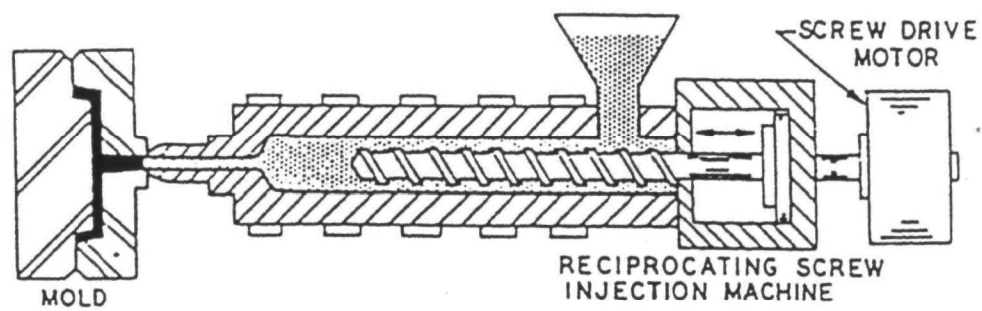


Exhibit 6-4d. Reciprocating screw injection machine.

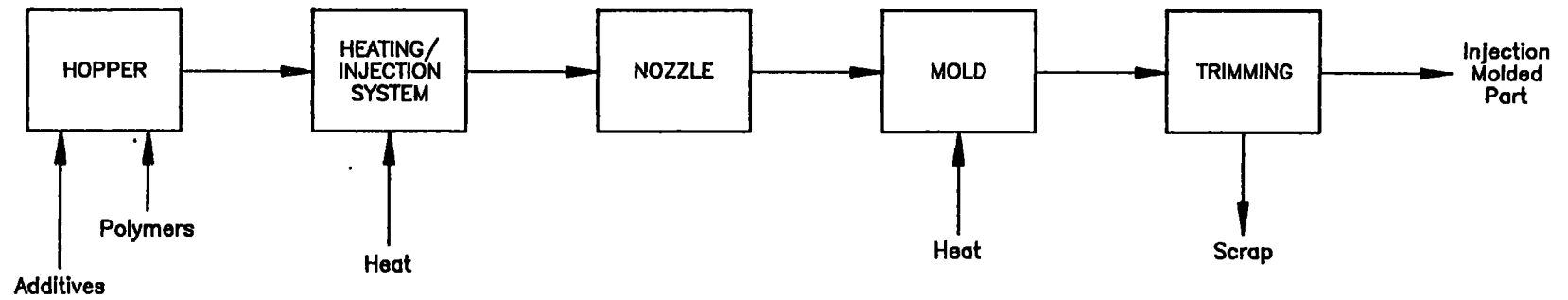


Exhibit 6-5. Cyclical injection molding process for thermosets.⁵

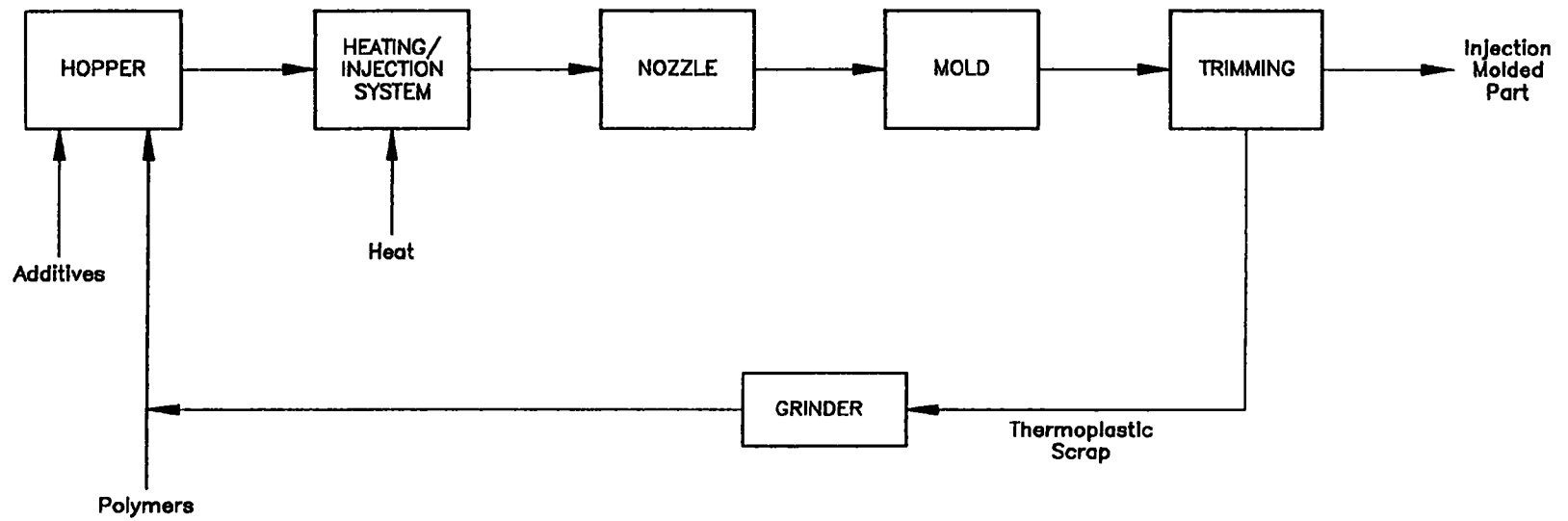


Exhibit 6-6. Cyclical injection molding process for thermoplastics.⁵

range from 10 to 35 seconds; however they can be as short as 1 second for very small parts (*e.g.*, gumball containers) and as long as 120 seconds for larger, more intricate parts (*e.g.*, garbage cans).

Injection molding operations are relatively automated and require minimal manpower. Except for scrap grinding and recycle of thermoplastics, employee manpower requirements are similar for both thermoset and thermoplastic molding processes. Exhibit 6-7 lists estimated manpower requirements to operate a typical injection molding machine.

**EXHIBIT 6-7. MANPOWER REQUIREMENTS FOR OPERATING AN
INJECTION MOLDING MACHINE**

Unit	Workers/Unit/8-hr Shift
Mixing/Blending	0.5
Molding	0.5
Trimming	0.25
Scrap Grinding (Thermoplastics Only)	0.25

Plasticizing the feed. The feed hopper of the injection machine can be loaded by mechanical machinery or manually by the machine operator. The polymer feed is usually granular or in the form of small pellets. In addition to the raw polymer, additives are also included in the feed to create desired characteristics in the polymer melt and the final molded product (such as color or ultra-violet resistance). Plasticizing entails raising the temperature of the pelletized or granular plastic feed to the point where it will flow under pressure. This is accomplished by simultaneously heating and pulverizing the granular solid until it forms a melt at an elevated and uniform temperature and pressure with uniform viscosity.¹ This process step takes place in the heating (plasticizing) cylinder, which is a simple heat exchanger. Most cylinders have heavy steel walls with highly polished and hardened inner surfaces, and are typically surrounded by variable electric heating elements. The size of the heating cylinder on any given machine is usually determined by the volume of the parts to be molded. The heating cylinder of the

injection-molding machine is the primary element, since it is responsible for conditioning the melt before its injection. Exhibit 6-8 presents typical processing temperatures for thermoplastics and thermosets often used in injection molding processes.

Injecting. During the injection step, the molten plastic from the injection cylinder is transferred through various flow paths (*i.e.*, runners) into the cavity of the mold, where it takes the shape specified by the mold cavity. The melt in the cylinder is forced out through the injection nozzle by a reciprocating screw, an injection plunger, or a combination of both, depending on the type of machine. The injection of the molten resin occurs at pressures as high as 20,000 psi. Molten resin from the injection nozzle enters the mold through a system of runners. The runner system for a single-cavity mold is simply a straight sprue (a hole leading to the mold cavity), but for multicavity molds, the system may be complex in order to distribute the material to each cavity. Exhibits 6-9 through 6-12 show the typical cycle of the injection process.

Molding. Molds, made of high-quality, non-porous steel, are vented to allow air, moisture, and other gases to be forced out by the incoming melt, thereby avoiding bubbles and gaps in the molded product.¹ Molding allows the plastic to solidify in the mold, which is kept closed by the clamped platens of the machine. The molds are held together with great pressure to ensure that the mold halves are not separated by the force exerted by the pressurized injection of the melt. The molds remain closed until the molded product has cooled sufficiently. The cooling period is the most time consuming segment of the injection molding cycle. Thermoset materials require that heat be applied to the mold during the molding period to complete polymerization. Sometimes thermoplastic materials are cooled within the mold by the circulation of non-contact cooling water.

Mold Ejecting. Mold ejection takes place after the clamping unit is opened. The ejection of the molded part is usually accomplished by knockout pins or springs in the mold activated mechanically or hydraulically by the machine. Some operations use jets of air to eject the molded part. Once the product is ejected, the mold finishing cycle can begin, commencing with the plasticizing step.²

**EXHIBIT 6-8. TYPICAL PROCESSING TEMPERATURES FOR
COMMONLY USED THERMOPLASTICS AND
THERMOSETS**

Polymer	Processing Temperature (°C)
<u>Thermoplastics</u>	
Acrylic Resins	180 - 250
Acrylonitrile-Butadiene-Styrene (ABS)	180 - 250
<u>Fluoroplastics</u>	
Ethylene-Tetrafluoroethylene Copolymer (ETFE)	260 - 330
Fluorinated Ethylene Propylene Copolymer (FEP)	200 - 260
Polyvinylidene Fluoride (PVDF)	260 - 330
Nylon 6	260 - 290
Nylon 6/6	270 - 300
Polyacetal	185 - 225
Polycarbonate	280 - 310
<u>Polyester</u>	
Polybutylene Terephthalate (PBT)	232 - 260
Polyethylene Terephthalate (PET)	27 - 300
<u>Polyethylene</u>	
Low Density Polyethylene (LDPE)	160 - 240
High Density Polyethylene (HDPE)	200 - 300
Ethylene Vinyl Acetate (EVA)	200 - 280
Polyphenylene Oxide	280 - 340
Polyphenylene Sulfide	315 - 330
Polypropylene	200 - 275
Polystyrene	180 - 260
Polyvinyl Chloride	160 - 210
Styrene-Acrylonitrile (SAN)	180 - 240
<u>Thermosets</u>	
Diallyl Phthalate	170 - 180
Melamine Formaldehyde	160 - 170
Unsaturated Polyesters	232 - 260
Urea Formaldehyde	150 - 160

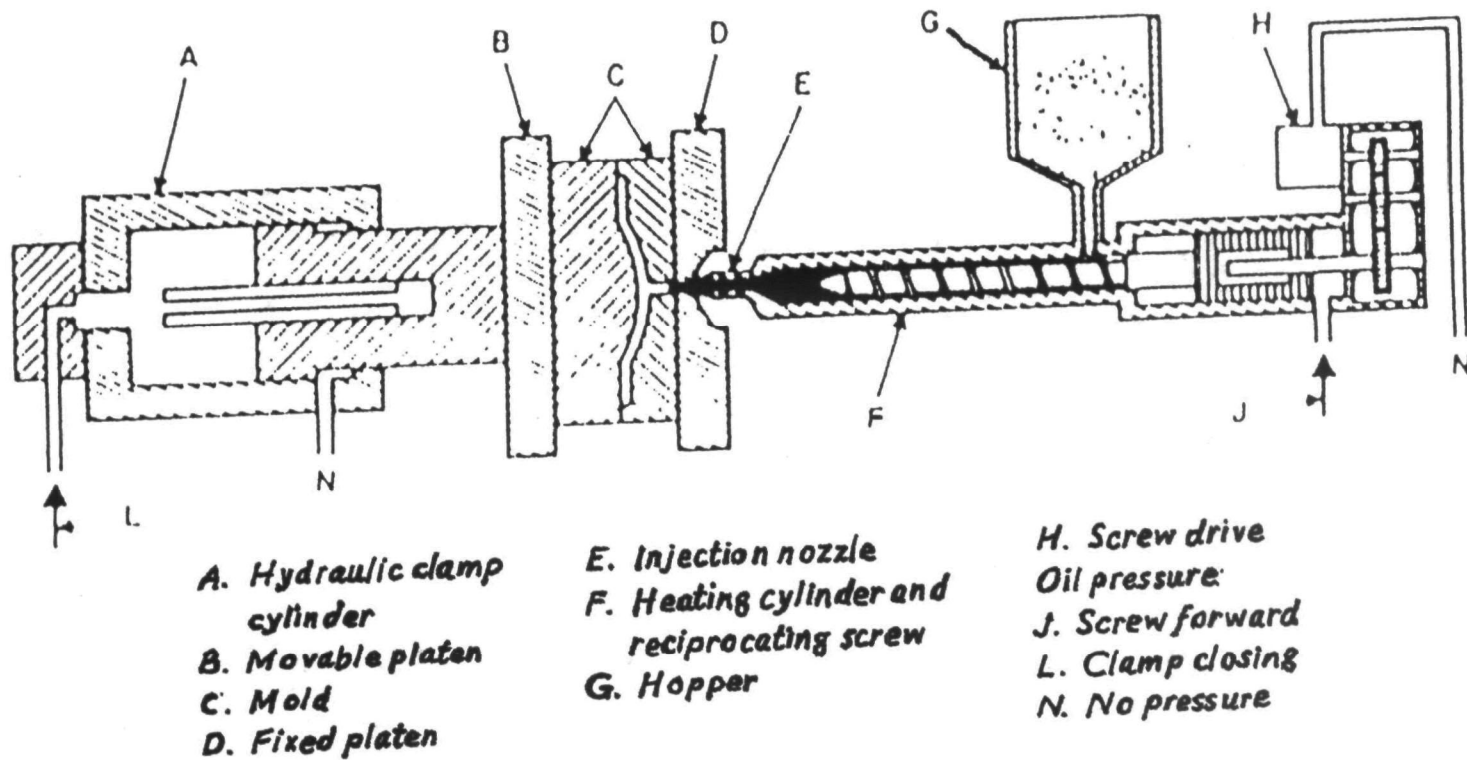
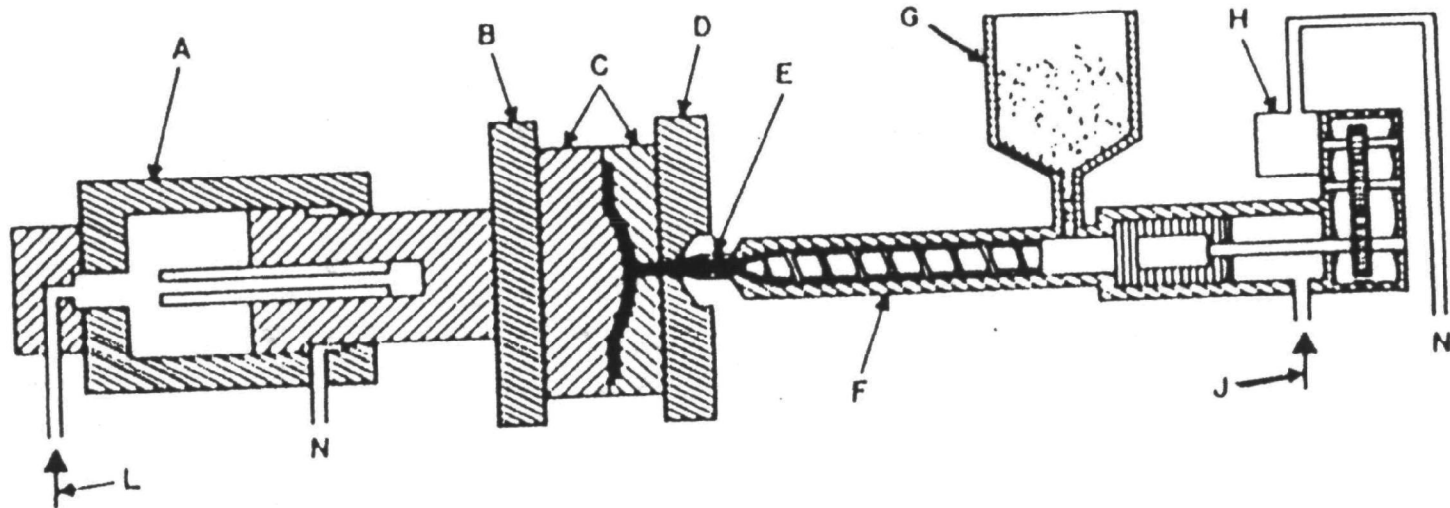


Exhibit 6-9. Injection-molding cycle--melt ready for injection.¹

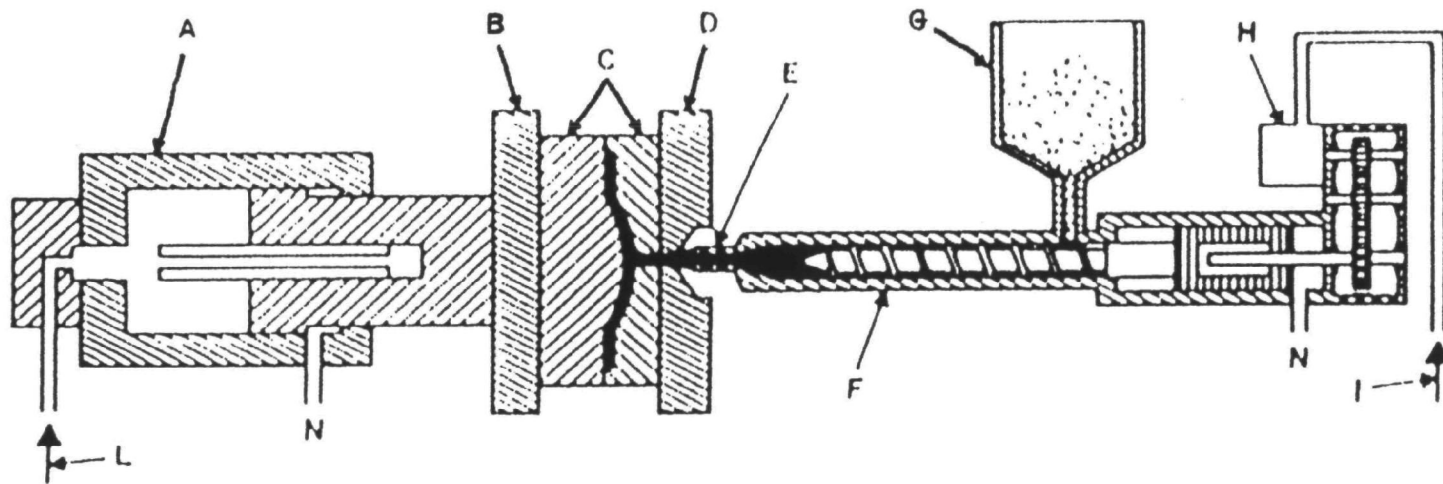
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- | | | |
|------------------------------------|--|-------------------------|
| <i>A. Hydraulic clamp cylinder</i> | <i>E. Injection nozzle</i> | <i>H. Screw drive</i> |
| <i>B. Movable platen</i> | <i>F. Heating cylinder and reciprocating screw</i> | <i>Oil pressure:</i> |
| <i>C. Mold</i> | <i>G. Hopper</i> | <i>J. Screw forward</i> |
| <i>D. Fixed platen</i> | | <i>L. Clamp closing</i> |
| | | <i>N. No pressure</i> |

Exhibit 6-10. Injection-molding cycle--melt being injected.¹

(reprinted with permission from Weir, Glifford, *Introduction to Injection Molding*, Society of Plastics Engineers, Inc., Greenwich, Connecticut, 1975.)



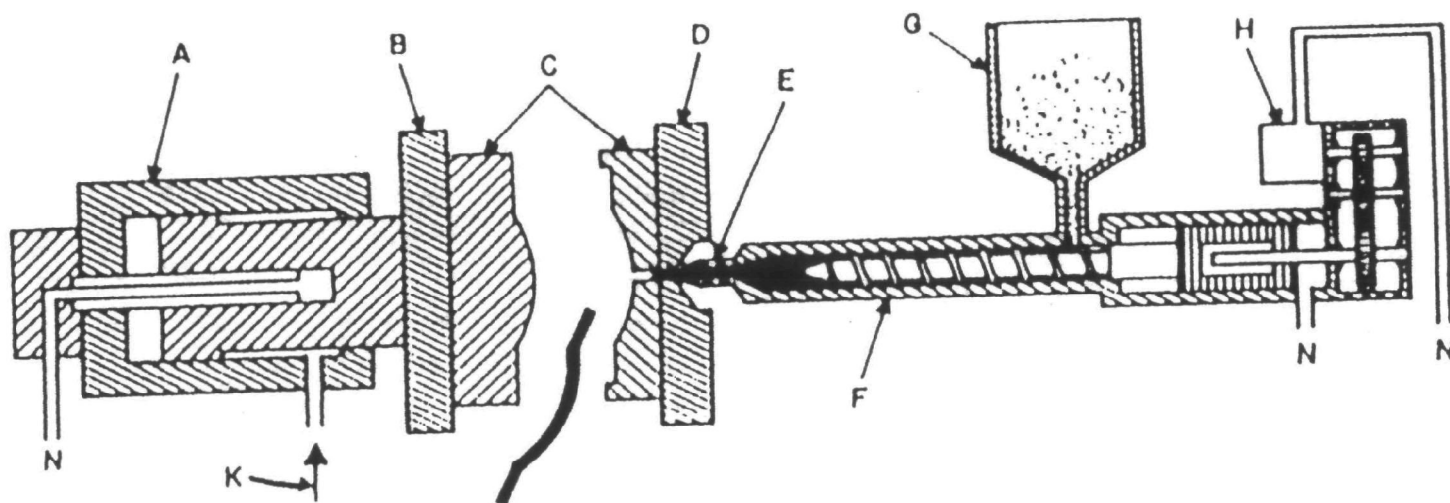
A Hydraulic clamp
cylinder
B Movable platen
C. Mold
D. Fixed platen

E. Injection nozzle
F. Heating cylinder and
reciprocating screw
G. Hopper

H. Screw drive
Oil pressure
I. Screw drive
L. Clamp closure
N. No pressure

Exhibit 6-11. Injection-molding cycle--mold closed for part cooling; melt being plasticized.¹

(reprinted with permission from Weir, Glifford, *Introduction to Injection Molding*, Society of Plastics Engineers, Inc., Greenwich, Connecticut, 1975.)



A Hydraulic clamp
cylinder
B Movable platen
C. Mold

D. Fixed platen
E. Injection nozzle
F. Heating cylinder and
reciprocating screw
G. Hopper

H. Screw drive
Oil pressure
K Clamp opening
N No pressure

Exhibit 6-12. Injection-molding cycle--part ejection.¹

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Mold Finishing. Depending upon the end use of the molded part, some means of finishing and/or decorating may be required. The finishing of a molded product may consist of removal of sprues resulting from solidification of plastic in the runners, trimming excess plastic (flash), decoration of the product, or the assembly of two or more pieces. Flash is excess plastic attached to the product caused by worn or misaligned mold components, the use of improper cycle conditions (*i.e.*, excessive temperature or pressure), or the use of an improper grade of plastic material. Decoration includes post-molding treatments such as application of color, trim, and/or labels.²

6.3 IDENTIFICATION AND CHARACTERIZATION OF EMISSION POINTS AND WASTE STREAMS

The primary waste streams generated at injection molding facilities include the following:

- Solid Waste
- Air emissions
- Operating fluid leaks
- Coolant fluids
- Noise pollution

Exhibit 6-13 summarizes the probable point sources and contaminants (indicated by X) from injection molding operations.

Solid Waste. A large volume of solid waste is generated by rejected products, sprues, flash, and other excess plastic produced by the injection molding process. Fortunately, most thermoplastic waste can be recycled back into the feed. Thermoset plastic waste must be disposed of or ground up and used as a filler to increase the viscosity of other polymers.

EXHIBIT 6-13. SOURCES AND TYPES OF EMISSIONS FROM INJECTION MOLDING OPERATIONS

	Air Emissions					Solid Waste		
	Particulates		Volatiles					
	Polymer	Additives	Monomer	Additives	Decomposition Products	Polymer	Plasticizer	Additives
Hopper	X	X						
Heating/Injection			X	X	X			
Mold			X	X	X			
Trimmer	X	X				X	X	X
Grinder	X	X						

Air Emissions. Injection molding operations have the potential to release particulate and hydrocarbon emissions to the atmosphere. Particulates are released during the addition and mixing of polymer feed in the hopper. Particulates are also created by trimming the product and grinding thermoplastic sprues, runners, and other scrap to be recycled. These particulates consist of particles of polymer and additives.

Emissions of volatile organic compounds are liberated from vents in the heating/injection cylinders and the molds. These emissions consist of traces of monomers, additives, and decomposition products. Decomposition products occur when the processing temperature reaches the decomposition temperature, which varies according to the type of plastic being molded. Exhibit 6-14 presents those decomposition products which could be formed during injection molding operations. Because styrene is a commonly used compounding material, specific decomposition data is presented in Exhibit 6-15.

Operating fluid leaks. Oils, greases, hydraulic fluids, etc. may leak from equipment if it is not maintained properly.

Coolant Fluids. Typically, water is used as a cooling agent to hasten the molding process. The cooling water may become contaminated with greases from the mold. Thermal pollution is another difficulty, as the coolant will absorb a great deal of heat and should not be returned directly to a river or lake to prevent detrimental effects to biota.

Noise Pollution. Operating injection molding equipment (especially the grinders used to recycle thermoplastic scrap) produces a great deal of noise which can result in accelerated worker fatigue and hearing loss. The level of noise pollution often depends on the age and condition of the molding and grinding equipment.

EXHIBIT 6-14. POSSIBLE INJECTION MOLDING DECOMPOSITION PRODUCTS

Polymer	Highest † Processing Temp. (°C)	Decomposition Temp. (°C) ‡	Decomposition
Acrylic Resins	250	320	*
ABS	240	300	*
Diallyl Phthalate	175	285	*
Fluoroplastics	330	300	HF
Melamine Formaldehyde	170	182	*
Nylon 6 and 6/6	290	300	*
Phenolic	205	300	*
Polyacetal	225	250	*
Polybutylene	190	300	*
Polycarbonate	310	330	*
Polyester (thermoplastic)	300	300	Acetaldehyde
Polyester (thermoset)	260	275	*
LDPE	240	100	Ketone Carbonyl
HDPE	300	100	Groups form
EVA	2870	100	Due To Oxidation
Polyphenylene Sulfide	330	700	*
Polypropylene	275	300	*
Polystyrene	260	300	*
PVC	210	100	HCL
SAN	240	300	*
Urea Formaldehyde	160	182	*

* Decomposition products are not formed at or near injection molding temperatures.

† The highest possible temperature reached by the normal injection molding of all formulations of the polymer listed.

‡ The lowest temperature at which decomposition products begin to form.

EXHIBIT 6-15. STYRENE EMITTED FROM THERMOOXIDATIVE DEGRADATION
(μ g/g, lb/ton)^a

Temperature (°C)	Polystyrene	Impact Polystyrene	Acrylonitrile- Butadiene-Styrene	Styrene- Acrylonitrile
197	-- ^b	--	7800, 15.6 (68) ^c	--
200	Trace	--	--	--
208	--	--	2300, 4.6 (32)	--
218	--	--	--	2700, 5.4 (32)
224	--	310, 0.62 (3.4)	--	--
240	520, 1.04 (8.0)	--	--	--
250	740, 1.48 (7.0)	280, 0.56 (3.8)	--	--

^a Uncontrolled emissions.

^b "--" Not measured.

^c Styrene yield is given in parenthesis as the percentage of total loss in weight.

6.4 POLLUTION PREVENTION, RECYCLING, AND POLLUTION CONTROL SYSTEMS

6.4.1 Pollution Prevention

Most of the pollution associated with injection molding operations can be avoided or minimized through proper plant operations. Many potential pollution problems can be avoided if care is taken to address the following topics:

- Proper plant layout
- Employee training
- Scheduling of work orders and jobs
- Inventory control
- Equipment maintenance
- Segregation of waste streams

Proper plant layout. If a plant is laid out inefficiently, the operators are forced to constantly relocate to monitor the machines for which they are responsible. This may prevent necessary adjustments from being made at the proper time because the operators are busy elsewhere. Problems may develop and remain unchecked for several days or longer. If the problems are severe, the product run may be ruined, resulting in wasted raw materials and unusable off-specification products. An operation that is efficiently arranged with easy operator access to all important machine controls will help to prevent errors of this type by allowing operators to perform all their tasks within a relatively small area. Exhibit 6-16 shows an example of a properly laid out operation, with arrows indicating controls/indicators which must be monitored by an operator.

Employee Training. A solid employee training program will have beneficial effects on operation efficiency of the plant. Workers who are well trained in the operation of their machines and in troubleshooting procedures will produce more product in less time with less waste. Poorly

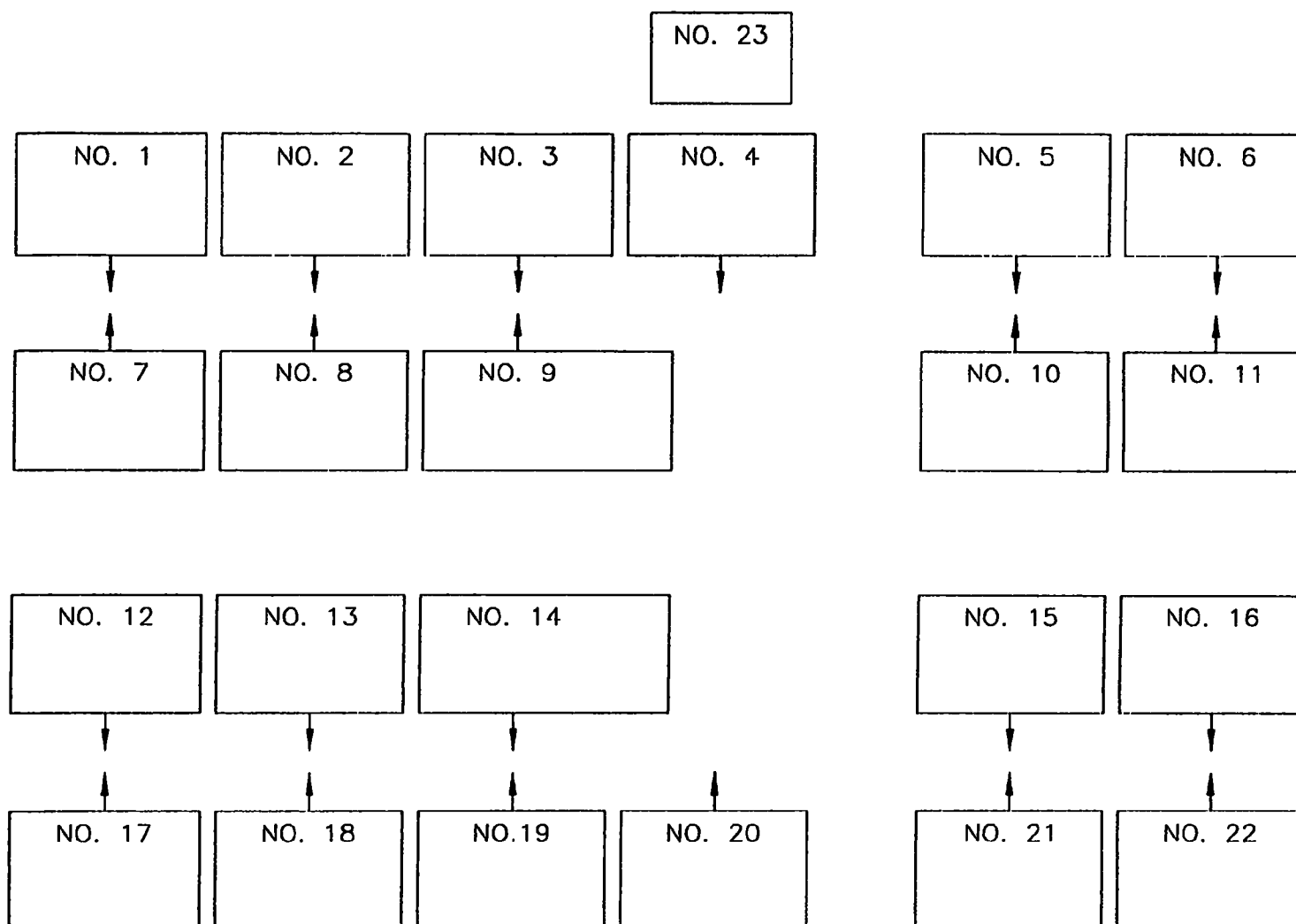


Exhibit 6-16. Model injection molding plant machine layout.

trained workers will take longer to recognize potential problems in the molding process, and may not understand how to deal with the problems once they are identified. This will result in more frequent waste from rejected products. Well-trained employees are also more likely to request maintenance for malfunctioning equipment, and thereby avoid serious mechanical problems through preventive maintenance.

Scheduling of work orders and jobs. The order in which jobs are completed should be determined by two significant factors: product color and raw materials availability. The color being applied to the plastic must be considered during production scheduling decisions to ensure first quality end products. Progressing from light colors such as yellow or pink to darker ones like blue or black will prevent the lighter colored resins from being discolored by residues from darker ones. Darker resins will not usually show discoloration from small amounts of resins having lighter hues.

The second aspect of scheduling involves ensuring that correct amounts of raw materials are on hand by requiring work orders from customers which define the amount of product desired. This is especially important if the job requires special or proprietary raw materials. Excess raw materials remaining after a job is completed may be wasted unless they can be used for something else. Preferential treatment should be given to customers who commit to long runs, as large batches make it possible to avoid purging the machines often, which causes large amounts of waste plastic and downtime.

Waste plastic can also be minimized by using a purging foam for equipment cleaning. The foam is fed through the molding system like the plastic feedstock. It shortens the cleaning process and eliminates solvent cleaning waste.

Inventory control. In addition to careful ordering of raw materials and additives according to work orders, any inventory left over should be carefully catalogued and stored in an orderly fashion. This will facilitate use of any leftover materials and prevent waste. If records of excess

raw materials and additives are not maintained, the inventory will not be used efficiently and valuable materials may be entirely wasted.

Equipment maintenance. A regular program of equipment maintenance is essential. Poorly maintained equipment is more likely to malfunction and result in rejected parts and waste. Machines that are not regularly maintained are also likely to develop leaks of oil and hydraulic fluid. These leaks are an environmental hazard and may cause low fluid levels in the machines, producing equipment breakdown and failure. The blades on grinders of recycling scrap thermoplastics should be sharpened regularly to prevent unnecessary strain on the motor due to difficulty in shredding the plastic. A regular program of maintenance on operating equipment has the goal of keeping all machines in prime operating condition and stopping potential problems before they happen.

Segregation of waste streams. The current technology has not produced an economical method of separating mixtures of different polymers. For this reason, waste from machines using different feedstocks should be kept separate. If waste thermoplastics are segregated, they can be recycled and returned to the same process that they resulted from. Thermoset plastic wastes which cannot be recycled should not be mixed with reusable products so they can be disposed of. Careful waste segregation is an important part of a good recycling program, and is essential for an economically sound plastics molding operation. Similarly, all waste maintenance liquids (e.g., hydraulic oils, greases, and degreasers) should be separated. Another waste minimization option for maintenance liquids is to consolidate maintenance liquids. Rather than using five lubricating oils, a facility may be able to use two.

6.4.2 Recycling operations

Thermoplastic sprues, runners, and scrap generated by the trimming of product flash can usually be ground and recycled to the hopper feed. Virgin resin and regrind are usually mixed in a 4:1 ratio. As previously mentioned, it is important to segregate waste streams to avoid mixing different polymers.

Typically, scrap grinders are used to reduce runners, sprues, and reject parts to uniform small-size particles that can be blended back into the molding material in the hopper. In small molding facilities granulators are installed alongside or beneath each molding machine to regrind material from the individual machines. This provides for a mechanical or manual feedback to the hopper. Larger injection molding facilities may have a centralized area for all scrap grinding and recycling.

A typical scrap grinder consists of three blades, two rotating and one stationary, housed in a suitable chamber with a feed hopper at the top and a screen beneath which permits material to pass through when it has been reduced to the proper size. There are numerous types of blades designed for grinding of different types of plastics. Blades will operate more effectively if sharpened on a regular basis. Blade maintenance should also be included in the maintenance schedules. Sharp blades allow for easier grinding (both in the cutting of the plastic material and by causing less strain on the grinder). In addition, sharp blades yield a finer regrind which can be incorporated more easily into the molding process. Plastics can be categorized into three main categories with respect to their behavior in grinding operations:²

Energy-Absorbing Plastics. Most thermoplastics (*e.g.*, low density polyethylene) are considered to be energy-absorbing plastics. These plastics are somewhat flexible, impact resistant, and easily granulated.

High Impact Plastics. These plastics (*e.g.*, ABS) are extremely hard and are not easily broken. These plastics will tend to shatter when exposed to great stress.

Friable Materials. These plastics (*e.g.*, Phenolic resins, styrenes, etc.) break apart easily without application of extreme stress. Granulation of friable materials usually causes large amounts of dust and airborne particulates.

Important topics to consider in choosing recycle granulators include²:

- The general type of granulators- under-the press, beside the press, or a central recycling system (this will depend on the size and arrangement of the overall operation)
- Throughput requirements- what hourly production rate is required
- Physical properties of the plastic to be recycled- this will determine the type of blades that must be used
- Choice of screens- this will depend on the size of the machines and the size of regrind granules desired

6.4.3 Pollution Control Systems

Pollution resulting from injection molding operations is mostly minor and easily controlled. The remainder of this section discusses control strategies for the emissions described in Section 6.3:

- Solid Waste
- Air emissions
- Operating fluid leaks
- Coolant fluids
- Noise pollution

Solid Waste. The most efficient way to deal with thermoplastic waste is to recycle it. Thermoset scrap may not be recycled directly because it cannot be remelted, although it may be ground up and used as filler material to increase the viscosity of other resins. However, because any plastic waste which cannot be recycled is comprised of inert plastic material, it poses limited environmental disposal problems.

Air emissions. The quantities of VOC released by the injection molding process depend largely on the speed of the molding cycle and the polymers being molded. For instance, polystyrenes operating at fast cycles will emit more fumes than polyethylenes operating at the same speeds. Normally, emissions rates are relatively low resulting in more health and safety concerns than

environmental concerns. For this reason good ventilation of the manufacturing area is essential, with hoods containing fans over each molding machine.

Particulate emissions from the feed hoppers and grinding of scrap must also be controlled. Use of exhaust fans and a baghouse will effectively and cheaply alleviate this problem.

Operating fluid leaks. Use of catch pans with drain plugs will allow for easy removal of any fluids that leak from the machines. The fluids may be collected and removed for disposal by a licensed disposer.

Coolant fluids. If water is used to cool the molds, it may be contaminated by greases etc. from the molds. The water will also be carrying waste heat and should not be returned to a river or lake because of the possibility of thermal pollution harming biota. Cooling water should be returned to ambient temperature and reused. A cooling tower may be used to remove waste heat from coolant water. The plant water should also be consistently monitored for calcium (*i.e.*, hard water) and algae growth. Hard water may result in scale deposits throughout the piping system. Scale will cause inefficient machine operation and degradation of hydraulic fluids.

Noise Pollution. The noise resulting from the operation of molding machines and recycle grinders can be reduced by use of a system of baffles surrounding the machines. Baffle systems constructed of wood and acoustical insulation are highly effective, however, simple systems made from sheets of heavy canvas will usually suffice.

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8. U.S. Environmental Protection Agency. *Economic Impact Analysis of Effluent Limitations and Standards for Plastics Molding and Forming Industry*. EPA-440/2-84-025. Office of Water Regulations and Standards. December 1984.

EXHIBIT 6-17
ANDERSON TOOL AND PLASTICS CORP.
WORK ORDER

JOB INFORMATION	TEMPERATURE
Customer-	Front-
Part Description No.-	Spare Front-
Job No.-	Rear-
Mold No. - -Cav._ -K.O.-	Spare Rear-
Machine No.-	Nozzle-
Dimension-	Adapter-
TIME	REMARKS
Job Start-	
Hrs. Required-	
Days Required-	
Job Completion-	
WEIGHT	
Shot Weight- - ozs.	
Part Weight- - ozs.	
Pieces per lb.- -/sets	
Lbs. per hour-	
Parts per hour-	
Material-/Blend No.	
Machine Time	
Inj. forward-	
Inj. Hold-	
Mold Open-	
Inj. Delay-	
Mold Close-	
Overall Cycle	
Pressure Inj.-	
Accumulator-	
CARTON INFORMATION	
Carton No.-	
Quantity Required-	
Pieces Per Carton-	
Existing Cartons in Stock-	