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ENVIRONMENTAL TECHNOLOGIES APPLICABLE TO WASTEWATER POLLUTION ABATEMENT IN THE ST. LAWRENCE RIVER SYSTEM

Canada

ENVIRONMENTAL TECHNOLOGIES APPLICABLE TO WASTEWATER POLLUTION ABATEMENT IN THE ST. LAWRENCE RIVER SYSTEM

A REVIEW OF THE LITERATURE AND DIRECTORY OF EXPERTS

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CHAPTER ONE

INTRODUCTION

The Problem

Over the past three centuries the impact of human settlement has taken its toll on the St. Lawrence River ecosystem. The stresses on the system have resulted from growth in human populations along the St. Lawrence and its associated waterways, and the growth of industries that take advantage of the natural resources, including water, in the area of the St. Lawrence River watershed.

Many of the industries that have been established along the St. Lawrence River and its feeders use large volumes of water in their processing operations and produce as waste, chemicals, heavy metals and other effluent materials that are hazardous to aquatic and human life. One of major sources of pollutants is contaminated process water that is discharged directly, or with minimal treatment, into the river system from pulp and paper manufacturing, the chemical industries, and mining and metallurgical industries.

Many of the water pollution problems related to the mining industry result from acid mine drainage, the name given to leachate from mine tailings and mining operations. Another source of pollutants are landfill sites in which solid wastes from industrial operations have been dumped. Chemicals and metals in the sites leach into the groundwater and thereby into rivers, lakes, and wells.

Air pollution from industries on the St. Lawrence also cause concern as oxides related to acid rain are a by-product of metallurgical industries, and sulfides and various other noxious and toxic gases are by-products of the chemical and pulp and paper industries. Many plants have scrubbers in their smokestacks to remove some of the pollutants before the air is discharged to the atmosphere. Wastewater, solids, and sludges from scrubbing operations contain hazardous materials. Therefore, although air pollution is a major problem among industries along the St. Lawrence, we are only concerned in this study with liquid and solid wastes from scrubbing operations.

Another source of chemical and metal pollutants is the surface finishing industry. Surface finishing includes the various physical and chemical processes used to improve or change the appearance or surface characteristics of a product. Surface finishing encompasses cleaning, electroplating, anodizing, galvanizing, and metal, paint and other coatings. Pollutants include metals, cyanides, oils, greases, highly acidic or alkaline spent liquors, and solvent containing sludges. Surface finishing processes are used in the metals processing industry as well as in various manufacturing industries. Many of the companies in this category are small.

Regulations

Recognition of the extent to which industrial operations cause water and land pollution, and regulations to reduce pollution levels have been slow. Canada and the United States have abundant supplies of fresh water and have been depositing untreated municipal and industrial sewage into the rivers and lakes for more than a hundred years. Yet it has only been in the past 25 years or so that governments have acknowledged that pollution is a major problem in North American waters and have taken actions to regulate the levels of pollutants discharged into water bodies or dumped in landfill sites.

In Canada, water pollution comes under the the Fisheries Act. Subsection 33(2) of the Act prohibits deposit of deleterious substances into waters frequented by fish. Regulations under sections 33 and 34 of the act include:

- Pulp and Paper Effluent Regulations which regulate total suspended solids; oxygen-demanding decomposible organic matter produced as waste from a mill; and toxic wastes deposited by a mill (EPS 1-WP-72-1, 1971)

- Federal Metal Mining Liquid Effluent Regulations and Guidelines which limit the concentrations of arsenic, copper, lead, nickel, zinc, total suspended matter, and radium-226 in, and the pH of effluents from mining and milling operations. The regulations cover mining and milling facilities and associated smelters, pelletizing plants, sinter plants, refineries, acid plants and similar operations where the effluent from the operations is combined with effluents from metal and milling (EPS 1-WP-77-1, 1977)

- Petroleum Refinery and Effluent Regulations and Guidelines which regulate oil and grease; phenols; sulfide; ammonia nitrogen; total suspended matter; and any substance capable of altering the pH of liquid effluent or once through cooling water (EPS 1-WP-74-1, 1974)

- Chlor-alkali Mercury Liquid Effluent Regulations in which deleterious substance is defined as mercury from the operations or processes of a plant (EPS 1-WP-77-3, 1977)

- Metal Finishing Liquid Effluent Guidelines which regulate suspended solids; chromium; cyanide; copper; lead; nickel; and zinc (EPS 1-WP-77-5, 1977)

The Federal Regulations and Guidelines are applicable across Canada. Where provinces also have regulations on concentrations of hazardous materials in industrial effluents, the more stringent regulations apply to industries within the provinces. For example, Ontario has adopted a Municipal/Industrial Strategy for Abatement (MISA), under which the province is developing new regulations to control levels of municipal and industrial pollutants. Industries for which new regulations are being developed are petroleum industries, organic chemicals, iron and steel, inorganic chemicals, pulp and paper, mining, metal casting, electric power and industrial minerals. In these industrial sectors the MISA office has in progress a program for monitoring levels of pollutants. New regulations will developed as a result of the monitoring program and consultations with industry. As part of the process, the best and most economical technologies for treating industrial wastes are also being studied.

In the United States, the Environmental Protection Agency (EPA) sets the national environmental standards. Before 1972, the United States had water quality standards which set limits on permissible concentrations of various pollutants in water bodies. In 1972, the United States passed the Federal Water Pollution Control Act with the goal "to restore and maintain the chemical, physical and biological integrity of the nations's waters". Under the act, dischargers had to limit their pollutants to specified EPA determined effluent content quotas. Individual states can set up alternate limitations if the EPA limitations would not achieve the states's water quality standards. Various ammendments have been issued since then to address limitations on specific groups of chemicals and metals.

Hazardous wastes are regulated under the U.S. Resource Conservation and Recovery Act (RCRA). These so-called RCRA-wastes include specific chemicals or metals, as well as wastewaters and/or sludges from various manufacturing processes. The wastes are usually referred to by code numbers. The Hazardous and Solid Wastes Amendments (1984) prohibits placement of RCRA wastes in or on the land and gives dates by which the prohibitions take effect. These acts have resulted in efforts by the EPA and industry to find methods of treating wastes to comply with the regulations. The EPA has published a series of reports on best demonstrated and available technologies for treatment of some of the RCRA listed wastes. In addition, various handbooks on treatment technologies for different types of wastes based on work sponsored by the U.S. Environmental Protection Agency have been published commercially. Some of these publications are referenced in appropriate chapters of this report.

Most European countries have also recently developed stringent regulations for controlling industrial pollution in attempts to clean up the air and waterways in Europe. Regulations usually carry severe fines which now make some recovery technologies for chemicals and metals economically attractive.

Major Polluting Industries of Concern in the St. Lawrence System

The St. Lawrence River Action Plan is a federal-provincial program to clean up the St. Lawrence River. One of the main objectives of the plan is to reduce the liquid toxic wastes of the 50 largest industrial polluters along the St. Lawrence by 90% by 1993.

The fifty major polluting industries fall into the following industrial sectors:

- Pulp and Paper (15 companies)

- Metal Industries (12 companies total)
    - Aluminum (6 companies)
    - Copper and Zinc (2 Companies)
    - Carbon-based Metal (1 company)
    - Iron and Steel (3 companies)

- Chemical Industries (13 companies total)
    - Petrochemical (7 companies)
    - Inorganic Chemical (5 companies)
    - Explosives (1 company)

- Petroleum Industries (3 companies)
- Mining Industry (1 company)
- Surface finishing (1 company)
- Miscellaneous (3 companies)

The effluents of companies within each industrial category may have some similarities but the composition of the effluents depend on the raw materials used as input, the industrial processes used, and the nature of the products. For example, in the pulp and paper industry there are a number of generic methods of pulping and bleaching, each of which uses different chemicals. Chemicals are also added to the final paper processing stage to produce different grades and colours of paper. Likewise in the petro/organic chemical industry, though the input chemicals have some similarities, the desired final product determines the processes used in manufacturing, the chemicals added during the manufacturing process, and the pollutants that result from the different stages in the processing.

In mining and mineral processing, the composition of the wastes depends on the ores, the processes used for mineral extraction, and the extent of processing at the plant. Processes can range from refining to produce metal ingots for sale to forming sheet or tubular metal for incorporation into final products. More extensive processing at a plant incorporates surface finishing operations and therefore more and different types of waste streams. The pollutants from surface finishing also vary with the processes used.

Pollution Abatement

The most obvious way to reduce water pollution from industrial processes is to reduce the volume of water used in the process and hence the volume of water that requires treatment before being discharged to a receiving body. In some industries this is an attainable objective depending on the quality of the water needed for the processes. In some cases, cooling water can be recycled, and process water can be reused, sometimes after treatment to remove contaminants.

The industrial and manufacturing processes can be changed so that different and less harmful, or more readily treatable chemicals are used. For example, cyaniding in metal finishing may be replaced by nitriding, and hydrogen peroxide bleaching may be an alternative to chlorine based bleaching processes in paper making. Process changes, however, are not always possible because quality could be compromised.

Processes can also be monitored more carefully so that the optimum balance of chemicals to obtain the desired product are added. For this purpose, automatic process controls and monitoring equipment can be incorporated into the system to regulate chemical balance. In some plants, metals or chemicals can be recovered from effluents prior to treatment.

Waste Treatment

The effluent water from the various processes at the plant can be treated separately or they can be combined and treated together. Because the composition of the effluents from each plant is unique, a waste audit is required to determine the best treatment or combination of treatments for the plant. An audit involves an analysis of each waste stream to determine the composition of the effluent and the best method or methods of treating the pollutants in the wastewater. Some waste streams may require pre-treatment to eliminate toxic materials that may interfere with downstream treatment processes; some waste streams may have to be separated for different treatments; some may be combined for treatment. After the composition of the effluents has been determined, laboratory and pilot scale testing of potential treatment methods are usually necessary to determine the best and most economical method(s) for the particular plant and location that will comply with regulations. Some treatment methods require large land areas that a company may not have. It may also be more economical to ship some types of hazardous wastes to a centralized treatment facility than to treat them on-site.

The other major category of pollutants are solids generated as by-products of either the industrial/manufacturing processes, or from treatment of the liquid wastes. The solids are often in the form of sludges that contain a variety of hazardous materials that can leach out into the groundwater systems. Untreated or dewatered solid wastes have usually been dumped in landfill sites. In the United States and in many European countries there are now stringent regulations on what can and cannot be dumped in landfill sites. Hazardous materials must be rendered harmless by either removal of the harmful constituents or by converting them to a stabilized form so that they cannot leach out. Again, treatment of solids depends on the composition of the hazardous materials in the solids. Some treatments may result in the hazardous constituent being converted from a solid or liquid phase to a gaseous phase and therefore a series of treaments may be required.

Although the treatment technologies for the wastes and effluents from each industry and company within the industry may be different, there are a number of generic technologies that are used in the treatment of hazardous materials in wastewater and solid wastes. The following chapter will describe the generic technologies and their areas of application. Each of the remaining chapters will be devoted to a specific industry. A brief description of the general characteristics of the industry and processes used will be followed by a discussion of process changes and treatment technologies applicable to the industries. Research into new or improved technologies will also be discussed where applicable.

REFERENCES

EPS 1-WP-72-1. Pulp and Paper Effluent Regulations. Environment Canada, 1971

EPS 1-WP-77-1. Metal Mining Liquid Effluent Regulations and Guidelines. Environment Canada, 1977

EPS 1-WP-74-1. Petroleum Refinery and Effluent Regulations and Guidelines. Environment Canada, 1974

EPS 1-WP-77-3. Chlor-alkali Mercury Liquid Effluent Regulations. Environment Canada, 1977

EPS 1-WP-77-5. Metal Finishing Liquid Effluent Guidelines. Environment Canada, 1977

CHAPTER TWO

ENVIRONMENTAL TECHNOLOGIES FOR TREATMENT OF INDUSTRIAL WASTEWATER AND SOLIDS

Technologies for the treatment of industrial wastewater and solids fall into four general categories, namely physical, chemical, biological and thermal processes. Within each category there are a number of generic technologies that can be customized for use with different types of waste streams or solids. A wastewater treatment system for a specific processing operation will consist of the most appropriate and economical technologies that will result in treated effluent containing the minimum or less than the minimum levels of deleterious substances specified in the appropriate regulations. As more knowledge is aquired about the toxic effects of various components of industrial waste streams, and as technologies for measuring levels of pollutants improve, regulations may change. A treatment system that meets the regulations today, may not meet them tomorrow. Therefore in selecting technologies for treatment of waste streams, companies should be aware of the limitations of the different treatment processes.

The general categories of wastewater treatment processes are (Lorenz, 1989, Holden et al., 1989):

> **Physical processes**: these are based on differences in the physical properties of the contaminant. Examples are particle size of suspended solids, specific gravity of different components, and viscosity of components. Examples of physical processes are screening, sedimentation, reverse osmosis, distillation, filtration and gas transfer.
>
> **Chemical processes**: these are based on the chemical properties of the contaminant in the waste stream and change the chemical characteristics of the contaminant so that it can be rendered harmless or converted to a state where it can be removed from the waste. Examples are ion exchange, electrodialysis, dechlorination, coagulation, and precipitation.
>
> **Biological processes**: these incorporate biochemical reactions to remove soluble or colloidal organic impurities. Examples are biological filtration and activated sludge processes.
>
> **Thermal processes**: these use high temperatures as the means of destroying or detoxifying hazardous wastes. Thermal technologies include incineration, pyrolysis, vitrification and some oxidation processes.

Treatment can also be categorized as primary, secondary or tertiary. Primary treatment normally consists of separating suspended solids from the waste stream by processes such as filtration or sedimentation. This can be as simple as allowing the water to remain in settling ponds for a period to adding chemicals to enable small suspended particles to agglomerate prior to filtration. The wastewater may be filtered through a sand, charcoal, or mixed media filter to remove suspended solids. Activated carbon filters are used to remove organic materials. In some industries, such as pulp and paper, pretreatment is necessary before the primary treatment stage to remove large particles of suspended matter, such as sand and gravel, that may damage equipment downstream in the treatment process.

Secondary treatment removes biodegradable and toxic components from the effluent. These may be physical, chemical or biological processes.

Tertiary treatment removes colour and odour from the effluents.

The sludges resulting from the various treatment process may contain hazardous materials that have to be removed or stabilized before landfilling. Processes include removal of contaminants by chemical or biological means and dewatering of the sludges to decrease the water content. Where hazardous material cannot be removed, thermal treatment technologies such as incineration, cementation and vitrification can be used to contain the contaminants in a state where they cannot leach into the environment.

The major generic physical, chemical and biological processes will be described in this chapter.

Physical Processes

Screening

Screening is used in industries such as pulp and paper and mineral processing to remove debris and other large solid particles so that they will not reduce the efficiency of later treatment processes or damage equipment such as pumps and valves. Coarse screening devices include bar screens, belt screens, perforated plates, and wire mesh.

Filtration

Filtration is similar to screening but is used to clarify the wastewater by removing finer particles. Suspended solids of less than 100 ppm can be removed by passing an aqueous stream through one or more types of filter media such as sand, granular activated carbon, powdered carbon, and garnet. Use of activated carbon filters, which remove suspended solids, adsorb tastes and odors, and control organics is increasing. Different filter designs can increase the filter surface area and solids removal rate. Filtration is also used to dewater sludges and concentrate the solids into a paste or solid cake for disposal or further processing. The rate of filtration can be increased by using pressure or gravity filters.

Filtration systems are also used in conjunction with ion exchange and membrane unit processes.

Sedimentation

Wastewater can also be clarified by removing suspended solids by sedimentation. Where gravity sedimentation is used, the water is directed to holding tanks, ponds, or lagoons and held for enough time to allow modt of the suspended solids to sink to the bottom of the holding tank. The solids form a sludge that can be removed for further treatment or disposal and the water is discharged or treated further. Settling tanks often have conical bottoms so that sludge can be removed by opening a valve and draining the sludge from the tank. Settling ponds or lagoons usually require a large land area. When the sludge reaches a certain level the ponds are drained and the sludge is removed by earth handling equipment.

Chemical additives such as flocculants and coagulants can be added to enable very fine or colloidal particles to agglomerate and be removed by sedimentation.

Where space is limited, various kinds of equipment that increases the surface area of the settling tank and thus shortens the water retention times can be used.

Flotation

Flotation is generally used only in large treatment facilities. Material that floats to the top of the tank or pond is skimmed off by mechanical skimmers. If the suspended matter in the wastewater is very fine and settles slowly, dissolved air flotation can be used. In this process, tiny gas bubbles are introduced into the bottom of the tank and become attached to the solid particles, enabling them to float to the top.

Flotation can also be used to separate oil-water mixtures, oil-oil mixtures, or different density materials. Bennett (1988) reviews procedures for removing oil from wastewater by air flotation.

Flotation cells are commonly found in mineral processing industries and are being used increasingly for treatment of industrial wastewater. They have advantages over conventional technologies including lower capital costs, space savings, and low maintenance.

Distillation

Distillation is the separation of more volatile components of a liquid mixture by vapourization and condensation. The mixture is heated in a distillation vessel, the more volatile components vapourize and pass up through the column where they are cooled and condenses. The process can be either continuous or batch. Distillation is used in chemical industries for purification and can be used to recycle solvents.

In waste treatment, distillation is used to recover and concentrate volatile components. Solids from the bottoms of distillation vessels usually contain hazardous materials that can be disposed of by thermal destruction methods such as incineration. As there is also the potential for volatile organic vapours to escape into the atmosphere, distillation has to be carefully monitored.

In a continuous distillation system, the liquid should be free flowing (viscous liquids need pretreatment) and must contain negligible amounts of solids. Organic peroxides, pyrophoric organics and most inorganic wastes are not suitable candidates for distillation. Industrial wastes suitable for distillation include (Rogers and Brant, 1989):

- Plating wastes containing an organic component
- Aqueous wastes containing phenol
- Polyurethane waste containing methyl chloride
- Ethylbenzene-styrene mixtures
- Waste solvents - usually mixtures containing keytones
- Alcohols and aromatics
- Waste lubricating oils.

Solvent Extraction

This process is used for liquid-liquid extraction, especially for extracting organic compounds from aqueous solutions and for separating specific components from solids by a liquid in which the component dissolves.

Solvent extraction is used to extract phenols from wastewaters from petroleum refineries, coke oven and phenol resin plant operations (Berkowitz, 1989). Research has been conducted into the use of solvent extraction for treatment of other wastewaters including removal of PCBs from transformer oils, removal of water and oil from sludges in metal working and petroleum refining, and removal of acetic and formic acid from liquors used in treating wood with bisulfite.

Membrane Separation Technologies

Membrane separation can be used for volume reduction, recovery or purification of a liquid phase, and concentration or recovery of a contaminant or solute.

The technologies included in this category are reverse osmosis, hyperfiltration, ultrafiltration and electrodialysis (MacNeil, 1988; MacNeil and McCoy, 1989).

The conditions needed for osmosis to occur are that there must be two solutions of different concentrations (or a pure solvent and a solution), and a semipermeable membrane separating the solutions. The solvent will flow through the membrane into the concentrated solution. In reverse osmosis, pressure is applied to the more concentrated solution and the solvent is forced through the membrane into the less concentrated solution. The solvent can be recovered and the soluble contaminant is concentrated for further treatment. Reverse osmosis has been used in the electroplating industry to recover metals from electroplating baths (McNeil, 1988; McNeil and McCoy, 1989) and by chemical manufacturers to remove organics from wastewaters (Chemical Engineering, 1989).

Hyperfiltration and ultrafiltration separate high molecular weight ionic or organic components from water through use of a semipermeable membrane with small pore size and application of pressure. The high molecular weight components are too large to pass through the pores. Hyperfiltration is used for components of molecular weight 100 to 500, and ultrafiltration for components with molecular weight over 500 (McNeil, 1988; McNeil and McCoy, 1989). These filtration technologies are being used to remove toxic metals from metal finishing wastewaters, to concentrate oily wastes from metal finishing rinse waters, and to recover oil from waste oil emulsions in metal machining and rolling operations.

Liquid membrane separation - formerly used in the uranium industry has been resurrected by UNC Inc. to apply to extraction of other metals from wastewater (Lorenz, 1989)

Stripping Processes

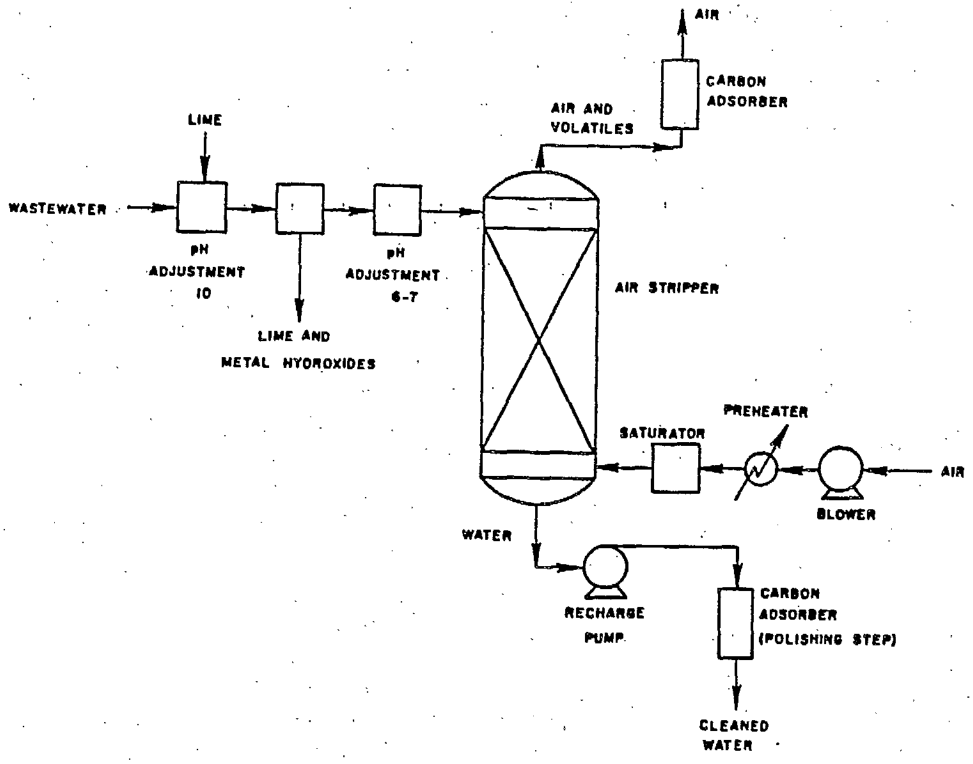

Figure 2:1. Air stripping schematic

Source: Breton et al. Treatment technologies for solvent containing wastes, 1988, p. 262.

Volatile organic compounds in concentrations less that about 100 mg/l can be removed from dilute aqueous waste streams by air stripping. In the stripping process, dissolved molecules are transferred from a liquid into a flowing gas or vapour stream in a packed tower with countercurrent flow of air and water (Figure 2:1). In air stripping, the flowing gas is air. A packed tower air stripper can remove greater than 99% of volatile organics from water. In steam stripping, the vapour stream is steam. Less volatile or more soluble compounds, and higher concentration organics in waste streams can be removed by steam stripping. Steam stripping can also be used to treat spent solvents contaminated with nonvolatile impurities (Boegel, 1989). The compounds stripped off are released to the air, adsorbed on carbon, or passed through a catalytic converter.

In the catalytic conversion process, the stripped off contaminant is passed over a catalyst and heated to a high temperature so that the contaminant is broken down into harmless components which can then be released into the air.

Activated Carbon Adsorption

Activated carbon can be used to remove a variety of organic and some inorganic contaminants from liquid and gaseous waste streams. In the carbon adsorption process, the contaminated water is passed through column reactor vessels containing granular activated carbon (GAC), a highly porous material which adsorbs the hydrocarbon contaminants. Adsorption is a result of electromagnetic interactions among nucleii and electrons. GAC adsorption can remove as much as 99.99% of the organic compounds found in water.

Designing a GAC system is complex and requires an understanding of adsorption kinetics and system steady state conditions. A variety of reactor configurations can be used (Figure 2:2). Factors that must be taken into consideration include the type and number of contaminants as each contaminant competes for carbon pore space; the contact time; the solubility of the compound to be removed; and the presence of metal contaminants in the wastewater that may have to be pretreated before carbon adsorption.

Chemical Processes

Ion Exchange

In wastewater treatment, ion exchange is used to convert hazardous components into a form in whichthey can be reused. Ion exchange is suitable for wastewater containing low levels of heavy metal contaminants. The metals can be regenerated and the water recycled or discharged. Ion exchange has also recently been used for purifying concentrated metal containing solutions such as steel-pickle liquors and recycling the liquor (Brown, 1989). Some exchange resins are selective for certain metals and can be used to remove a toxic metal from a solution containing a high concentration of non-toxic metal.

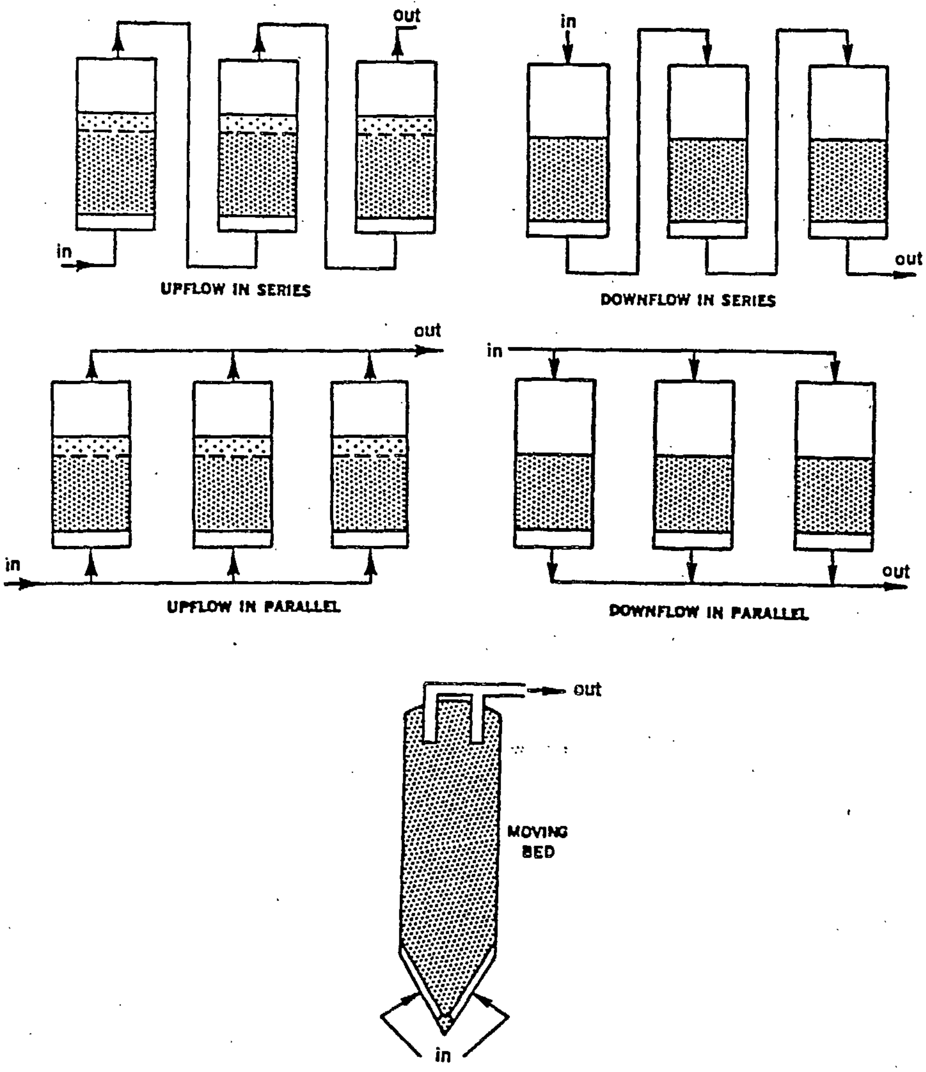

Figure 7.6.2. CARBON BED CONFIGURATIONS

Source: Reference 12.

Figure 2:2 Carbon bed configurations

Source: Breton et al. Treatment technologies for solvent containing wastes. 1988, p. 321

In the ion-exchange process, electrolytes are adsorbed from solutions through reaction between ions in the solution and localized sites on the adsorbent, or ion exchange resin. The reaction is essentially a reversible double decomposition in which one of the reactants is free to move through the solution and the other is held fixed to the solid. For example:

$$Na^+ + {}^+H\text{-}S = H^+ + Na^+\text{-}S$$

where S denotes the solid surface.

Most common ion exchange resins are polystyrene based. Properties of the resins vary and they function over different pH ranges.

Normally the ion exchange reaction takes place in a vertical column in which the resin is fixed. The solution passes through the column and the metal ions react with the ions on the resin. The resin can usually be regenerated in place.

Ion exchange in the electroplating industry can be used to recover metals from rinsewaters and plating solutions. Examples include (Brown, 1989):

- Recovery of chromic acid from plating rinse water;
- Recovery of metals from acid copper and nickel plating rinsewater
- Recovery of metals from mixed rinsewaters
- Effluent polishing by using resins that selectively remove low concentrations of toxic metals from high-flow effluent streams

Ion exchange can also be used to treat industrial cooling tower blow-down that contains chromate (used as a corrosion inhibitor in cooling towers), and for acid purification and recovery.

Ion exchange is used extensively in the nuclear industry to remove radioactive contaminants from evaporator condensates and for purification of radioisotopes.

Electrolysis

Electrolysis is a common technology for refining ores and it is now increasingly being used for recovering metals from waste streams in electroplating, rolling mills and electronics industries. Electrodes are immersed in a chemical medium and a current is passed between them. At the cathode (negative electrode), the metal ion is reduced to the elemental metal and at the anode (positive electrode) gaseous oxygen, nitrogen or hydrogen evolves. Electrolytic technology has been used to recover various heavy metals, including gold, silver, cadmium, nickel, nickel-iron alloy, copper, and zinc from wastewaters and can be used to recover some metals from crystals and sludges (Aguwa and Haas, 1989). Recovered metals can be reused.

Coagulation and Flocculation

Coagulants or flocculants may be added to wastewater to increase the sedimentation rate of suspended or colloidal materials. In the flocculation process the fine particles aggregate through particle-particle interactions under appropriate electrolytic conditions or by attachment to long chain polymers. The mechanisms by which flocculation occurs have been studied by a number of researchers. A summary of theoretical developments is given by Mishra (1989).

Polymer flocculants are usually the most effective, forming larger, heavier floc particles which settle faster and form a denser sludge. Flocculation is often used in removing heavy metals after chemical precipitation (see Figure 2.3). The sludges usually require treatment to remove or stabilize hazardous components before disposal.

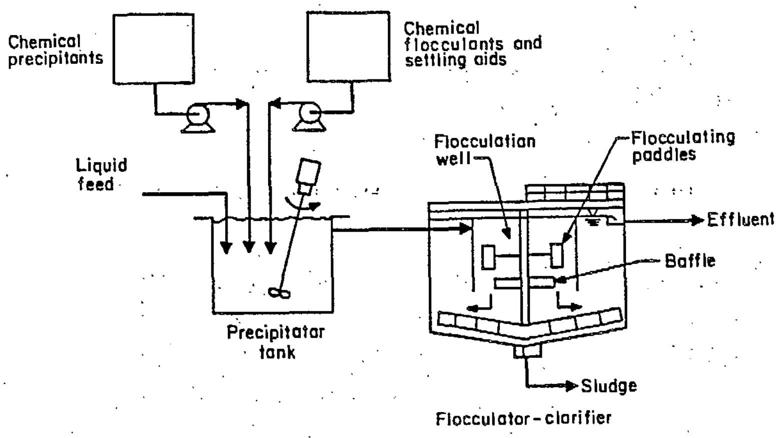

Figure 2.3: Chemical precipitation

Source: Standard Handbook of Hazardous Waste Treatment and Disposal, 1989, P. 7.22

Chemical Precipitation

Chemical precipitation can be used to treat hazardous constituents that can be converted through addition of chemicals under appropriate pH and reaction conditions to an insoluble form and then filtered out. Metals amenable to precipitation include arsenic, barium, cadmium, chromium, copper, lead, mercury, nickel, selenium, silver, thallium, and zinc (Chung, 1989): Corrosive wastes and spent pickle liquors from steel finishing processes can also be treated by chemical precipitation.

Industries that are candidates for this technology include metal plating and polishing, ferrous and non-ferrous metals, mining, inorganic pigments, and the electronics industry. Cyanide must be removed from the waste stream prior to treatment and hexavalent chromium must be converted to trivalent chromium.

Chemical Oxidation and Reduction

In oxidation-reduction (redox) reactions the oxidation states of the reactants change. When electrons are removed from an atom, ion or molecule the substance is oxidized; when they are added, it is reduced. The substance in the altered state has different chemical and physical properties.

Oxidation-reduction processes are mainly used to treat low concentration metal-bearing wastes and inorganic toxic wastes such as sulfides, cyanides, and chromium and for organic wastes such as phenols and sulfur-containing organic compounds (Fochtman, 1989). Oxidation reagents include sodium hypochlorite, calcium hypochlorite, hydrogen peroxide, potassium permanganate and ozone. Reduction reagents include sulphur dioxide and sodium borohydride.

Ozonation

Ozone is a very strong oxidant that reacts with a large variety of organic and inorganic compounds and has been used to treat hazardous wastes in many industrial sectors (Novak, 1989). Ozonation has also been used in conjunction with ultraviolet radiation to detoxify wastewater containing aromatic and aliphatic polychlorinated compounds, aliphatic amines, ketones, and alcohols. The process will not degrade low molecular weight chlorinated organics.

Dehalogenation

Dehalogenation is a relatively new technology for halogenated hydrocarbon wastes and many potential applications are still in the research stage. Halogenated hydrocarbons include PCBs, chlorinated dioxins, and halogenated benzo- and dibenzofurans. Commercial processes are available for removing or reducing the amounts of PCBs from oils or fluids. The effectiveness of the processes depends on the nature of the oil, the halogenated hydrocarbon concentration, and other chemicals in the oil that may interfere with the reaction (Kornel, 1989).

Solidification, Stabilization and Encapsulation

These are treatment processes used to reduce the mobility of pollutants so that wastes can be landfilled. In solidification processes materials are added to the waste to produce a solid. This can, but does not necessarily involve a chemical bond between the toxic component and the additive. Stabilization involves a chemical reaction with the toxic component to give a more chemically stable non-toxic form. Encapsulation involves complete coating or enclosure of a toxic particle(s) with a new substance (Wiles, 1989).

Pozzolan cementation is one of the processes used to contain toxic contaminants. "Pozzolanic concrete is the reaction product of fine grained aluminous siliceous (pozzolanic) material, calcium (lime) and water" (Breton et al. 1988, p. 661). The reaction takes place at normal temperatures and the product is a strong, slow hardening cement. The pozzolanic process is used mainly in inorganic waste treatment. High concentrations of organics tend to prevent the formation of a high strength product,

Biological Processes

Biodegradation is the "molecular degradation of an organic substance resulting from the complex action of living organisms" (Biodegradation Task Force 1978). There are many natural living organisms involved in biodegradation processes at the micro and macro levels. Genetic engineering has produced various microorganisms that will degrade hazardous chemicals in wastewater and in waste dumpsites. Biological degradation processes include aerobic systems in which oxygen is required and anaerobic systems where microbial action takes place in the absence of oxygen. In the aerobic category are trickling filters, activated sludge, aerated lagoons and rotating biological contactors.

In a trickling filter or activated sludge system, a microbial community that will convert organic compounds to new cellular material and inorganic, non-hazardous chemicals, such as carbon dioxide and water, is cultivated. A knowledge of the specific chemical compositions of the waste streams is necessary before selecting or engineering microbes able to decompose the hazardous constituents of the stream. Other factors that have to be considered are variations in composition of the waste stream, nutrient requirements, pH, oxygen supply and temperature. A microbe population can be killed off by extreme conditions or sudden changes in chemical composition of the waste, and microbe populations can take a long time to regenerate and stabilize.

Trickling Filters

A trickling filter (also known as a biofilter tower) is a fixed film, attached growth system, that consists of a bed of stones, corrugated plastic sheets, redwood slats or other material three to six feet deep through which the wastewater trickles down. Bacteria gather and multiply on the filter media and consume most of the organic matter in the wastewater.

Activated Sludge

Activated sludge is a suspended growth, mixed culture system. A mixture of wastewater and biological sludge is agitated and aerated to stimulate the bacteria to break down the organic matter more quickly. After aeration, the sludge drops out in a final clarifier. About 25% of the sludge is returned to the reactor vessel to keep the biological process alive.

Oxygen is supplied to the system through agitation of the wastewater surface so that oxygen is adsorbed from the atmosphere, by passing compressed air through the reactor vessel, or a combination of both methods.

In a fluidized bed aerobic reactor, oxygenated wastewater is used to fluidize a bed of sand. This allows greater surface area for biological growth.

A sequencing batch reactor is a cyclic activated sludge system.

In an activated sludge process, aeration serves a number of functions including mixing effluent from primary treatment with the returned activated sludge; keeping the sludge in suspension; and supplying the oxygen required in a biological oxidation process.

The U.S. Environmental Protection Agency found that trickling filters were as effective as activated sludge in removing priority pollutants (Lorenz, 1989).

Ganczarczyk (1983) gives a detailed account of the activated sludge process and some of the factors that have to be considered in operating and maintaining an activated sludge system.

Aeration Lagoons

Lagoons, oxidation ponds (ditches) or stabilization ponds are large, shallow ponds in which wastewater is treated through the interaction of sunlight, algae, and oxygen. About one-third of all secondary treatment plants use oxidation ponds, usually without primary treatment.

Generally, lagoons or ponds that receive settled wastewater and consequently function only as secondary treatment devices are known as oxidation ponds. Those that receive raw wastewater and function over the entire range of treatment are called stabilization ponds or lagoons. Stabilization ponds require no mixing.

In facultative lagoons, part of the solids settle to the bottom where anaerobic decomposition takes place. Less mixing energy is required in these systems.

An industrial aeration application is in pulp and paper secondary treatment systems for improved biological oxygen demand (BOD) removal and reduced basin retention times. In the chemical industry, aeration processes handle heavy chemical oxygen demand (COD) loadings in the industrial organic, pharmaceutical and agricultural chemical sectors. In the textile industry, additional BOD concentrations in ponds and lagoons have increased the demand for improved oxygen rates. In the petroleum industry, there is need for improved biological treatment of refinery wastewater.

Rotating Biological Contactors

These consist of a series of closely spaced vertical disks, often made of plastic, mounted on a shaft. The disks are placed in such a way that about 40% of the surface area is immersed in wastewater. When rotated about the shaft, the disks carry a film of wastewater into the air where it absorbs oxygen. In completing the rotation, the oxygenated film mixes with the reservoir of wastewater. The disks perform several functions:

- provide a medium for the build-up of microbial growth
- bring microbial growth into contact with wastewater
- aerate the wastewater reservoir.

Aerobic Digestion

Aerobic digestion is used to treat the organic sludge resulting from biological processes. Aerobic digestion is similar to the activated sludge process in that biological decomposition takes place in a tank equipped with an aeration device. Fixed surface aerators are usually used. Submerged aeration is preferred in colder regions where freezing may be a problem. Mechanical aeration is preferred in batch systems.

Anaerobic Treatment

Anaerobic digestion is a sequential, biologically destructive process in which hydrocarbon molecules are converted in the absence of oxygen to carbon dioxide and methane by microorganisms called methanogens.

Anaerobic digestion has a number of advantages over aerobic processes. Anaerobic digestion produces about 20 times less solids (sludge) for disposal and sludges tend to be easier to dewater; energy requirements are less because power is not needed to drive aerators; high organic destruction rates can be attained; and the methane (biogas) produced in the process can be used as a fuel.

Biological upset is one of the major problems with anaerobic digestion. Heavy dosages of toxic material can lower the pH and inhibit sludge decomposition and methane production. Changes in the pH can be corrected by adding buffers such as calcium hydroxide. Waste streams may require pretreatment to remove toxic materials and heavy metals prior to digestion.

Anaerobic treatment has been used for municipal sludge stabilization and for treatment of easily biodegradable wastes such as food industry effluents. Full scale systems are now being used in some pulp and paper mills.

In anaerobic filter reactors, the bacteria form a thin biofilm on a surface within the reactor. These reactors can be fixed bed or fluidized bed. The other major reactor configuration is the Upflow Anaerobic Sludge Blanket (USAB) which consists of a tower containing sludge granules of active biomass. The water passes up through the sludge blanket.

In two stage reactors, different types of organisms specific for different organic compounds are in the two reactors. The first reactor can degrade organic molecules to simpler forms suitable for methanogenesis in the second reactor.

Land Treatment

This involves spreading wastes on the land or placing waste in a shallow pit and using biological decomposition to treat the waste. Land treatment, particularly the form of treatment referred to as land farming, is most often used to dispose of organic solids and sludges, such as the waste by-products of the petroleum industry.

Aquatic Treatment

Aquatic plant systems are shallow ponds with floating or submerged aquatic plants. Floating plants derive their carbon dioxide and oxygen needs directly from the atmosphere and their minimal nutrient requirements from the water. Submerged plants absorb oxygen, carbon dioxide and minerals from the water column.

A number of aquatic plants support the growth of bacteria which metabolize waste. Aquatic treatment systems could be compared to trickling filters with built in clarifiers.

Other technologies

FMC produces 100 types of a seaweed based product called carrageenan that is expected to find use in food processing and industrial wastewater treatment to remove proteins. There is promising work underway to use carrageenan and its byproducts to recover precious metals from wastewater streams, such as those of the electronics industry (Lorenz, 1989).

Thermal Treatment

Thermal treatment is a destructive mechanism that uses heat to break down organic contaminants, including PCBs and dioxins, in waste waters and solids. The types of organic materials that can be destroyed depends on the temperature that can be attained in the process and the medium containing the contaminant.

High temperature technologies include rotary kiln incinerators and fluidized bed incinerators which use combustion technology; infrared incinerators that use near-infrared radiation to pyrolyse the feed material; plasma incineration in which the waste is pyrolysed at temperatures over 5000 C using an electric arc to form a plasma which on cooling forms hydrogen, nitrogen, carbon monoxide, HCl, and particulate carbon; in-situ vitrification, a process used to convert soils to durable glass and in which the organic constituents are pyrolysed (Johnson and Cosmos, 1989; Cheremisinoff, 1988).

Many of the thermal processes were developed to treat contaminated landfill sites and can be used to treat dewatered sludges. Some of the thermal processes, e.g., plasma pyrolysis, can also be used to decompose toxic wastewaters.

In some areas, a central incineration facility can serve a number of plants. Wastes are trucked to the incinerator site and the costs of incineration are usually based on the type of waste. Problems with incineration technologies stem from fears that if temperatures are not high enough, pollutants will merely be changed from a solid or liquid phase to a gas phase and escape into the environment. Many communities are therefore reluctant to have permanent incinerators sited near them or to have potentially dangerous chemicals trucked through them on a regular basis (Chemical Engineering 1988). Some of these objections can be overcome by mobile thermal treatment services where the treatment unit is trucked to the site and the waste is treated on-site (Cheremisinoff 1989b).

Sludge Treatment

Many of the sludges produced as by-products of wastewater treatment processes contain hazardous chemical and metals that must be removed by appropriate chemical or biological methods or stabilized before landfilling.

Sludges can be dewatered by a number of methods including vacuum filters, belt presses, filter presses, centrifugation, or evaporation lagoons (Kellog, 1989; Cheremisinoff, 1989a). Some sludges have to be conditioned first to improve their dewatering efficiency. This is usually done by adding chemicals to the sludge to enable the solid particles to agglomerate into larger particles or flocs.

The dewatered sludge (sludge cake) can be either landfilled or subjected to thermal treatment for destruction or stabilization. Depending on their organic and moisture content, some sludges can be used as furnace fuel.

Emerging Technologies

Irradiation

Gamma radiation processes for treatment of municipal waste are at the demonstration stage in Canada through Nordion's Sludge Pasteurizing System (SPS) project (Swinwood and Wilson, 1988; Gay, Wilson and Swinwood, 1988). The possibility of using irradiation to degrade the lignin in pulp and paper mill wastes has been studied by a number of researchers (e.g., Meshitsuka and Nakano, 1976; Kahn et al., 1987). Research on using gamma radiation for treatment of pulp and paper mill wastes is currently being conducted in Canada the the Whiteshell Nuclear Reseach Establishment.

Photocatalytic Processes

A photocatalytic water purification method that makes use of semiconductor powders that can be activated by solar or artificial UV light has been developed by Photocatalytics (Lorenz, 1989).

Best Demonstrated Available Technologies

The Environmental Protection Agency in the U.S. is conducting studies and issuing reports on Best Demonstrated Available Technologies (BDAT) for chemicals, metals, wastewaters and sludges from a number of processes.

The EPA defined available technologies as those that are both demonstrated and achievable. Demonstrated technologies are those currently used on a full scale basis to treat the waste of interest or a waste judged to be similar. EPA will also consider as demonstrated treatment, technologies that are used to separate or otherwise process chemicals and other materials on a full scale basis, some of which are applicable to waste treatment where the waste is similar to raw materials processed in industrial applications.

The agency determines whether the technologies are commercially available and whether they substantially reduce the toxicity of the waste or the liklihood of migration of hazardous constituents from the waste.

Treatment technologies are considered commercially available if the treatment method can be purchased or licensed, or if the services of the facility offering the technology can be purchased, even if the technology itself cannot be purchased.

EPA reports on best demonstrated available technologies applicable to industries of concern are cited in appropriate sections. Some handbooks outlining best available treatment for hazardous wastes are also available (e.g., Breton et al, 1988; Freeman, 1989; Palmer et al., 1988; Wilk et al., 1988).

The Municipal/Industrial Strategy for Abatement (MISA) office of the Ontario Government is planning to produce documentation on best available technologies economically achievable (BATEA) for pollution control in conjunction with its program to introduce new regulations on effluent discharge limits for various industrial sectors.

Biological treatment for mineral industry effluents is being studied by the CANMET laboratories of Energy Mines and Resources (see for example, Gould et al., 1988; McReady et al., 1990; Bechard et al. 1989).

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CHAPTER THREE

PULP AND PAPER INDUSTRY

Of the 50 major polluting companies on the St, Lawrence River System, 15 are in the pulp and paper sector. The mills are classed by the type of pulping processes or the source materials used as follows (Centre Saint-Laurent, 1989):

Sulfite chemical pulping (5 mills)

Thermomechanical or chemithermomechanical pulping (6 mills)

Chlorine-bleached kraft pulp mills (2 mills)

Recyclable materials for manufacture of fine or tissue paper (2 mills).

In 1989, 14 of the mills had primary treatment facilities. None had secondary treatment.

A mill may use one or more generic chemical or mechanical pulping processes, but within a mill there are variations in some of the process stages. The processes used by any mill are dependent on a number of factors including the varieties of wood available to the mill; whether the mill will use any recyclable materials; the age of the mill; the number and types of process upgrades that have been implemented; the availability and costs of energy; the availability of water; the availability of chemicals; the type of paper or paper products that will be produced by the mill (ranging from cardboard to fine tissues); the demand for the mill's output; and environmental regulations.

The yield of pulp is defined as the quantity of pulp or paper produced divided by the amount of wood entering the mill. Yields from the various processes range from 30% to 95%. The remainder is waste in solid, liquid or gaseous form. The types of waste depend on the processes and chemicals used. The organic wastes take oxygen from the water and therefore reduce the oxygen available to fish and other aquatic life; many of the chemicals are toxic to aquatic life, some are carcinogens, and some are also persistent in the environment. Suntio et al.(1989) have identified 250 chemicals present in pulp mill effluents and provide data on the amounts produced, bioconcentration, potential and toxicity.

Effluent from pulp and paperB mills is regulated under the Fisheries Act. Regulations are outlined in Environment Canada's Pulp and Paper Effluent Regulations (EPS 1-WP-72-1, 1971). The regulations are currently in the process of being revised but revisions will not be announced until later this year.

Deleterious substances are prescribed as (EPS 1-WP-72-1, 1972):

(a) total suspended solids

(b) oxygen-demanding decomposable organic matter produced as waste from a mill (biological oxygen demand (BOD) and chemical oxygen demand (COD))

(c) toxic wastes deposited by a mill

The regulations give permitted deposits of total suspended solids and BOD from the various stages in the pulp and paper processes in mills using different types of pulping and bleaching processes. The permitted deposits are different for existing and for new or altered mills.

Some of the provinces have or are developing provincial regulations. New effluent regulations for the pulp and paper sector will be introduced in Ontario in the early 1990s under the MISA program. The monitoring stage of the process for developing new pulp and paper regulations is currently underway (MISA 1989).

Bonsor et al. (1988) compare pulp and paper mill effluent regulations in the United States and some European countries with those of Canada. In the U.S., the most recent regulations are more stringent than in Canada and it is expected that they will become even more stringent. In Sweden and Finland, BOD effluent regulations reduced BOD levels by close to 90% from 1955 to 1985. More recently, emphasis has been on reducing the levels of organically bound chlorine. In West Germany, under the Waste Water Charges Act of 1976, polluters are charged fees based on the quantities of pollutants discharged. Bonsor et al. (1988) calculated if the fees applied in Ontario, a small mill would pay about one million dollars per year.

Waste Reduction

A major way of reducing waste is to introduce new or improved processes that will increase the yield of pulp or paper products and thereby reduce the amount of waste, while maintaining the product quality desired. New process technologies that use and produce fewer hazardous materials or that produce more easily treatable hazardous materials can readily be incorporated in new mills but can be expensive and difficult to incorporate in older operations. However, some new or improved technologies can be fitted retroactively into different stages of existing processes.

Luonsi et al. (1987) outline some ways of reducing hazardous waste in a pulp and paper mill. The most basic is good housekeeping to reduce accidental spills which can result in significant discharges of harmful materials to water bodies. Good housekeeping includes regular maintenance and checking of valves, pumps, pressure gauges, etc. to reduce incidences of equipment failure. Training and education programs for mill employees help to reduce spills caused by human error.

Incorporation of modern process control and monitoring equipment enables early detection of abnormal conditions and allows for optimum operating conditions to be maintained at the various stages of the process. This results in minimization of chemical use. Overdimensioning of critical process equipment to contain spills reduces the possibility of sudden overloading of treatment processes.

Other measures include recirculating and reusing process effluents; changing over to production methods and equipment with lower water consumption; separating and regrouping different kinds of wastes; chemical recovery; and developing less polluting production processes.

Improved end-of-pipe treatments can reduce toxicity levels by significant amounts. In some mills, waste streams are combined before treatment. This can dilute the harmful constituents in the waste streams and reduce the efficiency of the waste processing treatment. In addition, the treatment method used may not be adequate to treat all hazardous materials in a combined waste stream. Segregating and regrouping the waste streams so that each can be treated by the optimum method to remove hazardous materials can significantly reduce the toxicity levels in the final discharge.

In the Environmental Protection Service Training Manual (EPS 6-EP-83-1, 1983), "The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices", the processes used in the various stages of converting raw wood to pulp and/or paper and the waste products produced at each stage are described. This report will briefly summarize the processes and describe some of the new technologies and research being conducted to improve the processes and reduce or eliminate waste from the various stages.

Raw Wood Handling

Wood is shipped to a mill by truck or water and is stored at the mill. Newer mills tend to have wood shipped by truck and use dry mechanical methods for handling the wood. The waste from dry handling methods consists of sand, soil, bark and pieces of wood. This is normally shipped to landfill sites.

In older mills, where wood is or used to be shipped by water, water "flumes" may be used to move the raw wood to the debarking operation. Sand and grit, bark fines, and organic leachates from the bark accumulate in the flume. In some mills the flume water is also used in debarking.

Debarking removes the bark from the logs before chipping. In a debarking drum, as the logs are rotated they fall against each other, and the bark is loosened and removed. In a dry drum process, the bark is used directly in furnaces. In a wet barking process where water is used to help loosen the bark, the bark has first to be dewatered before being used in the bark furnace. Bark can also be removed by hydraulic jets (used mainly in B.C.) or by mechanical strippers fitted with rotating knives.

Chipping reduces debarked logs to wood chips by means of rotating knives. Chips are screened to remove sawdust, slivers, and oversized chips.

The effluent from the wet handling and debarking processes contains suspended solids in the range of 40kg per oven dried tonne (ODt) of wood processed. A woodroom effluent treatment clarifier can reduce suspended solids to 3kg/ODt.

The effluent also contains varying amounts of organic matter (BOD) depending on the source of the water for the debarking process. If water from another waste stream in the mill is used in the debarking process, the BOD can be double.

Bark is usually stored and burned as fuel. Leachates from bark storage (especially from the wet debarking process) can produce harmful effluents. Effluent is also obtained from bark pressing equipment used to dewater wet bark.

New or Improved Technologies

Converting from a wet to a dry woodroom process will eliminate liquid effluent. Dry handling tends to require more land space than wet processes and also requires investment in woodhandling equipment. To meet the ever increasingly stringent effluent quality measures in Finland, the Schauman Company has, among other things, changed over to dry debarking in its plants (Skogman and Lammi, 1987). Some Canadian mills are also changing to dry woodhandling processes.

Pulping

Pulping loosens and separates the fibres in the wood. This can be done by chemical or mechanical processes. The two major chemical processes are the kraft or sulfate process and the sulfite process. The major mechanical processes are groundwood pulping, refiner mechanical pulping, and thermomechanical pulping.

Chemical Processes

Kraft Pulping

The kraft process can be used with most types of wood. It uses an alkaline solution of about 10% Na_2S and NaOH - also known as white liquor - in which the chips are soaked to impregnate them and cooked at about 165 C. The spent or black cooking liquors are cycled to a chemical recovery system where the chemicals are regenerated. The washing process that separates the pulp from the black liquor is called brownstock washing. The liquid leaving the washers contains toxic organic materials that are resistant to biological treatment.

Washing efficiency depends on the dilution factor and the number of stages of washing installed. Increasing the washing efficiency reduces the organic material and chemicals in the effluent discharged to the sewers. Adding more stages of washing equipment or modern equipment can increase efficiency.

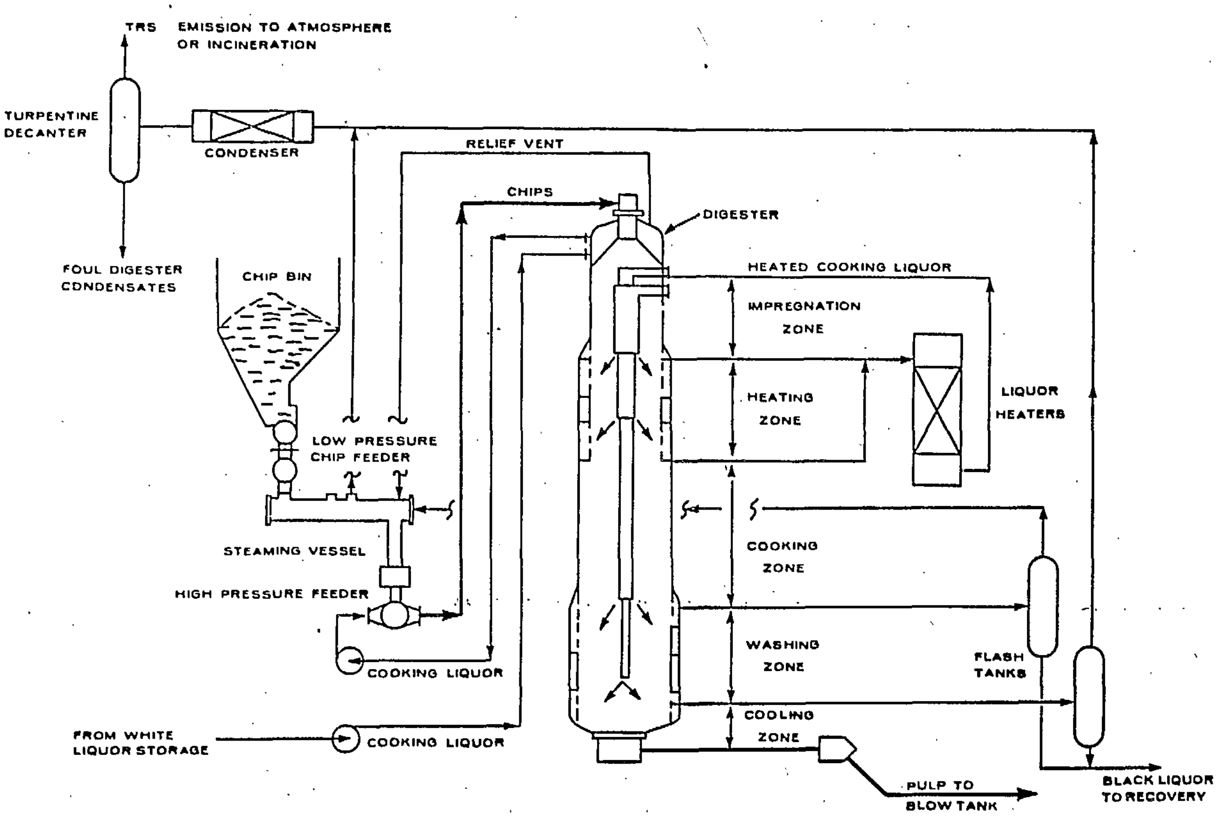

Figure 3:1. Typical continuous kamyr digester for kraft pulping

Source: The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices, EPS 6-EP-83-1

Pelton (1989) notes that the efficiency of the brownstock washing operation is important because the performance of downstream operations such as bleaching and black liquor recovery is dependent on it. Poor washing can lead to higher bleaching costs, excessive chemical loss, and increased effluent treatment costs. Brownstock defoamers can be used to increase washing efficiency.

PAPRICAN conducted a study in 1988 that shows certain types of oil based defoamers used in the brownstock washing stage cause the formation of precursor compounds that in turn form dioxin when chlorine is added (Pulp and Paper, 1989). Tests are being done on effluent, sludge and pulp from Canada's 47 bleached pulp mills. A study on 104 mills in the U.S. will provide data for regulations on dioxin in the U.S.

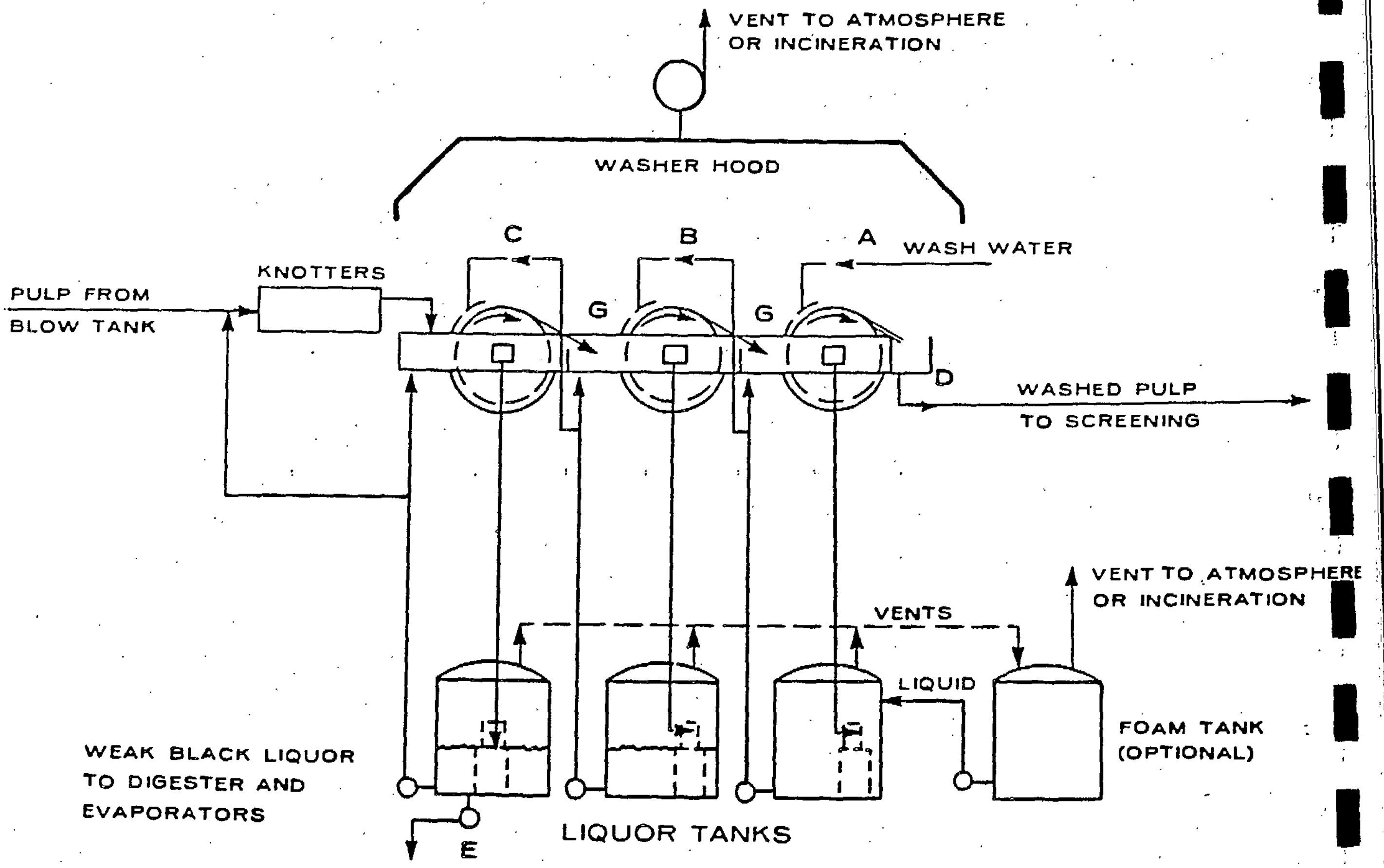

Figure 3:2 Brownstock washing process

Source: The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices, EPS 6-EP-83-1

Turpentine is one of the by-products of the kraft process. The turpentine is in the condensed vapours from the digester which are routed to a turpentine recovery system. The residue from this contains chemicals such as terpenes, terpinol, and methanol which are toxic to fish.

The effluent from the washing process contains high BOD levels. Other major liquid wastes are bleaching effluents and evaporator condensates.

Some of the major pollution problems are encountered in kraft mills. Kraft mills are banned in West Germany and kraft pulping is being replaced by other methods in Sweden and Finland. Some Canadian companies are looking at alternative pulping methods.

Sulfite Pulping

Sulfite pulping is used for spruce, fir, balsam, western hemlock, birch, and poplar.

The cooking liquor is SO_2 (obtained by burning sulfur) absorbed in an alkaline base solution. Limestone was the most common base but this is being replaced by soluble bases such as magnesium, sodium or ammonium. The spent cooking liquors go through a chemical recovery process or are drained to the sewer and the pulp is washed by rinsing with white or fresh water.

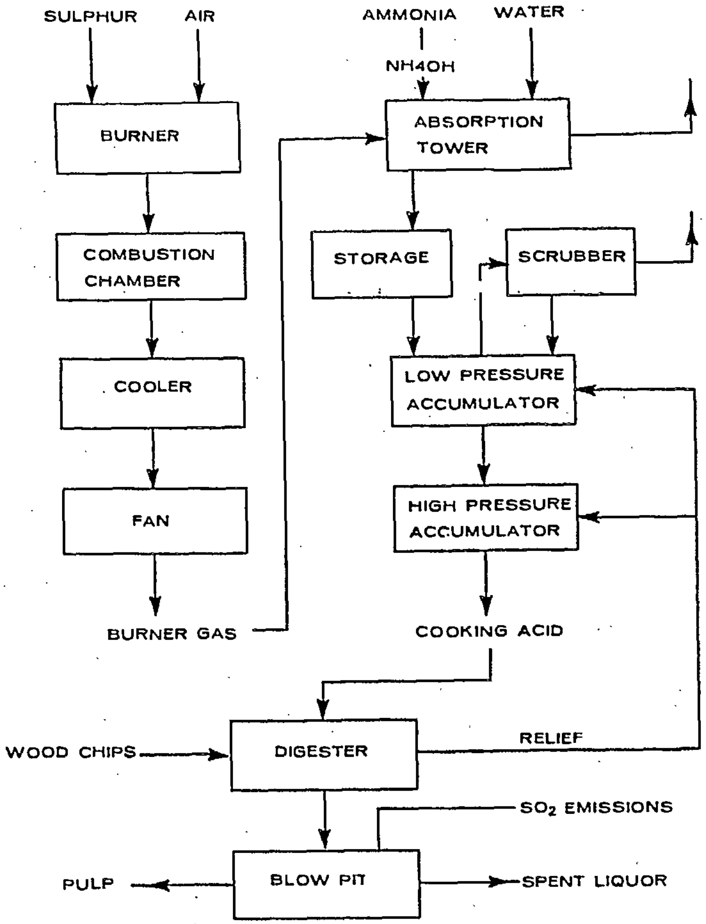

Figure 3:3 Sulfite pulping process

Source: The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices, EPS 6-EP-83-1

The BOD and effluent toxicity can be reduced by raising the pulping yield. This can be accomplished by installing a refiner system. In high yield sulphite pulping, the chips are partially cooked in the digester and the defibering is completed in refiners where wood chips are passed through double or single revolving disc refiners. The pulp from this process is chemimechanical pulp (CMP).

Semichemical Pulping

The chipped wood is first treated chemically in a digester and is then mechanically defilibrated in a disc refiner. The spent cooking liquor contains organic acids which cause disposal problems. Fluidized bed reactors has enabled these liquors to be preconcentrated to 30-35% solids and then burned. The spent liquor can also go to a kraft mill.

Mechanical Pulping

Mechanical pulping gives yields of greater than 80%. Pulp quality depends on the operating pressure in the defibering operation.

In Stone Groundwood Pulping, logs are forced into contact with a revolving grindstone in the presence of water. In pressurized systems, grinding is done in pressure vessels under elevated pressure. In some mills, hardwoods are pretreated by soaking in sulphite and sodium bicarbonate liquor at elevated temperature and pressure to give chemigroundwood pulp.

Refiner Mechanical Pulp is produced by passing woodchips through revolving disc refiners.

In the Thermomechanical Pulping (TMP) process, chips are steamed under pressure and then defibered under pressure in a disc refiner.

Chemithermomechanical Pulping (CTMP) is similar to thermomechanical pulping but sodium sulphite is added to the steaming vessel.

The water from pulping processes contains suspended solids and soluble organic materials from the wood. The BOD from these organic materials decreases as the yield of pulp increases. Therefore, any process that will increase the yield of pulp will reduce the BOD levels.

The toxicity of pulp mill effluent originates from the wood. Toxic materials are washed from the wood and wood pulp at various stages of production. Principal toxic constituents in pulp waste streams are shown in Table 3.1 (Thakore et al, 1989).

Different processes generate different amounts of toxicity depending on the process characteristics and wood species. Studies on behaviour of toxicity on pulp fibers showed that in the kraft process toxic compounds can be removed from pulp fibers during brownstock washing. In the chemithermomechanical pulp (CTMP) process, the low solubility of toxic compounds, together with adsorption properties of the fiber makes toxicity removal by washing difficult. As a result in an integrated groundwood newsmill complex, most of the toxicity from the CTMP process is carried on in the fibres into the newsprint mill and is distributed evenly into the large common white water system.

Effluent Source	Toxic Material	
	Major	Minor
Debarking	Resin acids	Diterpene alcohols
Mechanical Pulping		
Softwood	Resin acids	Diterpene alcohols & fatty acids
Hardwood	Juvabione and unknowns	Resin acids and fatty acids
Kraft Bleaching		
Acid	Quinones and chlorocatechols	Unknown
Alkali	Chlorinated phenols resin acids and fatty acids	Liquid pitch and dispersant

Table 3.1 Principal toxic constituents of pulp mill waste streams

Source: Thakore, Collins and Smiley, 1989

Process Improvements

The Baie Comeau mill of Q&O Paper Company is changing from sulphite pulping to thermomechanical pulping (TMP). As Rodden (1989a; 1989b) points out, the mill was almost forced into TMP because of environmental considerations. The switch from sulphite will reduce BOD considerably and increase pulp yield from 50% to 95%. Use of TMP will also reduce the mill's process steam demands and the need to make steam, and hence reduce energy requirements.

After losing its competitive position because of lack of modern production facilities and low cost producers, the Tasman Paper company in New Zealand considered a number of options for its Kawerau Mill in the Bay of Plenty, and decided on kraft mill modernization (Allison and Johnson, 1989). The option included installation of larger, more efficient digesters, and enhanced delignification before bleaching to reduce chlorine chemical demand. The capacity of the mill will be increased significantly without increase in effluent discharge to the environment.

The Institute of Paper Science and Technology in Atlanta is conducting research on the use of high temperature electrochemistry in chemical pulping for promoting delignification reactions in pulping. (Pulp and Paper Canada, 1989a).

Current applications of biotechnology in the pulp and paper industry include treatment for alcohol and yeasts in spent liquors, for slime control, and for wastewater treatment (Hakulinen, 1987). Applications under development include biological pulping and bleaching and biofibre production, as well engineering microorganisms for treatment of wastes that cannot be treated by conventional biological methods.

The Kobe Steel Company Ltd. in Japan has developed a new biopulping process in which 80% of lignin in pulpwoods can be decomposed at normal temperature and pressure by a microbe that is highly efficient in lignin decomposition. The process is still in the R&D stage but the company is optimistic about it being successful (Pulp and Paper Canada, 1989d)

A new pulping process that combines petrochemical process and alcohol distillation technology with standard pulping techniques has been developed by Repap Enterprises Corp. Inc. Called the ALCELL (trademark) pulping process, it uses ethanol and water solution to dissolve lignin from wood chips in an extractor under controlled temperature and pressure. The lignin separation and liquor recovery system separate the by-products (sulfur-free lignin, wood sugars and volatile components) and recycles the ethanol to the extraction stage. This closed cycle, environmentally friendly pulping process has been demonstrated at a plant at Newcastle, New Brunswick with all systems operating successfully (Pulp and Paper Canada, 1987, 1989b).

Bleaching

The colour of pulp ranges from dark brown to creamy white. About half of this is used in its unbleached state; the other half is bleached to produce white paper. Kraft pulp is the most difficult to bleach. Sulphite pulps can be bleached to high brightness using a three stage sequence of chlorination, caustic extraction and hypochlorite bleaching. Kraft pulps normally require a five or six stage sequence to achieve the same brightness (see Figure 3.4) (EPS 6-EP-83-1, 1983)

The chlorination (C) stage involves addition of chlorine to the pulp and then washing and thickening. The wash filtrate contains high BOD levels and chlorolignin compounds.

In the alkaline extraction stage, sodium hydroxide is added to the pulp. This removes resinous materials, pentosans and low molecular weight hydrocarbons and residual reaction products from the C stage.

This is followed by at least one, usually more, oxidative bleaching stages using sodium hypochlorite (H) or chlorine dioxide (D).

The most common kraft bleaching sequences are CEDED and CEHDED.

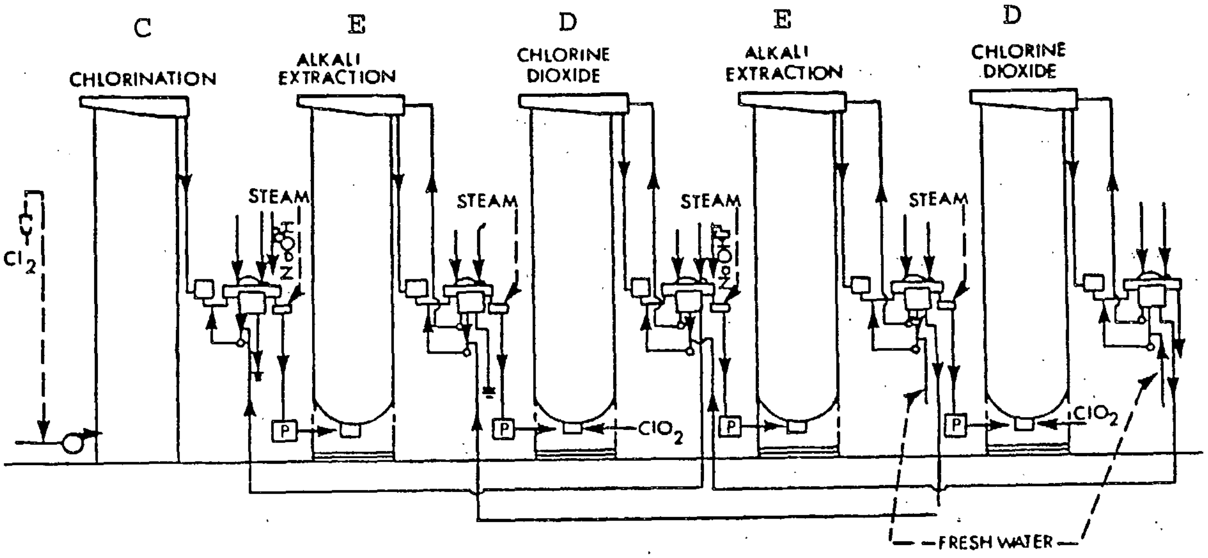

Figure 3.4: Flow diagram of a five stage bleach plant (CEDED)

Source: The Basic Technology of the Pulp and Paper Industry and its Environmental Protection Practices, EPS 6-EP-83-1

The filtrate from the C stage is the most toxic stream in a mill using the kraft bleaching system, followed by unbleached decker filtrate, the chlorination effluent and combined mill outfall.

Process improvements in bleaching include (EPS 6-EP-83-1):

- Chlorine dioxide substitution which is partial substitution of chlorine by chlorine dioxide in the first stage
- Increased use of sodium or calcium hypochlorite

- Oxygen bleaching (oxygen delignification) which consists of treating the pulp with oxygen under pressure. This eliminates the chlorination and caustic extraction stages and has been found to reduce BOD by 50%, COD by 40% and colour by 60%. In Canada, oxygen delignification systems are installed at the Eddy Forest Products mills in Espagola, Ontario and at the Champion International Mill in Hinton, Alberta. Installations of oxygen delignification plants are planned for 1990 at the Diashowa Company mill, Peace River, Alberta and the Canfor mill, Port Mellon, B.C. (Bonsor et al. 1988)

- Papribleach process based on application of ammonia to chemical pulps. It is unknown if this process is being used on a commercial basis.

- Rapson-Reeve closed cycle bleaching. This process was used at the Great lakes Forest Products Co. mill at Thunder Bay but had to be abandoned after several years due to a variety of reasons including corrosion (Bonsor et al, 1988). The system has the following features: 70% substitution of chlorine dioxide for chlorine in the first bleaching stage; countercurrent washing in the bleach plant; minimal external water input to the bleach plant; a salt recovery process to remove sodium chloride from the white liquor; a steam stripper to treat evaporator condensates; spill control provisions.

Environmental Problems Related to Pulp Bleaching

In the kraft pulp bleaching process, 45 to 90 kg organic material is dissolved per tonne of pulp production, most of this (75 to 90%) in the chlorination and extraction stage. (Reeve and Earl, 1989). When elemental chlorine is used, some of the chlorine atoms are covalently bonded to the organic molecules resulting in about 5 kg of chlorinated matter per tonne of pulp produced. Chlorinated dioxins and furans are among the compounds that have been found in bleached pulp products. It is believed chlorinated organic compounds in pulp and paper, and mill effluents have toxic, long term environmental effects, though extensive studies in Sweden have not resulted in a clear cut relationship. However, in 1986, the Swedish National Environmental Protection Board established limits on discharge of chlorinated organics to take effect in 1989 and recommended two methods of attaining the limits: oxygen bleaching combined with aerated lagoon treatment or oxygen bleaching together with high substitution of chlorine dioxide in the chlorination stage.

In Canada, Ontario has recommended a limit of 1.5 kg adsorbable organic halogen (AOX) per tonne of pulp. Quebec plans to limit organochlorine compounds to 1.5 kg/tonne of pulp by 1993. Ten mills in Quebec will be affected.

Although kraft mills are no longer allowed to operate in West Germany, about 850,000 tonnes of bleached sulphite pulp are produced annually (Reeve and Earl, 1989). Mill effluent is regulated and taxed, based on the amount of COD discharged and the effluent toxicity. Plans are also underway to regulate and tax organically bound chlorine.

A number of organizations are conducting research into ways of reducing organochlorine discharges from kraft bleaching processes. One of these is substitution of chlorine by chlorine dioxide in the kraft bleach process. In Sweden, chlorine dioxide is being substituted for chlorine in many mills. In Canada, trials at three mills has shown that increasing chlorine dioxide substitution in the chlorination stage from 10 to 30% to 50% decreases chemical consumption and costs, while maintaining pulp strength and improving bleach plant effluent quality. One of the mills in the trial has now adopted substantial substitution for its softwood production and is evaluating substitution on its hardwood production (Pryke, 1989).

Liebergott (1989) reported that increasing chlorine dioxide substitution to 70% produced less AOX and less chlorinated phenolic compounds in bleach effluent.

At the Aracruz pulp mill in Brazil, Manfredi et al. (1989) conducted laboratory and mill trials using sodium hypochlorite, a by-product of manufacture of chlorine based bleaching chemicals, and found that application of very small charges of sodium hypochlorite in dilute solution allowed savings in chlorine dioxide charges of up to 30% and gave a substantial improvement in effluent colour.

Bonsor et al. (1988) suggest in a report to MISA that in-plant controls and process modifications to minimize formation of toxic substances should be emphasized over secondary treatment for kraft pulp mills in Ontario. The authors believe that adopting a best available technology approach to regulating effluent would require all mills to install secondary treatment that may divert finances from more environmentally and economically beneficial in-plant measures for improving effluent quality. The report recommends that R&D on chlorine-free bleaching should be encouraged.

Idner and Kjellberg (1988) compare oxygen bleaching of sulphite pulp with conventional pulp bleaching in relation to pulp quality, emissions, and costs. Installing an oxygen bleaching stage in a softwood sulfate pulping line decreases emission of COD and total organic chlorines (TOCl) from the bleach plant by about 40% and BOD by 25%. For a birch sulfate line the decrease is about 30%. Production costs can also decrease depending on local conditions. There are also cost benefits in effluent treatment because of lower emissions. The authors report that 18 new oxygen bleaching plants were planned to go into operation in Finland before the end of 1989.

Axegard (1987) found that for an oxygen delignified softwood kraft pulp, formation of adsorbable organically bound halogen (AOX) and total organic chlorine (TOX) is linearly proportional to consumption of elemental chlorine. Below about 10 kg chlorine per tonne of pulp, practically no chlorinated phenols were detected.

In a pilot plant study using spent bleaching effluents from a German sulfite pulp mill, Milstein et al. (1987) used polyimine to precipitate organic matter from the chlorination and extraction stages, separately and mixed, as a water insoluble complex. Colour, COD, and AOX in the C stage were reduced by 92%, 65% and 84% respectively and in the E stage by 76%, 70% and 73% respectively.

Hall et al. (1989) tested wastewaters from several process streams in four kraft mill bleach plants to assess their suitability for anaerobic treatment. Several samples were found to have adequate COD concentration that may be suitable for high rate anaerobic treatment. They suggest that if anaerobic technology can be developed for higher strength chlorination and extraction stage effluents, more than 86% of organochlorine compounds produced in kraft mills could be treated biologically.

The effluent from bleached kraft mills is usually acidic and has to be neutralized to meet pH discharge requirements and to facilitate biological treatment of the effluent. Calcium carbonate ($CaCO_3$) is the most commonly used neutralization chemical. Good process design and proper process control can minimize $CaCO_3$ use. Blackwell et al (1988) describe a system used by Celgar Pulp, Castlegar, B.C., that involved addition of calcium carbonate to bleach plant effluent, followed by mixing with mill sewer flows to obtain the desired pH. They found a final pH of 6 instead of 7 can cut calcium carbonate use and toxicity in half. A full scale system is now in operation.

Paprican has started operating a new pilot bleaching plant to conduct research and development of new bleaching techniques and to demonstrate their feasibility for both chemical and mechanical pulps (Pulp and Paper Canada, 1988a).

DuPont has established a pulp and paper technology laboratory at Deepwater, New Jersey. Areas under investigation include reducing sodium silicate use during bleaching of mechanical pulp and alternatives to chlorine based bleaching agents (Pulp and Paper Canada, 1988b).

Stock Preparation

Following bleaching, the pulp is prepared for papermaking which involves blending pulps, adding chemicals and fillers and mechanical treatment necessary to enable the fibres to form a sheet of paper.

Paper Machines

The stock then goes to the paper machines where it is dewatered, pressed, rolled and dried. The excess water contains BOD, and chemicals fillers, etc. that were added to the stock. These are usually in low concentrations.

Waste Treatment

Primary Treatment

Primary treatment normally removes 80-95% of suspended solids from the effluents and about 10% of the total BOD. Gravity clarifiers, settling basins, and air flotation units are used.

Larger particles settle out quite readily but settling problems occur with fine particles and colloidal materials which contribute considerably to the BOD loading. For these, flocculating or coagulating chemicals can be added. Flocculating chemicals used in the pulp and paper industry include alum, ferric chloride, and polyelectrolytes (Mangravite, 1989). Research is being conducted with synthetic polymers to increase the flocculation efficiency of the process.

Chemical precipitation can cause problems through chemicals remaining in the effluent and/or by forming sludges that may be difficult to treat.

Reductions in volume of wastewaters through increased recycling opens opportunities for research into more efficient clarifiers for use with smaller volumes of water.

The solids removed by settling processes form a sludge that must be dewatered before land disposal or burning in a heating unit. Flocculants and coagulants improve the dewatering process.

Primary treatment includes sludge dewatering on belt presses or vacuum filters, and cone or vee presses.

Secondary Treatment

Secondary treatment is used to remove BOD caused by dissolved organics in the effluent. Biological processes, which are normally used at this stage include aerated lagoons, activated sludge, rotating biological contactors, and trickling filters. In these processes, naturally occurring microorganisms convert dissolved organic materials to environmentally benign materials. The efficiency of biological systems is dependent on the composition of the influent stream, the retention time, the availability of nutrients (carbon, oxygen, nitrogen and phosphorus), and the microorganisms in the treatment system.

Biological treatment systems are more efficient in treating low molecular weight pollutants than high molecular weight materials such as resin acids and chlorinated lignins.

Aerated Lagoons

In aerated lagoons, effluent is treated for 3 to 10 days. Lagoons have a number of advantages over other methods but require a large area of land. Nitrogen and phosphorous have to be added to pulp and paper effluents to improve the nutrient conditions. Oxygen is provided by surface aerators or by pumping air or oxygen into the tanks.

Activated Sludge

Activated sludge processes use very high concentrations of biologically active material and the BOD reduction rates are much more rapid than in the lagoon systems. Activated sludge systems produce large amounts of suspended solids. Most of the sludge is returned to the treatment system - the remainder is dewatered and disposed of.

Mobius (1987, 1989) conducted pilot plant experiments to try to improve COD elimination in activated sludge treatment of pulp and paper wastewater. Experiments were conducted with varying hydraulic retention times and oxygen concentrations on a variety of wastewaters from activated sludge treatment plants in West German paper mills. It was found that aeration cascade reactors gave better COD elimination than completely mixed aeration tank reactors at similar hydraulic retention times, sludge loading, and dissolved oxygen. In aeration cascade reactors a decrease in BOD sludge loading will increase COD elimination. Hydraulic retention times of greater than 6-8 hours had no significant influence on COD elimination and concentration of dissolved oxygen in the aeration tank had no effect on COD elimination in the 1-4 mg/l range.

Pulp and paper companies in Finland have been operating full scale activated sludge treatment plants for a number of years, and report considerable success in reducing BOD and COD. In an activated sludge treatment plant with extended aeration at the Wilh. Schauman Company in Jakobstad, Finland, it has been found that total reduction of BOD is 90-95%, of COD, 50%, and chlorinated phenols in the range 60-75 % depending on the wood used in the pulping process (Skogman and Lammi, 1987).

The Metsa-Serla company operates five activated sludge processes at company operations in Finland (Kettunen, 1987). Experience has shown that in activated sludge processes it is essential to control variations in water composition entering the treatment system and that the systems themselves require continuous control. Dewatering and disposal of biological sludge are some of the main problems that have been encountered and are areas where development work is required. The authors caution that pilot trials must be conducted with water from the mills in which the plants will be installed. Systems are not automatically transferable because of the different effluent characteristics.

In Finland, 13 activated sludge treatment plants were constructed between 1983 and 1987 and more are planned to meet new guidelines for BOD, COD and toxic organic chlorine criteria for effluents. Objectives for BOD reduction in present plants in Finland were between 60 and 85% but most plants operate at efficiencies greater than the objectives (Luonsi et al., 1987).

Disposal of biological sludges resulting from activated sludge treatment plants poses a number of problems as the sludges tend to be difficult to dewater. Biological sludge ranges from 10 to 15% of all sludge handled by the Finnish plants (Saunamaki, 1987). Biosludge can be thickened separately in a centrifuge with several kilos of polymer per tonne of sludge added. It may also be possible to stabilize biosludge prior to dewatering by aerobic or anaerobic procedures. Wet oxidation prior to dewatering has been found to make sludge easier to handle in a belt filter press.

Experimental laboratory scale work on dewatering processes (Kyllonen et al., 1987) on a number of sludges from different mills found that thermal treatment improved the filterability of all the sludges; ultrasound treatment reduced filterability because of decomposition of the sludge particles; and enzymatic treatment gave inconclusive results. Optimum treatment for a specific sludge may be a combination of different treatments depending on the composition of the individual sludges.

Two stage activated sludge processes have been tested on a laboratory scale in Finland by Mehner et al. (1987) who point out that each mill requires a customized process to selectively treat the characteristics of the wastewaters to be treated by each unit. The researchers found that a two stage activated sludge process, with the first stage consisting mainly of bacteria and the second of bacteria and protozoa can tolerate relatively high suspended solids concentrations and that sludge yield was low, perhaps because of biodegradation of settleable matter.

A modified activated sludge process for treating nutrient deficient wastewater consisted of an anoxic/anaerobic unit combined with a small contactor or aerator unit and a conventional activated sludge process. In this system, low effluent phosphorous concentrations result because the phosphorous is kept bound to the biomass.

In the third pilot plant, wastes were pretreated in an anaerobic system prior to aerobic treatment. This procedure reduces the organic loading of the effluents and reduces excess sludge.

Conventional activated sludge treatment processes require a BOD:P ratio of 100:0.6 (Vaananen, 1987). As wastewaters from pulp and paper mills are nutrient deficient, phosphorous usually has to be added with the result that phosphorous in the effluent is increased. If phosphorous is not added there are problems with bulking sludge. Vaananen showed in both pilot and full scale experiments in two kraft mills in Finland that phosphorous concentration can be reduced to 1.2 mg/l (total P) by adding 100 mg/l ferrous sulfate to the aeration basin in activated sludge treatment of kraft pulp mill wastewaters.

Phosphorous in the effluent can be lowered by controlling the level of phosphorous and maintaining it at optimum ratio, i.e., nutrient feed equivalent to nutrient demand. Reliable sensors are needed to enable an optimum ratio to be maintained. Removal of phosphorous can be improved through anaerobic processes (Vaananen, 1987).

Anaerobic Treatment

Anaerobic technology is primarily for treatment of soluble organic materials. In an anaerobic treatment system organic matter is broken down by bacteria in the absence of oxygen resulting in the production of methane (biogas) and carbon dioxide. Anaerobic technology is now common for treating wastewaters in agricultural and food processing industries as well as in municipal sludge treatment. Some pulp and paper wastewaters are also suitable for anaerobic digestion but pose more problems because of the presence of chemicals used in the pulping process that may be toxic to various strains of bacteria. The effluent from pulp and paper mills varies in composition from mill to mill and within the same mill as it is dependent on the type of wood being used in the pulping process and the chemical treatment used to produce various grades of paper.

At a number of mills, especially in Europe, full scale anaerobic treatment facilities are now in operation. At least three full scale units are operating in Canada (Maat, 1989).

The first full scale anaerobic waste water treatment plant in Finland was at the Anjala paper mill of Tampella Ltd., (Lehtomaki, 1987). Installation was combined with other improvements to the mill to reduce and pretreat wastewaters. Called the TAMAN anaerobic process, the treatment plant consists of a two stage anaerobic process which creates better growth conditions for different species of anaerobic bacteria and is more resistant to changes in loading and concentration of toxic compounds. The reactor can treat an average of 11000 m^3 waste water per day. BOD reduction in the region of 80% has been achieved during the startup period.

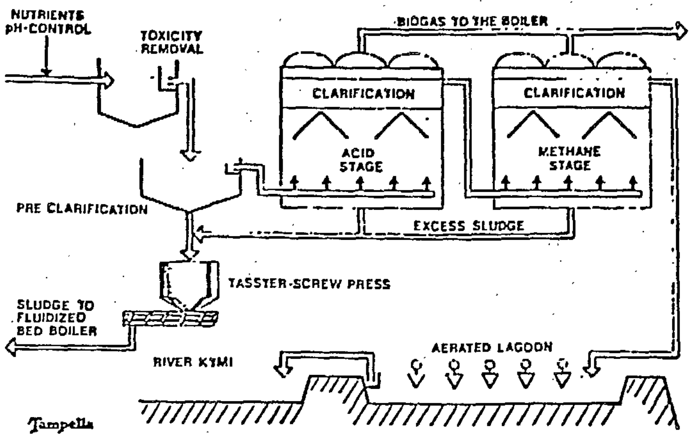

Figure 3:5 TAMAN aerobic process

Source: Lehtomaki, 1987

The potential deleterious effects of solids shocks on the anaerobic reactor have been eliminated by using gravity thickeners to increase solids retention capacity. Combined sludge and biosludge are dewatered by belt and screw presses.

Research into anaerobic treatment for pulp and paper wastewaters is being conducted at Environment Canada's Wastewater Technology Centre. Wastewaters from several pulp and paper mills have been tested to estimate the reduction in levels of BOD and COD that may be attained through anaerobic digestion, and the effects of constituents in the wastewaters that may inhibit anaerobic digestion (Hall et al., 1989, 1988). Chemical and batch biological tests were conducted on 43 waste streams from 21 pulp and paper mills that produce pulp by different processes. Streams sampled included woodroom effluents, bleach plant extracts, spent liquors, evaporator condensates, and combined effluents. Filterable COD concentrations ranged from 140 mg/l in combined kraft effluent to 115,000 mg/l in a sulphite digester liquor. The suggested optimum concentration range for anaerobic treatment is from 1000 to 30,000 mg\l of filterable COD. Anaerobic inhibition characteristics for the samples were also measured, i.e., factors that have an inhibitory effect on microorganisms, using as reference effluent from the Sturgeon Falls mill, where a demonstration anaerobic unit was being tested. The effluent from the Sturgeon Falls mill exhibits a moderate degree of inhibition although the demonstration scale unit shows that the level of inhibition can be tolerated in a continuous flow process. This implies that processes similar to that at Sturgeon Falls could be used on effluents with greater inhibitory characteristics.

Forty-nine percent of the wastewaters contained adequate concentrations of filterable-COD and showed relatively low levels of inhibition. These will be studied further for possible anaerobic treatment. Wastewaters from thermochemical and non-sulfur pulping showed low levels of anaerobic inhibition whereas bleach plant effluents had the highest levels. The highest filterable COD removal efficiencies were obtained with recovery plant effluents and the lowest with bleach plant effluent. The researchers list the types of wastewaters found to be most suitable for anaerobic treatment.

As a result of the investigations pilot and demonstration scale units have been installed at five Canadian pulp and paper mills.

The reactor selected for the Sturgeon Falls mill was the Upflow Anaerobic Sludge Blanket (UASB) which was developed at the University for Agriculture at Wageningen, the Netherlands (Hack and Habets, 1987). The UASB reactor is loaded with a layer of granulated or flocculant anaerobic sludge. The wastewater percolates up through the sludge layer and bacteria digest the organic material present in the sludge, generating methane and CO_2 in the process. A small part of the organic matter is used for new cell growth that takes place in the form of granules with good settling ability. Biogas is removed by three-phase separators at the top of the reactor. A gas free zone above the collectors allows for settling of the finely dispersed solids. Clarified effluent exits from the top of the reactor. Granular sludge can be used to seed other reactors. In the Netherlands the UASB reactor has been used to treat paper mill effluent since 1984. Plants achieve about 70% COD and 80% BOD removal. Biogas can be used as fuel in the mill.

At the Sturgeon Falls demonstration plant, after eight months of operation under normal mill conditions, the following conclusions could be drawn (Prong et al., 1987):

- steady state operation at volumetric loading rates greater than 20 kg/COD/cubic metre/day could not be maintained
- at loading rates up to 19 kg COD/m^3-day, the plant consistently obtained 85% or better BOD removal
- biogas production rate followed closely the volumetric loading rate indicating a healthy and acclimatized biomass
- when the reactor is operating well and the biomass is not overloaded, there is net granular sludge growth.

Plans were to install a full-scale four reactor BIOPAQ-UASB package plant at Sturgeon Fall.

Consolidated Bathurst set up an anaerobic pilot plant test at their chemithermomechanical (CTMP) pulp mill at Bathurst New Brunswick, in 1986 (Schneider et al., 1988). The three systems tested were a contact reactor, a two stage fluidized bed process, and an upflow anaerobic sludge blanket reactor. Data for BOD and COD removal during the startup period are given. The pilot tests were run for nine months (Wilson et al., 1988). The company planned to conduct tests to determine how the systems responded to various types of upset conditions.

At the Lake Utopia Paper Limited neutral sulfite semichemical mill, St. George, New Brunswick, a full scale anaerobic treatment plant is being constructed after results of pilot plant studies showed that a system was feasible for the wastewaters from the plant (Ferguson et al., 1988).

The effect of temperature on laboratory scale anaerobic digestion of pulp and paper sludge from a CTMP mill has been examined by Puhakka et al. (1987) who found that the digestion process for volatile suspended solids was superior at mesophilic (30-38 C) temperature ranges than at thermophilic (50-60 C) ranges. The supernatent COD solids from the mesophilic process was 30-50% less than for the thermophilic process.

Microorganism growth in an aerobic system depends on a variety of factors including pH, temperature, residence time, nutrient composition, and redox potential. Biomass loss can be reduced through biomass retention and recycling together with removal of solids. Various studies have looked at methods of increasing residence time of the contact between wastes and microbes. In one of these, Ajvasidis and Wandrey (1987) looked at methods of immobilizing microorganisms on surfaces so that they will be retained in the reactor. Colonization velocity depends on porosity and pore diameter of the medium used in the reactor. A fixed bed loop reactor with sintered glass was used to treat sulphite evaporator condensate in laboratory scale experiments. High molecular weight chlorolignins were precipitated by chemical means and the supernatant was treated anaerobically. At a residence time of 11h, 84% of the COD was eliminated at loading rates up to 100 kg cod/m3 per day. Reticulated sintered glass produced even better results. Further experiments are underway to scale up the process.

The U.S. Environmental Protection Agency funded pilot anaerobic studies with a fluidized bed reactor system (Anitron system) have been conducted on pulp and paper wastewaters. In the reactor a fixed film of microbial growth occurs on the media (usually sand) which are hydraulically supported as a fluidized bed by the incoming wastewater and recycled effluent (Sutton and Bezler, 1988). The wastewaters had high volumetric loadings of 24, 35 and 102 kg COD/m^3-day. Over the test period, COD reductions of 92, 86 and 60% respectively and BOD reductions of 93%, 83%, and 67% were achieved.

Anaerobic treatment studies of sulfur containing effluents from CTMP mills have been conducted in France on fixed bed reactors with upflow and downflow feed modes (Pichon et al., 1987). The effluent contains sulfur compounds which are toxic to methanogenic bacteria. It was found that it is necessary to acclimatize bacteria with increasing concentrations of sulfur compounds. The reactor functions with a COD:S ratio of about 10:12. Upflow reactors were found to be more efficient than downflow with a maximum loading rate of 3.5 kg COD/m3-day corresponding to a sulfur content of 800 mg/l. Efficiency can be increased with a hybrid sludge-bed/fixed-bed reactor.

Research on combined anaerobic/aerobic treatment of TMP/CTMP effluents is being conducted by Branion and Lo. The project will focus on the ability of various process operations to remove toxicity and BOD and will attempt to optimize a treatment process. (Pulp and Paper Canada, 1989c)

Qui et al. (1987) describe a two stage pilot scale anaerobic/aerobic process to treat kraft pulping wastes from the evaporator and caustic extraction stage bleaching effluents. They found that a large percentage of the BOD in the combined wastes could be removed in the anaerobic stage at loadings of up to 15 kg COD/m^3-d. The effluent, after treatment, had less than 30 mg/l BOD and suspended solids, and varying amounts of COD depending on the CE fraction being treated. A third of the sulfur in the influent water was removed as hydrogen sulfide gas in the anaerobic stage. Most of the remaining sulfur was oxidized to sulfate in the aerobic stage. The aerobic stage polished the effluent and reduced the BOD and odour to generally acceptable levels. In the latter stage of the study, the UASB reactor performance declined, perhaps because of metal toxicity.

Ghosh and Taylor (1988) conducted research on a novel anaerobic digestion technique using kraft pulp and paper mill effluents. The process provided for detoxification, hydrolysis and neutralization in a first stage reactor and optimization of coupled acetogenic-methanogenic fermentation an a second stage reactor. The first stage reactor is an upflow with gentle mechanical mixing. Detoxification is accomplished by recirculating scrubbed gases to removed sulfides and other volatiles. The second stage is a hybrid upflow reactor providing for enhanced biological solids retention and separate gas collection.

Brewer (1988), in a review of the status of anaerobic technology R&D, notes that specific research requirements in the pulp and paper sector include extending the range of digestible materials to include lignin and/or its degradation products; the need for improved chemical characterization of pulp and paper wastewaters and anaerobically treated effluents; development of design parameters to reduce toxicity due to chlorinated organics, resin acids and ammonium and sulfite; and cost comparisons between combined anaerobic-aerobic systems and aerobic systems alone.

Tertiary Treatment

Tertiary treatment, where used, further reduces suspended solids and BOD, and can be used to improve colour, odour, and taste and remove toxic contaminants.

Processes used in tertiary treatment are:

- activated carbon absorption
- massive lime treatment
- foam separation

Elimination of colour from bleach plant effluents can be accomplished by various processes including coagulation, membrane technologies, adsorption, ion exchange, photochemical processes and oxidation. Research into methods of eliminating the colour in bleach plant effluents indicated that hydrogen peroxide and ultraviolet radiation is not an economically competitive process (Prat et al., 1988).

Recycled Paper

Recycled paper pulp has to be purified in a deinking unit before further processing. Krofta et al. (1989) describe a total closed water system for water reclamation in deinking installations. The authors found that dispersed air flotation is the most effective method for separating ink from fiber and clay, with very small water and material loss. A totally closed system has zero wastewater discharge, and fibers, clays, chemicals, and water are recovered.

Complete Treatment Systems

Welander (1987) describes a multistage process consisting of primary settling and four biological stages for treatment of CTMP effluent. In the first biological stage the concentration of hydrogen peroxide from the bleaching stage of the CTMP is reduced by biocatalytic action. In the second, acidogenic stage, volatile fatty acids are formed and the remaining peroxide is decomposed. Al, Fe, and Ca salts are added to the effluent to detoxify compounds before the third, methanogenic anaerobic stage. The COD and BOD removal in the anaerobic stage are 60% and 90% respectively. The 4th, aerobic stage polishes the effluent and removes odour.

Riocell SA's mill in Rio Grande do Sol in Brazil has one of the most complete effluent systems in the world (Foelkel 1989). In response to concerns about environmental pollution from the mill, construction on the pollution control system started in 1980. Effluents from various areas, except the bleaching plant, are taken to the treatment plant by gravity feed. The effluent passes through a screening and grit removal system and then into a neutralization tank, into which bleaching effluents also feed. Neutralized effluents are fed into primary clarifiers for removal of suspended solids. Effluent is then homogenized in a lagoon with surface aerators, treated in a Unox activated sludge system, and then into a secondary clarifier. The biologically treated effluent from the activated sludge system has colour removed by flocculation with aluminum sulfate, followed by sedimentation. The effluent is then neutralized with lime, and put into a polishing lagoon before discharge into the river through diffusers. The sludges from the primary, secondary and tertiary treatment systems is thickened, dewatered in belt pressure filters. Research is being done on converting sludge and other solid residues to organic fertilizer. The treatment system removes 98 to 99% BOD, 91% COD, 97 % suspended solids and 90% colour.

Sludges

Options for sludge disposal include incineration (after dewatering where necessary, landfilling after treatment to remove to potentially harmful constituents, or agricultural uses. Pridham and Cline (1988) conducted research to find agricultural uses for pulp and paper mill sludge by determining the effect of various sludges and combinations of sludges on plant growth. In greenhouse experiments they found no toxic effects from the sludge on tomatoes, peppers and corn. Field tests show that paper mill sludge can be used as a soil conditioner and feltilizer.

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CHAPTER FOUR

METALLURGICAL SECTOR

In the metallurgical sector, 12 companies have been identified as being among the largest industrial polluters on the St. Lawrence River. They have been classed as follows:

Aluminum	6 companies
Copper and zinc	2 companies
Carbon-based metal	1 company
Iron and steel	3 companies

One mining company can also be included in this category.

The major activities of the companies are mining ores, extraction of metals from ores, and refining and processing the metals.

The pollutants depend on the types of ores used, the by-products from the metals extraction processes, the extraction and refining methods used, and the extent of metals processing done at the plant.

A review paper prepared for the Centre Saint-Laurent symposium, (June 1989), identified various environmental problems associated with metallurgical industries on the St. Lawrence.

Pollutants from an iron and titanium refinery are suspended solids as metal oxides and ore tailings. The metal oxides create problems of zinc leaching at pH 4.5. Effluents are not segregated. Effluents from the manufacture of ferroalloys from ferrous ores in an arc furnace in the presence of coke contain metal fines, metal oxides and trace amounts of other contaminants. Residues are buried at designated sites.

Steel is produced from iron ore or scrap iron. The metal is melted in arc furnaces and routed to hot rolling mills. Surface treatment is sometimes used. Pollutants include oils and greases containing a variety of pollutants; effluents containing large quantities of heavy metals in particulate form (mill scale). If surface or pickling processes are used, the liquors, soaps, detergents and sludges contain heavy metals at weak and acidic pH. Waters within the mills are not segregated so effluent contains a variety of pollutants from different parts of the processes. Other pollutants include sulfur dioxide, carbon monoxide and fluoride particles.

In the Metal Mining Liquid Effluent Regulations and Guidelines a mine is defined as "all metal mining and milling facilities and associated smelters, pelletizing plants, sinter plants, refineries, acid plants and any similar operations where the effluent from such operations is combined with the effluents from mining and milling" (EPS 1-WP-77-1, 1977). The regulations limit the concentrations of arsenic, copper, lead, nickel, zinc, total suspended matter and radium-226.

The regulations apply to the effluents from companies that combine their refinery effluents with mining and milling effluents.

Non-Ferrous Metals

ALUMINUM

The major source of aluminum is bauxite, an ore that contains hydrated aluminum oxides as well as silicon dioxide and iron oxide. Bauxite is imported into Canada, mainly from Brazil and Guyana, for metal extraction and refining here. As aluminum is extracted by electrolytic processes, one of the reasons Canada is a major producer of refined aluminum is the availability of relatively cheap hydro electricity.

Process Technology

The first step in the aluminum smelting process is to extract aluminum oxide, also called alumina, from the crushed ore, in what is known as the Bayer process. This is done by digesting the ore in a solution of sodium hydroxide at temperatures between 150 and 250 C. The iron and silicon oxides do not react and remain as a red insoluble sludge known as red mud, which also contains an insoluble alumino-silicate. If the alumina content is high enough, alumina may be recovered from the mud (Gilchrist 1989). The alumina is precipitated from the hydroxide solution and dried, or calcined, by heating to over 1000 C. Calcinationis the thermal treatment of the ore to decompose it and eliminate volatile products. This pre-refinement stage may be done before shipment, but the energy required for evaporation is a major cost.

Aluminum metal is extracted from the aluminum oxide in heated electric cells or pots by the Hall-Heroult process. The aluminum oxide is first dissolved in cryolite, Na_3AlF_6 at a temperature of about 1000 C in the pot, carbon rods are lowered into the pot and electric current is passed through the molten solution from the carbon lining of the pot to the carbon rod. In the process, the carbon rods decompose to form carbon dioxide. The molten aluminum is denser than the aluminum-cryolite solution and sinks to the bottom of the pot. Liquid aluminum is siphoned off into crucibles where it is kept in a molten state until it is ready to be used for fabrication into sheet metal or piping, or it is poured into molds to form ingots and allowed to cool and solidify. Toxic fumes and dust usually pass through a scrubber unit.

The basic aluminum smelting process has changed little in the past 100 years though improvements have been made to decrease power requirements and fluoride emissions (Peacey, 1989). The Bayer/Hall-Heroult process has a high energy consumption and the fluorine emissions cause problems in the electrolytic stage. A process that requires considerably less energy is the Alcoa process in which chlorine is added to alumina to form aluminum chloride, which is then decomposed electrolytically to form aluminum and chlorine. Difficulties with the Alcoa process include producing aluminum chloride of required purity while conforming to environmental standards (Grjotheim and Welch, 1989b). Cochran (1987) in a review of alternative technologies for producing alumina concludes that none of the technologies is economically feasible yet.

Welch (1988) and Grjotheim and Welch (1989a, 1989b) discuss recent technological developments in aluminum processing technology, which are mainly improvements to the Hall-Heroult process, such as improved cell design, changes in electrode materials, cathode design, and improved process controls. Johnson (1988) discusses mathematical modeling techniques used in the design of larger and more efficient cells. Saavedra et al. (1989) also believe that some of the major advances in aluminum technology in the next decade will be improvements to the Hall-Heroult process. They also discuss their research into a carbothermic process to reduce alumina as an alternative to the Hall-Heroult process. In the carbothermic process, coke is used as the reductant to produce either alloys or pure aluminum, depending on the processing routes. The results of pilot scale tests, and furnace designs are discussed. The authors believe that commercial scale carbothermic production will not occur before 2010.

Aluminum Wastes

The major pollution problems associated with production of aluminum are the large quantities of carbon dioxide gas, hydrogen fluoride gas (from reaction of cryolite with water), and red mud from the Bayer process which contains approximately 50% iron, titanium, silicon, non-extractable aluminum oxides and other minor constituents. The red mud is also very basic because it contains sodium hydroxide.

At some aluminum processing plants this mud has been pumped untreated into a receiving water body. At other plants, mud is pumped into red mud ponds where the solids settle out and the aqueous layer, which contains sodium hydroxide, is removed for recycling or is neutralized before being discharged.

The alkaline sludge, which contains metal contaminants, is dried and used as landfill.

Gilchrist (1989) states that the mud may be worked to recover alumina in it, if the aluminum value is high enough. The composition of the mud depends on the composition of the ore, and the efficiency of the aluminum extraction process. In many instances recovery of metals from the mud is not yet economically feasible.

Ho (1988) discusses research into methods of treating red mud. He found that addition of gypsum and copperas (a ferrous sulfate waste from the manufacture of titanium dioxide from ilmenite using the sulfate process, or from iron/steel pickling) overcame the salinity and sodicity of the red mud to enable it to be rehabilitated or reused to improve the water retention capacity of sandy soils that have good drainage and sufficient ground water dilution.

Kimmerle (1989) discusses some opportunities for waste reduction or recycling of aluminum process effluents at the Alcan Vaudreville plant. One of these is a thickened tailings disposal system for red mud using synthetic flocculants and an improved mud washing circuit. The thickened tailings do not segregate into sand, slime and water as in a conventional system but contain enough solids (>50%) to support a 2-10 degree slope in a dry mud stacking area. When the dried mud stack is deemed to be high enough, the land can be rehabilitated by use of fertilizer, top soil and vegetation.

Alcan is also looking at ways of recycling the fluoro-gypsum from its fluoride plant at Jonquiere and at new cathode materials to extend pot life and to eliminate generation of cyanides. The company used to operate a cryolite recovery plant but experienced operating problems.

A process for treating spent potlining by hydrolyzing the cyanides and encapsulating the carbon particles with gypsum to minimize leaching of water soluble fluorides has also been developed. Dross residues from the scum that forms when aluminum metal, alloys or scrap are melted contain a high percentage of aluminum. The company is planning to open a dross recycling facility in the U.S. mid-west to separate the metallic fraction from the non-metallic fraction and to upgrade it into useful products.

The acidic hydrogen fluoride gas can be removed by passing the waste gases through powdered aluminum oxide where it is converted to solid aluminum fluoride and can be recycled to the electrolysis process.

Ball and Bonner (1988) describe an aluminum die casting wastewater system that was installed at a facility in Alabama to comply with EPA discharge limits for the industry. The major sources of contaminated wastewaters are the die casting and cleaning operations. These contain copper, lead, zinc, phenols, toxic organics, and oil and grease. The treatment processes selected for the facility were oil water separation followed by chemical precipitation and activated carbon. The authors discuss the process of determining the chemicals, mixing energy, chemical doses, and chemical addition point to sustain treatment that would meet effluent requirements.

COPPER

Copper occurs naturally in ores as copper sulfide. Copper can also be recycled from scrap. Canada is among the major producers of copper.

Process Technology

Copper can be extracted and refined by a number of processes, the most common of which are pyrometallurgical procedures. About 80% of copper is extracted from sulfide concentrates by matte smelting. In this process, the ore is partially oxidized by roasting which removes some of the sulfur. It then goes to a matte smelter in which most of the copper and some of the iron goes to the matte (solution of metallic sulfides) which forms a bottom layer, while the rest of the iron as iron oxides goes to the slag (top) layer, which is discarded (Gilchrist 1989). The molten matte, which contains between 20 and 60% copper as sulfide with the remainder as iron sulfides is "blown" (oxidized). In this process, the iron sulfide is converted to the oxide and sulfur dioxide and iron oxide are slagged off until the vessel contains only cuprous sulfide. This is then blown to oxidize the sulfur and produce "blister copper" which is about 98-99.5% copper. The copper is then refined by electrolytic processes and cast into ingots.

In the electrorefining process, the impure copper is cast into anodes which are electrolyzed in a copper sulfate-sulfuric acid electrolyte to yield high purity cathode copper. During the electrolysis some of the impurities, including lead, selenium, silver and gold form an anode slime which stays on the anode or in the bottom of the electrorefining tank (Chen and Dutrizac, 1987). The anode slimes are treated to recover the metals.

The efficiency of extraction processes is dependent to some extent on the properties of the ores. Peacey (1989) outlines process developments over the past 20 years. Process improvements for conventional copper extraction methods are aimed at increasing the yield of metal from the ore and modernizing and improving tankhouse operations. Other major developments have been to improve matte grades (i.e., higher quality extract from the ore), to reduce energy requirements, and to control SO_2 emissions.

The basic electrorefining process has changed little over the years though improvements have been made to reduce impurities in the copper, and to increase recoveries and reduce processing costs.

Cooper (1989) outlines some of the technologies considered for retrofitting a copper smelter in Australia which had few technological changes since the 1960s. The technologies selected included proven smelting and anode furnace processes, pyrometallurgical slag cleaning and modifications to existing equipment.

Research is being conducted on plasma technology for metals extraction from ores. The VOEST-ALPINE company in Austria uses plasma technology for steelmaking and has a pilot plant for experimental work to extend the range of plasma technology (Muller et al., 1989). They have demonstrated extraction of copper from silicate copper ores using a plasma process. The copper extracted by this method had insignificant amounts of contaminants and copper yield was improved.

Roman-Moguel et al. (1988) describe an experimental process for refining copper scrap by gas injection to improve deoxidation conditions in a fire refining copper scrap plant. Dry air and hydrocarbon were used in the tests at scales of 16kg, 400kg, and 16 tonnes using two types of injections systems and either porous plugs or stainless steel tuyeres.

Copper Wastes

The major pollutants from copper smelting and refining are sulfur dioxide and the waste slags which contain a variety of metals that can leach out into water systems. Other pollutants include oils and greases, depending on the extent of processing of copper at the plant.

The sulfur dioxide can be converted to sulfuric acid in a sulfuric acid plant, which is a feature of many copper smelting operations.

Blowdown from conditioning towers which remove dust from the metallurgical operations off gas contains dilute sulfuric acid waste. Sulfuric acid is also obtained from the process that removes particulate materials from sulfur dioxide gas streams. Spent sulfuric acid from electrolyte solutions and sludges from copper recovery from electrolytic solutions are also sources of acid wastes (Wilk et al, 1988). The waste also contains copper, lead, iron, zinc, antimony, arsenic, bismuth and other metals.

Where the metals concentrations are high enough, or the metal is valuable enough, recovery would appear to be the best treatment technology. Hyvarinen et al (1989) describe a process for recovering selenium from copper refinery slimes by roasting at about 600 C in a sulfating atmosphere. A full scale production unit is in operation at the Outokumpu copper refinery in Pori, Finland. A precious metals recovery plant at the ER&S Company copper smelter at Port Kembla, Australia is used to recover gold, silver, palladium and platinum (Cooper, 1989).

ZINC

More than 50% of zinc is produced from mixed lead-zinc ores. Others are zinc-copper ores, and zinc with some cadmium. Various other metals are also present in zinc ores.

Process Technology

The zinc is separated from the lead and copper by comminution (fragmentation) followed by flotation. The ore is then roasted and calcined. The most common method of extracting zinc is leaching the calcine with sulfuric acid to dissolve the zinc, precipitating metal contaminants, acidification of the solution, and electrolysis between lead/silver anodes and aluminum cathodes (Gilchrist, 1989).

Another method of zinc extraction is reducing the zinc oxide calcine in retorts with carbon, vaporizing the zinc by heating to 1000 to 1200 C, and condensing the vapour to liquid zinc-zinc oxide (Gilchrist, 1989)

A third method is a zinc blast furnace, in which a hot sintered concentrate of zinc-lead ore and coke are heated at 800 C. Hot air is blown in, the lead is reduced and is collected in the hearth. Most of the zinc is reduced from the unfluxed sinter to zinc vapour which condenses. The zinc produced contains about 1.2% lead (Gilchrist, 1989).

Goto et al. (1989) discuss experiences with a pilot scale plant for injection smelting of zinc calcine and the feasibility of operating a 100,000 ton/year zinc injection smelting plant.

Main zinc extraction technology improvements have been to increase the amount of zinc extracted from the ores and increased mechanization of the tank houses. Attempts have also been made to reduce energy requirements (Peacey 1989). Kaneko et al (1989) describe a new cell design to reduce energy requirements in zinc electrowinning.

Taylor and Zunkel (1988) note that the primary zinc industry is in a better technological position than some of the other nonferrous metals industries as it has adopted new technology based on the roast-leach electrowinning process. Pressure leaching has enabled expansion of production without increasing roaster capacity.

Zinc Wastes

Pusateri et al (1988) note that more than three million metric tons of iron residues from zinc processing operations are impounded every year in lined or unlined storage areas. They believe that these will soon be classed as hazardous wastes sites by the EPA in the United States. They describe a flame reactor process for treating residues or for smelting zinc directly. The flame reactor has been proven to be viable for electric arc furnace dust from steelmaking for recovering recyclable zinc, lead and cadmium and producing a non-hazardous slag. Similar products can be produced from electrolytic zinc plant neutral leach and iron precipitation residues. The flame reactor can also be used as a low energy primary zinc smelter.

The residues from leaching zinc calcine contain lead, silver, and gold, and cadmium, copper and zinc combined as insoluble ferrites. Various processes which have been developed to extract lead, zinc, cadmium and precious metals from the residues and increase zinc recoveries and convert the residues into non-hazardous forms are compared by Taylor and Zunkel (1989).

Cadmium can be removed from zinc by fractional distillation and arsenic content can be reduced by treating with metallic sodium (Gilchrist, 1989).

Shabalina et al. (1989) are conducting research on the use of plasma technology for cleaning copper-zinc and converted copper-nickel slags. They report recoveries of copper and zinc of 65% and 83% respectively. Experimental work indicates that plasma technology is competitive compared with other prospective methods of slag cleaning.

TITANIUM

Quebec has the world's second largest deposits of ilmenite, an ore that contains titanium and iron.

Process Technology

In an iron and titanium refinery, iron and titanium are obtained from ilmenite ore that is first enriched and the ore tailings removed. The enriched ore is reduced in arc furnaces to remove oxygen and increase the titanium content. Pig iron and titanium slag are separated in the arc furnaces by densification. The slag contains about 60% titanium dioxide. The molten iron is sent to a steel mill. Ten percent of the titanium slag (Sorelslag) is processed by a sulfate process in titanium pigment manufacturing plants and the rest is exported.

In the extraction process, sulfuric acid is used to dissolve the titanium dioxide to form soluble titanyl sulfate $TiOSO_4$. Solid impurities are removed by filtration and and hot water is added to precipitate titanium dioxide hydrate which is dried to give titanium dioxide.

Titanium Wastes

The solution that remains after the titanium dioxide has been precipitated is extremely acidic and contains a high concentration of iron sulfate.

Trioxide Canada Ltd. has experimented with a process to produce gypsum (calcium sulfate) from the acidic wastes by adding lime. However, gypsum is mined in Canada and the extraction process produces much more expensive gypsum.

Ferrous Metals

IRON AND STEEL

Process technology

Iron is extracted from iron ore, which is impure iron (III) oxide, by heating the ore with coke and limestone (calcium carbonate) in a blast furnace. The major impurity is silicon dioxide. Coke is obtained from coal by heating the coal in air-tight ovens to a temperature of around 1200 C. Air, heated to 540 C is fed into the bottom of the furnace, the coke is ignited and burns to produce carbon monoxide which reacts with the iron oxide to produce carbon dioxide and liquid iron. The calcium carbonate decomposes to calcium oxide and carbon dioxide. The calcium oxide reacts with the silicon dioxide to produce liquid calcium silicate which is less dense than the liquid iron and rises to the top of the molten mixture where it can be tapped off and cooled to form slag.

The iron produced in the blast furnace has a purity of 90-95%. The molten iron, tapped from the bottom of the blast furnace is transferred to an oxygen furnace where, in the presence of oxygen and calcium oxide the impurities are converted to calcium salts and on cooling are added to the slag. The nearly pure iron contains traces of carbon and is called steel. Various additives can change the properties of the steel. For example, chromium is added to produce stainless steel.

The slags contain sand, iron, lime, soda ash plus various trace metals.

Foundry production processes involve charging selected raw materials and/or scrap metals into a melting furnace (cupola) or an electric arc furnace and heating the material in the presence of limestone flux until the metal is molten. Molten metal is then ladeled into molds into rough castings, which are processed by removing excess metal and cleaned to remove surface sands from the molds.

Process Technologies

Teoh (1989a and 1989b) discusses some recent developments in electric arc furnace (EAF) technology. Development in the 1960s and 1970s was spurred by the need to reduce energy consumption and increase tonnage in carbon steel. Developments in the 1980s that will continue into the 1990s are directed at improving quality, process optimization, and to achieve stringent environmental requirements at the lowest costs.

In older EAF technology, all the processes are performed in the same furnace. Newer technology splits the processes into three steps, preheating scrap in a separate vessel, scrap melting, and refining molten metal in an array of secondary or ladle refining processes. Teoh outlines recent developments in plant and process technology and discussed developmental work being done on DC arc furnaces, plasma furnaces, induction melting, bottom fuel injection systems, non-arc energy optimizing furnaces and scrap melters. (Teoh 1989a, 1989b; Steel Times International, 1989).

Kor (1989) discusses the "AISI Steel Initiative", a joint university-steel industry project to investigate new steel making processes. The results of an initial study conducted for the American Iron and Steel Institute (AISI) suggested that an in-bath smelting process in which iron ore is smelted to liquid metal while coal and oxygen are injected simulataneously was the most promising technology for the U.S. Features that make the process attractive and worthy of pilot plant studies include a relatively high production rate, 25% reduction in coal consumption, the possibility of producing steel directly and the flexibility to melt scrap. The pilot plant proposal has been endorsed by the AISI.

Plasma technology is also being used in the steel industry. Muller et al. (1989) list some of the advantages as lower operating costs and increased metals recovery which have been experienced at the VOEST-Alpine plasma steelmaking furnace in Austria. A plasma-arc furnace in Australia has recently started production of ferro-alloys from ore and metal fines (Kershaw et al., 1989). The furnace design is based on data from the Davy McKee plasma pilot plant in England. Metals recovery rates and power requirements under full scale operating conditions are not reported.

Hughes (1989) describes his concept for an integrated steel plant on a greenfield site for the year 2000 and notes that it is based on technology that is at least at the laboratory stage in 1988 as it takes a long time for technology to move from the laboratory through demonstration scale to full size. The steel plant he envisages will incorporate the Corex process for iron making. This splits conventional blast furnace reduction and smelting steps into two separate stages in different vessels and can use coal rather than coke. Hughes feels that a blast oxygen furnace steelmaking unit would be the main steel making process, despite the AISI initiative or other developments. Different casting processes are discussed as well as the incorporation of artificial intelligence and robotics in plant operations.

A new integrated steel plant at the Kwangyang work of the Pohang Iron and Steel Co. Ltd., in Korea that incorporates present-day state-of-the art technology is described by McAloon (1988). Pulverized coal injection is used in the blast furnaces, hot metal is desiliconized, combined blowing is used in the steel converters, and steel is continually cast and the slabs are hot charged in the rolling mill's reheat furnace. The plant is computer controlled.

At NKK's Fukuyama steel works in Japan, the blast furnace operation is controlled by artificial intelligence, consisting of a diagnostic expert system and a furnace heat control expert system (Sakurai et al., 1989). The system contributes to stable blast furnace operation and production of higher quality metal.

Before iron, manganese and lime can be recycled from steelmaking slags, phosphorous must first be removed as phosphorous adversely affects the mechanical properties of the steel. Fujita and Iwasaki (1989) discuss phosphorous removal by magnetic separation/flotation.

Etzel et al. (1989) discuss controlling carbide levels in desulfurization of grey iron slag so that the slag will not be hazardous. The method involves driving the reaction of the slag with calcium carbide to completion so that there is no residual carbide and hence no acetylene generation.

Iron and Steel Wastes

Petura and Schoenberger (1988) identify the major sources and types of hazardous wastes from iron and steel production as blast furnace operations, tin and chrome line wastes, spent pickle liquors and coke plant wastes. They discuss the concept of and problems in handling cross-media wastes where the primary waste stream may impact more than one medium. For example, off gases that pass through a scrubber unit may still contain constituents that are potentially harmful; scrubber waste solution contains particulate matter that will settle out to form a sludge, which after treatment may still contain contaminants. Transfer of a contaminant from a gas to a liquid medium does not provide a final solution to the problem of hazardous components in the gas. Regulations tend to apply to hazardous component of a gaseous, solid or liquid medium and not to the transfer of the constituent from one medium to another. The authors suggest that a new regulatory approach may be necessary for management of cross-media contamination.

Pollutants from electric arc furnace processes include dry dust wastes from grinding and shakeout operations; wastewater from the wet scrubbing process that removes particulate matter from the gaseous emission from cupola furnaces. The concentrated water results in a sludge that may be alkaline and which contains iron plus traces of cadmium, copper, chromium, nickel, lead, zinc and chemical additives. Sludges are also a by-product of slag quenching operations that are cooled by water.

Electric arc furnace waste has been classified as hazardous by the EPA. Avent and Morriss (1987) discuss some of the issues and alternatives for treating or reclaiming EAF wastes.

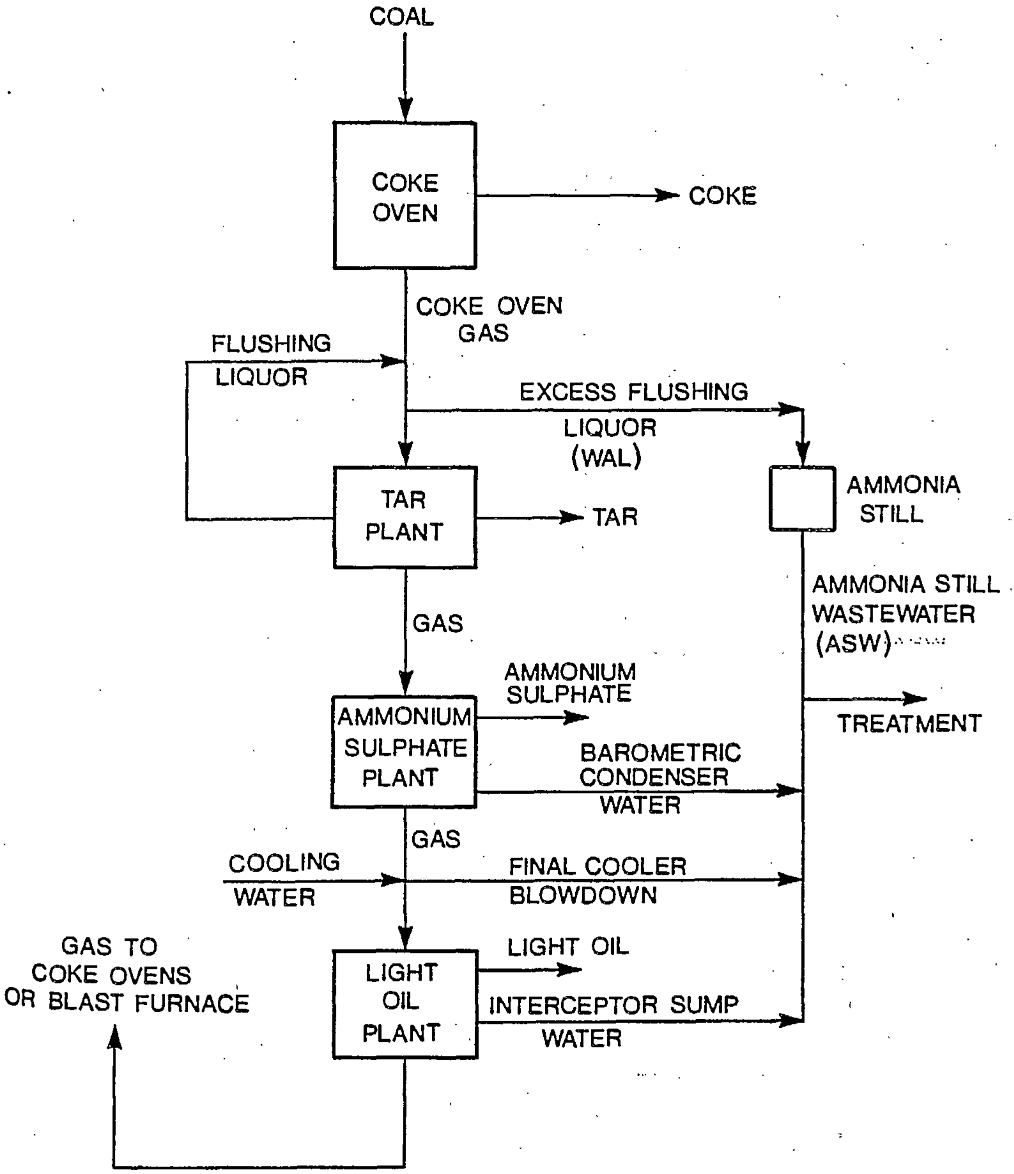

Figure 4.1: Major wastewater sources in by-product coking operations

Source: EPS Report 3/MM/1, 1984, p. 9

A number of by-products can be obtained from the off gases from the coking process. These include tars, light oils, phenol, ammonium compounds and naphthalene. The by-product coking process was (1984) used exclusively in Canada by the steel industry (EPS Report 3/MM/1, 1984). More than 40 toxic contaminants have been identified in by-product coke plant wastewaters (see Figure 4:1).

A number of tar-based coke plant wastes have been classified as either toxic or hazardous by the EPA. One of these is tar decanter sludge. Deer et al. (1987) discuss a number of ways of recycling tar decanter sludge and other tar-based wastes after processing by a process developed by AKJ industies in the U.S. The so-called AKJ process consists of adding a diluent to the sludge in a primary processing tank with a chopper grinding pump to reduce the size of particulate matter and mix the solution to bring it to a specified viscosity. The product can then be transferred to another tank to reduce particulate size further. The product can then be used as fuel or blended with other fuels.

Water Conservation

The iron and steel industry is one of the largest users of fresh water - it takes on average 40,000 gallons of water to produce one ton of steel with almost 50% of this used for cooling and 25% in processing. Water is used to scrub the gases from the furnaces and to cool the coke.

The blast furnace process produces most water pollution. Pollutants in wastewaters from iron and steel mills include suspended solids, pH, oil and grease, fluoride, iron, chromium, cyanide, phenols, and various heavy metals and toxic organics.

Changes in process technology to reduce water pollution include moving from blast furnace to electric melt furnaces. In Canada, more than 50% of steel is produced in electric furnaces. Experience in the US has shown that electric melt furnaces enable companies to comply with environmental regulations. Continuous casting of steel is used in Japan for most of its steel production and is also used more in Europe than in the U.S.

Recycling and reuse of water results in a reduction in volume of water per ton of steel produced. Where the quality of water in a process is not high priority, the water can be reused, for example, in flume flushing. Treating water for reuse in other operations can also be considered. At some steel plants in the U.S., total recycling has been achieved.

McGuire (1989) describes the water conservation practices of the Dofasco Steel company in Hamilton, Ontario. Dofasco uses about 20,500 U.S. gallons water per ton of steel produced. Ninety-seven percent of the water the company uses is pumped directly from Hamilton Harbour with the remainder coming from the city's system. With between 25% and 35% of the water coming into direct contact with raw materials, gases, or products, this results in about 7000 U.S. gallons of contaminated water per ton of steel. The remaining water is used for cooling and is not treated. The major water conservation techniques employed are:

- cooling towers/heat exchangers to recycle water
- contact process water conditioning to enable recovery of water for recycling. A filtration system is used for water from the hot mill and caster and an ion exchange system is used for the chromium contaminated water from the electrolytic coating lines
- condensation of water vapour from the boiler houses
- an evaporative cooling system for recovering waste heat from the melt shop fume collection hoods and reheat furnaces at the caster. If convective cooling were used vast quantities of water would be required.
- directing water from areas where high quality water is required to areas where lower quality water is needed so that water can be reused
- counterflow rinsing which can reduce rinse water requirements by 75%
- thermostatic control that ensures only sufficient water for cooling is being pumped in, especially for oil coolers, which results in 10,000 gallons water per minute savings.

Dofasco hopes by these and future water reduction techniques to reduce the water they withdraw from Hamilton harbour by more than 30 billion gallons per year and to reduce by 6% the city water that it uses.

Rao et al. (1989) discuss laboratory studies to determine the effects of using recycle water from mineral processing plants on froth flotation for the selective separation of minerals. They found that the presence of high concentrations of calcium or magnesium ions reduced the recovery of pyrochlore (a niobium mineral) and that organics in the recycle water led to lower selectivity. Sulfide flotation in the presence of copper, lead or iron ions also led to poorer selectivity. Biological treatment to lower the organics content and ion exchange treatment to remove metal ions improves flotation performance of recycled water.

Waste Treatment Technologies

Milling or concentrating an ore recovers metals from the ore and produces large quantities of finely ground rock particles or mineral tailings. The tailings are discharged from the mill as a slurry of solids in water to a tailings pond where the solids settle out and the water is recirculated or discharged to the environment (EPS 1/MM/3, 1988). Factors that should be considered in site selection, construction, operation and reclamation of tailings impoundments are discussed Mine and Mill Wastewater Treatment (EPS 2/MM/3, 1987). Specific problems and treatment for acid mine waters and for removal of cyanide and arsenic are also discussed.

Tailings management may require washing dissolved metals or salts, and dewatering or thickening prior to disposal in a tailings pond. Klepper et al. (1989) review some of the equipment, including thickeners, filtration equipment, effluent clarifiers and polishing filters, for handling tailings and effluent from mineral processing operations.

Reddy (1988) gives a brief literature review of some recent symposia papers on metal and mineral waste processing and secondary recovery. These include methods for improved recovery and recycling of scrap metals, and recovery of metals from slags, furnace dusts, sludges, spent liquors, and residues.

Palmer et al (1988) outline some of the recycling technologies for recovering metals from metals-bearing waste streams, as well as best practice technologies available for removing metals and cyanides from waste prior to disposal or further treatment. The appropriate technologies are dependent on the physical and chemical characteristics of the wastes and the chemical consituents of the waste. One or more treatment technologies may be required to remove different constituents.

In the mining industry solvent extraction of metal salts is used commercially to recover copper, nickel, cobalt, uranium, vanadium, and other metals from aqueous effluents (Palmer et al, 1988).

Microbiological metal recovery is an emerging technology for ore leaching and metal removal from process and waste streams. In metallurgical processes microbes act as aids in the dissolution of minerals in water solutions (bioleaching), as agents for altering the surface chemistry of mineral particles, and as selective accumulators of metal ions from dilute solutions (bioaccumulation) (Kawatra and Eisele, 1989).

Bioleaching is used commercially to recover copper from dumps of low grade sulfidic ores and waste materials. Research is being conducted on using microorganisms to recover other metals from low concentration wastes and from waste solutions (Olson et al., 1989). Applications include increasing gold recovery during cyanide leaching; aiding dissolution of uranium in acid solution; bioleaching of nickel and cobalt from low grade ores; reducing the amount of selenium in process wastewaters; adsorption of metals such as radium from wastewater streams (Kawatra and Eisele, 1989). Research on bioleaching is being conducted by the biotechnology group at CANMET (see, e.g., Tsezos et al., 1989; Bechard et al. 1989; McCready et al. 1990).

Wilk et al. (1988) and Palmer et al. (1988) outline neutralization treatment and recovery technologies for corrosive containing wastes. Many of these are also applicable to metal/cyanide containing wastes from the surface finishing and petroleum refining industries. Well established technologies include treatment with limestone, lime or caustic soda. Treatment however, must take into consideration quantity and quality of sludges produced as by-products.

The most common chemical treatment is neutralization of free acid and removal of metals by precipitation as hydroxides by addition of lime to the effluents. The lime is added before the effluent is discharged to tailings ponds so that the hydroxides settle out in the ponds. Metal hydroxides are amorphous solids and colloids with low settling rates. This results in sludge that is difficult to dewater. Separation can be improved by adding polymer flocculants or by recycling the sludge to a neutralization system to increase the precipitation rate (EPS Report 2/MM/3, 1987).

Various methods of treating cyanide in effluents are available (EPS 2/MM/3, 1987; Palmer et al, 1988; Wilks et al., 1988). Cyanide is mainly a byproduct of gold milling operations and of surface finishing operations.

In steel manufacturing, spent pickling liquors which contain up to 10% acid and 12% iron are a major source of pollutants. Eight to fifteen gallons of spent liquor are produced per ton of steel. Current disposal methods in use include deep well disposal which could result in groundwater contamination in the future; neutralization and treatment for solids and sludge removal; and metals recovery and regeneration of liquor (Palmer et al. 1988).

Surface treatment of metals usually involves an acid washing step. Recovery of acids for reuse involves removing metal contaminants. Solvent extraction and neutralization may not always be adequate to produce an effluent that meets environmental regulations. In an acid purification unit, acid is adsorbed from the concentrated solutions (e.g. etchants) and metal contaminants are allowed to pass through the system. The adsorbed constituent is subsequently removed by passing a regenerant through the resin resulting in a waste stream with a highly concentrated adsorbed constituent which is potentially recoverable. Acid purification has been applied commercially for successful recovery of steel pickling liquor, aluminum anodizing, etchants, and rack stripping operations.

Noma (1989) describes a method of acid recovery by diffusion dialysis using an new ion exchange membrane that is tolerant to both nitric acid and hydrofluoric acid. The acid recovery process is applicable to the steel and electroplating industries.

Extensions to an oil water separation plant at a steel mill in Britain that produces high quality rolled stainless steel strip splits the effluent into 10% oil and 88% water producing an oil that is sufficiently high quality to be resaleable and water that can be discharged to normal drainage systems without further treatment. The separation plant is a three stage process that uses coalescing separation and ultrafiltration processes (Iron and Steelmaking, 1989).

Arsenic from arsenic-bearing ores can be removed from wastewaters by precipitation as calcium or ferric arsenates.

Conventional treatment of wastewaters from the blast furnace and byproduct coking process are removal of suspended solids and physical and chemical methods to reduce concentrations of ammonia and cyanide. Processes that are used including alkaline breakpoint chlorination, ozonation, steam stripping, reverse osmosis and chemical oxidation (EPS 3/MM/1, 1984).

Pilot scale studies were conducted at the Wastewater Technology Centre in 1984 to determine the feasibility of biological treatment of these wastewaters (EPS 3/MM/1, 1984). A two stage fluidized bed process was used. The first stage was an anoxic denitrification fluidized bed reactor and the second an oxygenic nitrification fluidized bed reactor. The results showed that the technology is technically feasible for treating coke plant wastewaters and for combined stream of coke plant wastewater and blast furnace blowdown.

Research in the iron and steel industry is also being directed at pollution prevention, waste minimization and methods of treating or recycling wastes generated by the EAF process. Conventional end-of-pipe treatment technologies have the advantage of not interfering with existing production processes. However, Teoh (1989) notes that "a more rational and profitable approach is to understand exactly why a waste is generated from a process, and its linkage to raw materials and product quality to determine waste reduction opportunities". Some viable methods and process modifications that are currently available to reduce waste are outlined by McAloon (1987) Schochet (1988) describes a process for 100% recycling of EAF dust at a steel plant in the United States.

Sludge Treatment

Most of the metal hydroxide sludges from Canadian mining operations are mixed with tailings and disposed of in tailings ponds. Little is known about the stability of the metals hydroxides in the tailings ponds (EPS 2/MM/3 1987).

Treatment technologies for dewatering sludges include lagoon dewatering, vacuum filtration and centrifugation. Detoxification options include chemical treatment, solidification or stabilization, and toxic metal removal (Fontaine et al., 1988).

The U.S. Environmental Protection Agency regulates heavy metal and cyanide in wastewater and in sludges destined for landfill. The metal/cyanide waste disposal restrictions apply to liquid containing wastes that exceed the specified concentrations of total metals or cyanides in their leachates (Palmer et al., 1988). Cyanide wastes are defined as any wastes containing a carbon-nitrogen triple bond. A list of metal/cyanide containing wastes regulated under the U.S. Resource Conservation Recovery Act are given in Palmer et al., (1988). They list quench wastewater from metal heat treating operations, wastewater treatment sludges from explosives manufacturing, dust and sludge from electric furnace steel production, spent pickle liquor from steel finishing operations, decanter tank car sludges from coking operations, plus various copper, zinc, and iron compounds.

Considerable research has been conducted into methods of stabilizing metal containing wastes that result in a material from which the hazardous materials cannot leach out. These materials can then be landfilled or used for other purposes. The EPA defines stabilization, solidification and fixation as waste treatment that produces the combined effects of improvement of physical properties, encapsulation of pollutants, reduction of solubility and mobility of the toxic substances.

Stabilization/solidification technologies for treatment of metals containing wastes include:

- Cement-based techniques using pozzolanic or cementation reactions
- silicate-based techniques involve pozzolanic reactions that produce calcium silicates and aluminates that act as natural cement. This process can also be used to stabilize oily wastes.
- thermoplastic techniques
- sorbent techniques
- organic polymer techniques
- encapsulation techniques
- vitrification

Among the Best Demonstrated Available Technology reports published by the U.S. EPA that are applicable to the metallurgy industries are:

EPA/530-SW-89-017A. Best demonstrated available technology (BDAT) background document for cyanide wastes. Dec. 1988. This covers cyanide-containing electroplating and metal heat treating wastes.

EPA 530-SW-88-031L. BDAT background document for F006. August 1988. This covers wastewater treatment sludges from common and precious metals electroplating, except tin, zinc (segregated basis), aluminum, and aluminum-zinc plating on carbon steel; anodizing except sulfuric acid anodizing of aluminum; chemical etching and milling except where performed on aluminum; cleaning and stripping except when associated with tin, zinc, and aluminum plating on carbon steel.

EPA/530-SW-88-031D. BDAT background document for K016. August 1988. This covers emission control dust/sludge from the primary production of sludge in electric furnaces.

EPA/530-SW-88-013E. BDAT background document for K062. August 1988. This covers spent pickle liquor generated by steel finishing operations of facilities within the iron and steel industry.

EPA/530-SW-88-031M. BDAT for K087, August 1988. This covers decanted tar sludge from coking operations.

Bethlehem Steel Corporation in the U.S. has developed processes called DeTox and Super DeTox to solidify/stabilize liquid and solid wastes so that they can be disposed of as non-hazardous materials. The processes use lime and silica pozzolanic technology and appears to produce highly stable materials from steel waste. Research is also being conducted into the possibility of using the solids produced in large scale construction processes (Pamukcu et al, 1989).

Dobosz and Sebastian (1987) offer suggestions for reducing the volume of sludge waste from iron and steel mills at source. Sludges from neutralization from wastewaters from the drawing mill, forging shop and rolling mill may be reduced by substituting hydrochloric acid for sulphuric acid in the etching process; sludges from scrubbing operations can be reused, after processing by electromagnetic thickening, dewatering and briquetting, for pig iron melt; sludges from the etching batch may be separated from the oil emulsion and processed for use in blast furnaces.

The Waelz Kiln process can be used to recover zinc, lead and cadmium from bagroom dust from electric arc furnaces (Kern et al., 1988). The dust is mixed with coal, limestone and sand are added, and the mixture is heated to 1300 C. The zinc is reduced, volatilized and then reoxidized resulting in a zinc rich fume and an iron rich clinker. In the U.S., in 1988, more than 40,000 tons of zinc was recovered from 250,000 tons of EAF dust. By 1991, it is estimated that more than 20% of the output of zinc metal will be derived from EAF dust. As a result of this work, the EPA has recognized thermal treatment as best demonstrated treatment technology for dealing with EAF dust.

The iron-rich material has the ability to absorb heavy metals from aqueous solutions. Kern et al. (1988) suggest that landfills with a redundant lining of the iron-rich material could block ground water contamination from leachate and as a redundant treatment for conventional industrial wastewater plants.

Contos et al (1989) describe laboratory scale experiments to detoxify sludges produced from air pollution control equipment in foundries by using a proprietary metal inhibiting compound. After assessing degree of variability in the wastewater and the sludge from a number of foundries, they conducted various tests and found that by adding five percent dry weight of the metal inhibiting compound to the sludge, detoxification was successfully achieved.

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CHAPTER FIVE

SURFACE FINISHING

Surface finishing serves a variety of purposes including increasing the resistance of metals to corrosion, changing the surface properties of materials, and improving the appearance of products.

Three companies with major surface finishing operations have been identified as among the 50 companies contributing significant amounts of pollutants to the St. Lawrence River system. In addition to these three companies, metals companies with rolling mills and other metals processing operations also produce effluents and sludges from surface treatment operations. There are also numerous small metals finishing companies.

Metals surface finishing effluents fall under the Metal Finishing Liquid Effluent Guidelines (EPS 1-WP-77-5, 1977), which are intended to control the discharge of liquid effluents from metal finishing plants. However, the "guidelines do not apply to existing metal finishing plants which are captive of other operations such as steel companies, foundries, automotive manufacturers and airplane manufacturers where the effluents from the different components of the complex are not segregated and discharged separately". The guidelines are also "not to be construed as regulations under the Fisheries Act".

The guidelines give objectives for pH levels and the concentration of the following substances in effluents as (EPS 1-WP-77-5, 1977):

- total suspended matter	30.0 mg/l
- cadmium	1.5 mg/l
- chromium (total)	1.0 mg/l
- copper	1.0 mg/l
- cyanide (oxidizable)	0.1 mg/l
- cyanide (total)	3.0 mg/l
- lead	1.5 mg/l
- nickel	2.0 mg/l
- zinc	2.0 mg/l

In the United States, EPA metal/cyanide disposal restrictions apply to metal/cyanide containing wastes that exceed specified concentrations of total metals or cyanides in their leachates. There are at least 110 metal/cyanide wastes listed under the Resource Conservation and Recovery Act (RCRA) (for list, see Palmer et al., 1988, Table 2.2.1, pp. 7-9). This act, and the Hazardous Solids Wastes Amendment prohibit disposal of RCRA listed wastes in or on the land. Therefore wastes containing listed compounds must be treated prior to final disposal. The RCRA listed metals and cyanides include specific metals and metal compounds as well as metals-containing waste water and sludges from electroplating and coating facilities, petroleum refining, paint manufacturing, chemical production, and steel production and finishing. Cyanide wastes are defined as any wastes containing a carbon-nitrogen triple bond.

Some of the major industrial uses of metals and cyanides are in metal finishing, refining, photographic chemicals, plastics and organic chemicals manufacture, pigments, wood preservation, explosives, paint, metals parts fabrication, batteries, alloys, paper manufacture, and electrical and electronics applications (Palmer et. al., 1988).

The Environment Canada Report, "Overview of the Canadian Surface Finishing Industry" (EPS 2/SF/1, 1987), identifies the major Canadian manufacturing industries that use surface finishing (percent of market in 1983) as automobile parts (26%), steel strip mills (14%), hardware (12%), electrical appliances (10%), wire goods (10%), plumbing fixtures (6%), electrical equipment (5%), furniture (5%), pole hardware and heavy steel (5%), and electronics (4%).

Many surface finishing companies in Canada are small, with fewer than 10 employees. Only half of the 539 operations that responded to the Environment Canada survey treated their effluents prior to discharge.

Finishes in the automobile parts industry include plastics, nickel, chrome and zinc plating, anodized aluminum, and rust resistant oils and paints. Cold rolled steel is plated with zinc or tin. Hardware, wire goods, and steel furniture finishes include nickel-chrome, zinc, brass and bronze. Electrical appliances and plumbing fixtures can have nickel-chrome or zinc plate finishes. Hot dip zinc galvanizing is used in pole hardware and heavy steel. Copper plating is used for printed circuit boards, as well as nickel, gold, tin and tin-lead processes.

Processes used in surface finishing operations include mechanical processes, such as grinding or drilling that smooth surfaces or alter the shape of the product, chemical processes for cleaning surfaces and removing contaminants, and physical and electrolytic processes for applying coatings to the materials.

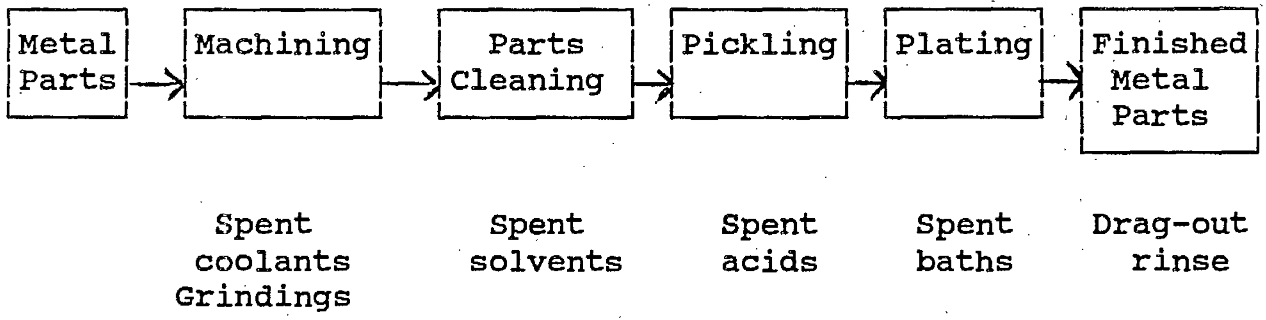

Fig. 5.1. Metal finishing operations and waste streams

Source: Sutter, 1989

A variety of products are used in these finishing processes. Abrasives and lubricants are used to improve mechanical processes and reduce heat build-up; solvents, soaps, detergents, oils, and acidic or alkaline solutions are used for surface cleaning; strong acids are used for pickling (removing surface scale); and coatings, such as plastics, paints, or metals can be applied by dipping the product in baths containing the coating materials, or through electrochemical processes.

Major Pollutants

The major pollutants in the surface finishing industry are (EPS 2/SF/1, 1987):

- Process wastewaters containing acids or alkalis, solvents, suspended solids including metals, and dissolved solids;
- Spent process concentrates such as acid baths containing dissolved metals, oils and suspended solids; alkaline baths containing fatty and oily substances; spent plating and coating concentrates with high metal content that may include hexavalent and trivalent chromium, cyanide and other toxic compounds.
- Sludges containing heavy metals, toxic chemicals (e.g. cyanides), solvents, and organic pollutants

In many cases, metal contaminants or toxic compounds in the liquids and sludges can be recovered and the process liquids can be recycled. The economics of the recovery/recycle process, however, may not make this an attractive option. In some cases, the contaminant can be converted to a less hazardous form, or treated to form a chemically inert substance prior to disposal.

Waste Minimization

Pollution from the surface finishing sector can be reduced or controlled in a number of ways, including better housekeeping to prevent and/or contain spills; reduction of product loss during pickling and cleaning operations; product substitution; process redesign and optimization of chemical use; reductions in use of water and other liquids; product recovery/recycling; and treatment technologies for waste liquids and sludges.

Alexander and Interrante (1989) describe a waste minimization assessment for a company that produced eleven types of hazardous wastes, including electroplating sludge, halogenated organic solvents, acids, silver containing photographic wastes and metals contaminated machine oil. They detailed the wastes generated, analyzed the waste minimization options and made recommendations for recycling and recovery options that would be economically feasible. These included recycling machining coolant, reduction in chemical use, and recovery of chlorinated solvents and the silver from the photographic process. They found the recycling/recovery options to be more cost effective than having the wastes trucked and disposed of at a waste disposal facility. They also note that increasing disposal costs will make recovery/recycle options more economically attractive in the future.

Housekeeping

Better housekeeping practices include reducing process solution wastage by using holding tanks to collect spills and leaks, increasing drag-out time at plating baths, oversizing equipment at critical points in the process, using process controls to optimize chemical use, and segregating acids, alkalis, cyanide and chrome wastes for separate treatment.

Product Substitution

The metals finishing industry produces some extremely hazardous wastes, including heavy metals that bioaccumulate in living organisms. One method of waste minimization is therefore metals substitution in finished products. In recent years, metals have been replaced by other materials, such as plastics, ceramics, or composites, in a variety of products.

Metals substitution is not always feasible. However, the raw materials in some processes may be substituted by potentially less harmful materials, or materials that will react to produce less hazardous or more easily treated waste, while maintaining product quality or performance characteristics. Considerable work has been done on elimination or substitution of cyanides, cadmium, and hexavalent chromium in plating processes. Palmer et al. (1988) give examples of some materials substitutions including replacing chromic acid with peroxide-based pickling liquor at a wire manufacturer, replacing hexavalent chrome with trivalent chrome systems for some coating applications, and use of ferric chloride or ammonium persulphate solutions for chromic-sulphuric etchants in some instances.

Cadmium, zinc and lead have been used as metal coatings for corrosion protection, but these metals are toxic and their disposal is regulated. Aluminum use is not restricted because of toxicity, and aluminum has good corrosion resistance and other properties that make it a good metal coating material. However, industrial scale electrodeposition has only recently been developed by Siemens R&D. This SIGAL process, which uses a non-aqueous electrolyte, gives a very pure aluminum coating and can be deposited on most technically importants metals (de Vries, 1987).

Cyaniding baths can be replaced by gas phase carbonitriding, a process which uses ammonia gas instead of cyanide to provide nascent nitrogen, a raw material substitution process that eliminates the need for a rinse phase.

Process Redesign

Process redesign options can include changing equipment and operating conditions, process controls to monitor and optimize reaction conditions, and incorporating new technologies into existing operations.

The EPA has reported the use of air dried, no-rinse chromate conversion coatings for steel, galvanized steel, and aluminum in the coil coating industry (Palmer et al., 1988)

Snyder (1989) discusses trivalent chromium plating technology that has been developed in the past 15 years and its use in various types of plating shops. The newer technologies overcome the problems of poor metal distribution, formation of hexavalent chromium during plating, and formation of dark coloured deposits that were experienced with earlier technologies. In addition to providing safer working conditions in the plating shops, trivalent chromium plating waste does not fall into the hazardous category that hexavalent chromium waste does. Sludge production and sludge disposal costs are both less than with hexavalent chromium.

Reduction in Water Use

Water consumption in surface finishing operations can be reduced in a number of ways, including (EPS 2/SF/1, 1987):

- counterflow rinsing
- spray rinsing
- use of conductivity meters so that slightly contaminated water can be used to full extent
- flow control valves
- delay over plating baths and rinse tanks so that liquids can drip back into the baths or tanks and thereby reduce dragout to the following tank
- drag-in/drag-out tanks before and after plating tanks.

Recovery/Recycling

Many of the metals recovery/recycling technologies are applicable to both surface finishing and metallurgical industries. Metals in process solutions can often be recovered and the solutions recycled. Metals can also sometimes be recovered from sludges before final treatment or disposal. Palmer et al. (1988, Table 5.2.1, pp. 73-75) summarize recycling technologies for metal containing waste streams. These include:

- Agglomeration, where small particles are gathered together into larger particles that can be more easily precipitated or filtered;
- Concentration, which includes membrane separation techniques (reverse osmosis, liquid membranes, Donnan dialysis, coupled transport); precipitation; extraction/leaching; adsorption (activated carbon, resin adsorption, ion exchange); thermal technologies (calcination, evaporation, crystallization, smelting); biological technologies; and flotation;

- Metal reduction, which includes electrolytic recovery; sodium borohydride; and thermal processes.

Recovery technologies depend on the constituents of the process solutions. Primary bath treatment recovery methods include electrolytic recovery, ion exchange, crystallization and evaporation.

Spent baths can be regenerated by removing contaminants. Insoluble metallic salts can be filtered out. Soluble salts have been removed from electroless nickel baths by crystallization followed by filtration.

Evaporation is used in the metal finishing and electroplating industries to concentrate and recover plating solutions, chromic acid, nitric acid/hydrofluoril acid pickling liquors, and metal cyanides from spent baths and rinsewaters. Chromic acid has been successfully recovered from rinse waters through ion exchange and by evaporation (Palmer et al., 1988).

Solvent extraction involves separation of a component from the waste solution by transfer to a second liquid. Solvent extraction is used in the mining industry to recover copper, nickel, cobalt, uranium, vanadium, and other metals from aqueous effluents. In the extraction process, the constituents to be recovered are transferred from an aqueous phase to an organic phase using an organic solvent as an extractant. In back extraction or stripping, the constituent to be recovered is transferred from the organic phase to a concentrated aqueous phase.

Solvent extraction is also applicable as a recovery process in metals finishing, though is less well developed (Palmer et al, 1988). It can be used, for example, to recover concentrated solutions, such as spent process solutions used in pickling and plating baths, or to treat low concentration wastewater streams, such as rinse waters used to remove dragout from pickling and plating baths. The process can involve more than one extraction stage. Pretreatment by precipitation and filtration to remove some constituents that might interfere with the extraction process, and post treatment to remove organics may also be required.

Scholler et al (1988) have been involved in development of a new system for recovery of heavy metals (zinc, nickel, copper, cobalt, cadmium, manganese, barium, strontium, lead, and mercury) from electroplating wastewaters with metals concentration ranging from 10 to 100,000 ppm. They developed a pilot scale pellet reactor for treating industrial wastes, based on pellet reactors that are in use for softening drinking water. In the reactor, a carbonate solution reacts with the metal in the wastewater to form a metal carbonate that crystallizes on seed material (e.g., filter sand) to form pure metal carbonate pellets. The fluid velocity is high to keep the grains in suspension. The pellets are removed and dissolved in acid to recover the metal. The process has the advantage of producing no sludge. A post-treatment filter removes any small suspended particles of metal carbonate or metal hydroxide.

The effluent from the pellet reactor can be discharged, further treated with hydroxide, or recirculated to a drag out bath. If additional treatment of the wastewater is required in an hydroxide precipitation plant, sludge volumes are considerably reduced, as are the amounts of treatment chemicals required. Backwash from the sand filter can be returned to an acid dragout or plating bath. The pellet reactor system is compact, relatively cheap, and can treat baths separately. The pilot plant results were favourable and implementation of the system with a partner in the electroplating industry was being negotiated.

Holbein and Blais (1989) describe a method of recovering metals from process wastewaters and spent concentrates using metal selective adsorbents and electrolytic metal recovery cells. The chelating-type metal adsorbents, which were developed in the early 1980s and are licensed under the trademark Vitrokele, selectively adsorb the target metals from the waste stream. The metal is recovered from the adsorbent in a high metal concentrate which can be treated electrolytically to recover the metal. The process has been used on electroless and electrolytic plating wastes, etching/milling wastes, incinerator wet scrubber waste waters and mining effluents.

Electrodialysis is a newer technology for recovering plating chemicals from rinse solutions. Electrodialysis is based on migration of ions through sets of alternate cation and anion exchange membranes that allow passage or +ve and -ve ions respectively. When current is applied, dissolved metals in the electrolyte are reduced and deposited on the cathode. Specific contaminants can be removed from waste streams without deposition of sludge. Electrolytic processes are most effective in removing gold and silver. Larger currents are required for cadmium, tin, lead and copper. Nickel recovery has been accomplished by electrodialysis, enabling reuse of the rinse water. Problems with electrodialysis include membrane fouling and local overheating. Recovery can be difficult from weak solutions.

Waste Treatment Technologies

The Canadian metal finishing liquid effluent guidelines (EPS 1-WP-77-5, 1971ide information on best practicable technology in 1977, the year they were issued. Treatment techniques for effluents are given in "Wastewater and Sludge Control in the Canadian Metal Finishing Industry" (EPS 3-WP-76-10, 1976).

As the wastes from surface finishing operations in the U.S. fall under the U.S. Environmental Protection Service RCRA regulations, considerable work has been done to identify methods for treatment and disposal of metals/cyanide containing wastes. Best practice treatment technologies for metal/cyanide containing wastes are published in the handbook "Metal/Cyanide Containing Wastes" (Palmer, et al. 1988). Treatment technologies for corrosive-containing RCRA listed wastes, including acidic wastes from metals cleaning and pickling liquors, and discussed in "Corrosive-containing Wastes: Treatment Technologies", (Wilk et al, 1988).

The U.S. Environmental Protection Agency reports on best demonstrated available technologies (BDAT) for metals and/or cyanides-containing wastewaters and sludges that have been published to date are:

> EPA/530-SW-89-017A. "Best Demonstrated Available Technology (BDAT) Background Document for Cyanide Wastes". Dec. 1988. This covers cyanide-containing electroplating and metal heat treating wastes.
>
> EPA 530-SW-88-031L. "BDAT Background Document for F006". August 1988. This covers wastewater treatment sludges from common and precious metals electroplating, except tin, zinc (segregated basis), aluminum, and aluminum-zinc plating on carbon steel; anodizing except sulfuric acid anodizing of aluminum; chemical etching and milling except where performed on aluminum; cleaning and stripping except when associated with tin, zinc, and aluminum plating on carbon steel.

Johannes et al. (1988) discuss the steps in developing design criteria for treatment of electroplating/metal finishing wastewaters and the factors that have to be taken into consideration, including recovery vs. treatment, in selecting the best treatment process(es) for a plant.

Many of the wastes in the surface finishing industry contain greases and solvents. The major U.S. industries generating RCRA listed solvent waste streams include paints and allied products, plating and polishing, metal coating and allied services, motor vehicle bodies and parts, aircraft equipment, and plastic materials and products (Breton et al., 1988). Treatment technologies for solvent containing wastes are discussed by Breton et al., (1988). These include many of the physical, chemical, and biological processes suitable for treating organic chemical wastes.

Wastewater Treatment

Metals in wastewaters may be in lower concentrations than in process solutions, or there may be a variety of metals in the wastewater that would make recovery of the metals for reuse uneconomical or infeasible. The concentrations of metals in the waste, however, still have to be reduced to acceptable limits. Metals can be removed from process wastewaters by a variety of methods, some of which are the same as those used for metals recovery or are modified to treat less concentrated solutions. Methods used for wastewater treatment include precipitation, ion exchange, adsorption, reverse osmosis, solvent extraction, membrane filtration, electrochemical treatment and evaporative recovery.

Precipitation

In precipitation processes, chemicals are added to the metal solutions to form insoluble metal salts which are precipitated from the solutions. Precipitation depends on pH, an excess of treatment ions to ensure complete precipitation, and effective removal of the precipitate. It may be necessary to pretreat waste streams to remove suspended solids, to adjust the pH, or to remove components such as cyanide, chromium, or oil before combining with other waste streams for treatment.

The efficiency of metals removal depends on metals in the solution and the pH (in mixed metals solutions the salts may be insoluble at different pH's); and the presence of complexing ions such as phosphates, tartrates, ethylenediaminetetraacetic acid (EDTA), and ammonia.

The advantages and disadvantages of established precipitation technologies, including lime, caustic soda, sulfide, and carbonate precipitation, are discussed by Palmer et al. (1988).

Hydroxide precipitation (sodium, calcium or magnesium hydroxides) is well developed technology and can be used to co-precipitate a mixture of metal ions. The major problems with hydroxide precipitation are gas emissions during precipitation and potentially hazardous sludge from which it is difficult to recover metals. (see Palmer et al., 1988 Table 10.1.20, p. 388-9)

Although magnesium hydroxide, $MgOH_2$, is a more expensive chemical, the cost of treating a plating waste stream with magnesium hydroxide is less than treatment with sodium or calcium hydroxide, as less chemical is required, lower sludge volumes are produced, and the sludge is easier to dewater (Teringo 1987). The method of treatment with $Mg(OH)_2$ to achieve optimum results is discussed.

Arumugam and Bhagat (1989) investigated the effects of metals concentration, pH, reaction time, coprecipitation with iron (III), and EDTA on the efficiency of caustic precipitation for removing nickel from electroplating wastewaters. They found coprecipitation with iron (III) did not affect nickel removal, but that precipitation was greatly inhibited by the presence of EDTA. The concentrations of nickel and EDTA, and the pH of the solution affected the precipitation rates to varying degrees. Their work emphasizes the necessity for careful analysis of wastewater streams and for monitoring treatment processes to achieve maximum metals removal efficiency.

Spent electroless nickel plating baths contain soluble nickel Ni(II), and reducing and complexing agents. Reducing agents are normally residual hypophosphite and phosphite species which have first to be oxidized to phosphate species before precipitation (Ying et al., 1989). The authors developed a three stage precipitation-oxidation-precipitation treatment process, using lime and potassium permanganate, that gave almost complete removal of both nickel and phosphorous from electroless nickel plating baths.

Sulfide precipitation enables heavy metals to be removed to extremely low concentrations. It can be used to remove lead, copper, silver, cadmium, zinc, mercury, nickel, thallium, antimony, arsenic, and vanadium (Palmer et al., 1988). Unless the pH is carefully controlled in sulfide precipitation, there is the possibility of hydrogen sulfide formation. It can also be difficult to recover some metals from the precipitates and metal containing sludges have to be treated.

Carbonate precipitation (calcium carbonate, limestone) and sodium carbonate Na_2CO_3 can also be used to remove heavy metals from wastewater, but the reaction times can be slow (Palmer et al., 1988).

Crystallization is used to precipitate metal contaminants in spent corrosive solutions by temperature reduction and settling or centrifugation. The process is limited to liquid wastes with appropriate solubility characteristics. It is used primarily by generators of large volumes of spent solutions, e.g., iron and steel plants. Copper recovery from sulphuric acid - hydrogen peroxide pickle liquors is being used increasingly in the U.S.A. and Europe.

One of the problems with conventional metal recovery processes such as precipitation is that complexed metals are not always removed efficiently and toxic sludges that are difficult to dewater are produced.

Coagulants or flocculants may be required for waste streams with dilute concentrations of constituents that become insoluble during neutralization/precipitation. The main types of inorganic flocculents are aluminum derivatives (e.g. alum - aluminum sulphate hydrate), iron derivatives and lime.

Synthetic organic flocculants are used almost exclusively in coagulation/flocculation of industrial heavy metal precipitates. Natural organic polymers used as flocculents include starch, plant gums (e.g. guar gum), cellulose derivatives, proteins and tannins. The major disadvantage of flocculation or coagulation is the production of metals-containing high water content sludge. The process cannot be used for small intermittent flows, and many of the coagulants form corrosive solutions (Landscheidt and Reuter, 1987).

Tare and Chaudhari (1987) evaluated the use of starch xanthate as a metal precipitant for industrial wastewaters. The metal xanthate sludge is easily dewatered and oxidation enables the metals to be recovered. They focused part of the study on the removal of hexavalent chromium. Results indicate that the heavy metals were removed more efficiently by the xanthates than by traditional reduction-precipitation methods and could be an alternative to traditional precipitation treatment.

Flotation can sometimes be used to remove metal contaminants. The metal contaminants have to be precipitated first by addition of, for example, a surfactant (ion flotation); by precipitation of the metal (precipitate flotation) or adsorbing the contaminant on to colloidal particles (colloid flotation). Chemical flotation is still at the bench or pilot plant level of research and the sludge is potentially hazardous (Palmer et al., 1988).

Chemical reduction is an established waste treatment process for reducing hexavalent chromium by sulphur based reagents (Palmer et al., 1988). Sodium borohydride has been used to a limited extent in some chloralkali and metal finishing facilities.

Treatment technologies for electroless finishing wastes include chemical precipitation and reduction, electrolytic reclaim, ion exchange, reverse osmosis and electrodialysis. Ion-exchange methods using strong alkaline resins treated with sodium hypophosphite can be used to remove excess phosphite from spent solutions. Ion exchange may be a more cost effective technique than precipitation. Gingras and Capaccio (1989) and Capaccio and Gingras (1989) describe wastewater treatment applicable to electroless nickel plating. In finishing baths, care should be taken in selecting the correct electroless metal formulation and in operating the baths to optimize bath performance and extend bath life. The authors advocate treating spent finishing baths and rinsewaters separately. The authors note that treatment technologies should be thoroughly tested to determine the optimum treatment chemistry for the wastewaters and sludges from a specific finishing operation.

Ion Exchange

Ion exchange is a well established technology for drinking water treatment. Ion exchange can also be used to selectively remove toxic heavy metals and metal cyanide complexes from dilute waste streams. In ion exchange processes, ion exchange resins absorb metal ions from water until the resin is exhausted. Regeneration of the resin with strong acid or alkali gives a concentrated metal salt solution. Depending on the purity of the metal salt solution, the metal may be recovered or the solution can be used as a plating bath. Water from the process may be recycled as rinsing water. Flow through operations, in which a bed or packed column of the exchange material or resin is used, is more efficient than batch mode operation.

Resins can be classified by functional (reactive) group and the type of exchangeable ions present. Cation exchangers have positively charged, mobile ions for exchange and anion exchangers have negatively charged ions for exchange. Chelating resins behave like weak acid cation resins but are highly selective for heavy metal cations. Solution pH affects the efficiency of the resin.

Ion exchange has been used to recover metal containing wastes from the metal finishing and electroplating industries. Nickel, for example, can be recovered as nickel chloride or nickel sulphate (Brown, 1988). Ion exchange can also be used to remove contaminants from hexavalent chromium baths so that baths can be reused (EPS 2/SF/1, 1987). In an acid purification unit, acid is adsorbed from the concentrated solutions (e.g. etchants) and metal contaminants are allowed to pass through the system. The adsorbed constituent is subsequently removed by passing a regenerant through the resin, resulting in a waste stream with highly concentrated adsorbed constituent which is potentially recoverable.

Research on ion exchange resins for treating industrial wastewaters from metal finishing operations is being conducted by a number of groups.

Karr et al. (1988) conducted research on a two-stage process for treating acidic electroplating wastewater with high zinc concentrations. Calcium hydroxide precipitation was used for the first stage and sodium sulfide precipitation and vermiculate ion exchange were tested and compared as second stage treatment processes.

The zinc-plating wastewaters tested had Zn concentrations ranging from 10,000 to 13,500 mg/l. The first stage calcium hydroxide precipitation removed >99% of the zinc, leaving the wastewater with Zn concentrations ranging from 12-50 mg/l. Effluent limitation for zinc is 2mg/l in the U.S.

In the second stage treatment experiments, it was found that sodium sulfide did not consistently provide adequate zinc removal. Vermiculite ion exchange was more effective at removing zinc, producing zinc concentrations of close to zero, but problems were encountered with ammonium in the wastewater which interfered with the process. Ammonia may have to be stripped before vermiculate ion exchange treatment. The vermiculate process was also almost twice as expensive as the sulphite treatment. Other studies (e.g., Harwood, 1980), have shown that metals can be recovered from vermiculite ion exchange media.

At the CSIRO Division of Chemicals and Polymers, in Australia, the water and wastewater group have developed an ion exchange technique for treating metal finishing wastewaters (Process and Control Engineering, 1989). The process uses a moving bed of magnetic resin which is cycled continuously between exhaustion and regeneration. Pilot plant tests on rinsewater from a nickel plating line reduced nickel concentrations from 35-50 mg/l to well below the 10 mg/l of the Melbourne and Metropolitan Board of Works limit.

As an end of pipe application, ion exchange resins have been used for selective removal of toxic compounds while allowing non-toxic dissolved ionic solids to remain in solution. Acid purification has been applied commercially for successful recovery of steel pickling liquor, aluminum anodizing, etchants, and rack stripping operations (Palmer et al., 1988).

Membrane Separation Technologies

A membrane allows preferential containment and transport of certain components in the waste stream. Membrane development remains a major focus of membrane technology research.

Reverse osmosis involves passing wastewater through a semipermeable membrane at a pressure greater than the osmotic pressure caused by the dissolved materials in the solvent. Reverse osmosis is a proven technology for treating electroplating wastewater. However, because of extreme pH (both acidic and basic), chemically resistant membranes are needed and are being developed. This recovery technology is capable of achieving zero discharge is some applications. One of the major disadvantages of reverse osmosis systems is membrane fouling which limits membrane life. Membranes can be very expensive to replace. Membranes available for reverse osmosis systems include cellulose acetate, aromatic polyamides and thin film composites.

Reverse osmosis can be used to recover metals from spent plating and rinse baths. The technology has been used successfully to recover nickel salts, zinc chloride, copper cyanide, zinc cyanide and cadmium cyanide from spent plating and rinse baths.

Donnan dialysis and couple transport appear to have some application for metal containing aqueous wastes but there are problems with membrane stability. Both processes use a concentration gradient to drive ions from a spent solution across a membrane into a stripping solution (Wilk et al., 1988). The waste is fed to one compartment and the stripping solution into which the concentrate will be extracted is fed to the other compartment. The major difference in the porcesses is the membrane and the transport mechanisms involved.

Ultrafiltration can be used to recover or treat electrophoretic paints, oil in water emulsions, and rinsewaters from alkaline metal cleaning baths. There are no known applications for recovery of metals from aqueous waste streams, except for precipitated materials. Ultrafiltration membranes are defined by the size or equivalent molecular weight of particles excluded (300 to 300,000 mol. wt. range). They are not suitable for separation of dissolved metal ions but are used for pretreatment or removing chemically precipitated metal species.

Carbon Absorption

Activated carbon adsorption involves separation of a substance from one phase (usually liquid or gas) and the concentration of the substance at the surface of an activated carbon adsorbate. Predominant use of activated carbon is for removal of organic contaminants with high molecular weight. However, bench, pilot and full scale studies have shown that carbon adsorption of many metallic compounds can be successful - absorption efficiency varying with compound. A few full scale systems have been used to treat chromium and mercury waste streams (Palmer et al., 1988). The carbon can be regenerated by using a strong acid or metal base. An economic incentive to recover the metal is needed. Spent carbon is usually disposed of in a secure landfill.

Biological Treatment

Biological treatment of metal-bearing wastes is still mainly in the experimental stage as heavy metals are toxic to most microorganisms. Dilute metal-bearing waste streams with metals concentrations of less than 10mg/L have been successfully treated biologically. Improvements in process tolerance for inorganic priority pollutants are still in the developmental stage (Palmer et al., 1988).

Thermal Destruction/Recovery Processes

Thermal processes for treating hazardous wastes include incineration, pyrometallurgical processes, evaporation and crystallization.

Most metal bearing hazardous wastes are poor candidates for incineration, which tends to be limited to organic wastes containing very low concentrations of metals. The ash content of a hazardous waste, i.e., that portion of the waste which is either a noncombustible solid or which will form a solid by-product in the combustion process, is an important incinerability indicator (Breton et al., 1988). Wastes with a high heavy metals content have a high ash content which may result in higher emissions of particulate matter and pollutant particles that may be hazardous.

Solvent containing wastes, such as those from painting or degreasing operations, generally have a low ash content and are candidates for incineration.

Pyrometallurgical processes include calcination and smelting. Calcination generally produces metal oxides, smelting produces pure metal. Use of these processes for treatment of metal bearing hazardous wastes from surface finishing is not well established but some furnace dust wastes are now being recovered using the processes (Palmer et al., 1988).

Thermal decomposition can be used to recover acid wastes, including sulfuric and hydrochloric acid pickling liquors (Wilk et al., 1988) The major application is recovery of hydrochloric acid from spent steel pickling liquors. A recent application is regeneration of waste sulfuric acid from the production of titanium dioxide pigments.

Sludge Treatment

Sludges from wastewater treatment in the surface finishing industry are usually classed as hazardous because of the heavy metals content. Sludges are usually difficult to dewater and flocculants or coagulants may be required to condition the sludge and improve its dewaterability. Flocculants, similar to those for water treatment can be used. Filter presses, centrifugation and other physical methods can also be used.

Bates et al. (1989) describe the design and installation of dewatering systems for plating waste sludges at three military installations in the United States with major plating and metal treating facilities. The systems are based on sludge conditioning by polymer addition and gravity dewatering on artificial media beds. The sludge cake is then trucked to hazardous waste disposal facilities.

The stabilization technologies for final disposal of sludges from the metallurgical industries are also applicable to metals finishing sludges. The constituents are bound into a solid that is resistant to leaching. The most common are lime/pozzolan and Portland cement based (Cheremisinoff, 1988).

It would not normally be economically feasible for a surface finishing company to operate it own stabilization plant. Most countries therefore have or are establishing hazardous waste treatment facilities.

There are a few hazardous waste disposal facilities in Canada. The Alberta Special Waste Treatment Centre in Swan Hills, Alberta, which opened in 1987, has facilities for treating and disposing of hazardous wastes. The facility is part of the Alberta Hazardous Waste Management Program which includes new legislation covering disposal of hazardous wastes (Zeiss, 1989)

The Stablex Company in Qu?bec has a plant that can handle inorganic wastes and Tricil (Sarnia) Ltd. has a plant in Ontario that can handle organic and inorganic hazardous wastes (EPS 2/SF/1 1987). The Ontario Waste Management Corporation is planning to construct a hazardous waste treatment and disposal facility near Smithville, Ontario

(OWMC, 1989) and the Manitoba Hazardous Waste Management Corporation has a proposal to construct a central treatment facility for Manitoba.

Hazardous wastes have to be trucked to the treatment facilities, which charge for their services. Charges are usually based on the types and quantities of wastes. Some companies also operate mobile hazardous waste disposal facilities, which are usually some form of incinerator or pyrolysis system. The metals content of sludges from metals finishing operations would not make them amenable to most of the existing mobile systems.

Paint sludges from surface finishing operations contain potentially hazardous solvents. A method of reducing the solvent content to zero and turning paint sludge into a powder of cured paint resin, in which heavy metals are encapsulated has been developed by Haden Drysys Environmental Limited (Product Finishing, 1989). The powder can be recycled into a variety of secondary coatings such as underbody paints and sealers, or can be safely landfilled At one car manufacturing plant in the U.S., a full scale "DryPure" system reduces the volume of sludge by over 90% to the final DryPure powder.

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CHAPTER SIX

CHEMICAL INDUSTRIES

The fifty companies identified as major polluters in the St. Lawrence River system are classed as follows (Centre Saint Laurent, 1989):

- Petroleum industry (3 companies)
- Chemical industries (13 companies)
    - Primary petrochemical (4 companies)
    - Secondary petrochemical (3 companies)
    - Explosives (1 company)
    - Inorganic chemicals (5 companies)

As synthetic organic chemicals are derived from petroleum, natural gas and coal, and as the waste products are similar, waste technologies for petroleum refining and for organic and petrochemical industries will be discussed in the same section.

Petroleum refinery effluents are regulated under Petroleum Refinery Effluent Regulations and Guidelines (EPS 1-WP-74-1, 1974). Under these, the following are prescribed as deleterious substances:

- oil and grease
- phenols
- sulfide
- ammonia nitrogen
- total suspended matter
- any substance capable of altering the pH of liquid effluent or once-through cooling water

Wastes from the petroleum refining and petrochemical industries may contain heavy metals and cyanides which are restricted under the Fisheries Act.

The Transportation of Dangerous Goods Act applies to the transportation of hazardous chemicals listed under the Act. A number of organic chemicals in concentrations of greater than 100 ppm are classed as hazardous substances under the act. These include trichloroethane, trichloroethylene, benzene, toluene, xylene. PCBs in excess of 50 ppm are also classified as hazardous materials. The Environmental Contaminants Act regulates the maximum concentrations of chlorinated biphenyls (PCBs) released to the environment. This affects thermal treatment technologies for destruction of PCBs.

In Ontario, petroleum refining effluent guidelines are being introduced under the Municipal/Industrial Strategy for Abatement (MISA) program. A list of priority pollutants has been compiled and refineries in Ontario have been monitoring their effluents for a year. From the data gathered, draft guidelines have been drawn up for review and discussion. These will form the basis of new legislation. Similar monitoring and review processes are in progress for the organic and inorganic chemicals sectors.

In 1987, the United States announced stringent standards for the organic chemicals, plastics, and synthetic fibers (OCPSF) industry category that require pretreatment of wastewaters prior to discharge into publicly-owned treatment works. Many of the standards promulgated for 47 pollutants are below 500 micrograms/l and for some the standards are of the order of 19 micrograms/l.

Many of the waste products of the petrochemical and organic chemicals industry are in the Resource Conservation Recovery Act (RCRA) list of hazardous wastes. Wastewaters and sludges containing RCRA listed compounds must be treated prior to land disposal.

PETROCHEMICAL/ORGANIC CHEMICAL INDUSTRY

Petroleum refineries process crude oils to produce a variety of petroleum products. In the refinery, crude oil is physically separated by distillation into fractions of different molecular weights. These fractions are then converted by chemical processes such as catalytic cracking, reforming, catalytic isomerization, polymerization, and alkylation to form other intermediate or final products, which can include, gasoline, fuel oils, lubricating oils, greases, waxes, asphalts, and petrochemicals or petrochemical feedstocks that form the raw materials for products manufactured by other industries.

The petrochemical/organic chemicals industry is complex because of the variety of products and processes used to produce intermediate and final products. Wastewater treatment is also complex and often has to be tailored to the specific chemicals produced as by-products of the manufacturing processes.

Primary petrochemicals are ethylene, propylene, butadiene, butylenes, benzene, toluene, and xylene (MISA 1988). Fuel co-products of petrochemical production include synthetic natural gas, liquefied petroleum gas, gasoline components, diesel fuel, home heating oil, and heavy residual fuel oil.

Other organic chemicals are produced through chemical reactions and purification. The raw or feedstock materials must be prepared or purified prior to chemical reaction. This stage can include distillation, vaporization, heating, compressing, and various chemical or physical purification processes.

The feedstocks then usually undergo reaction, often in the presence of a catalyst. In the reaction phase, in addition to the desired product, there are usually a number of by-products that must be separated by processes such as condensation, distillation, or absorption. Impurities remaining can be removed by processes such as distillation, extraction, crystallization, desulfurization, denitrification, or other physical or chemical means.

Waste Minimization

Waste minimization practices include source reduction, process changes, recycle/reuse, and waste exchange.

Source reduction

Source reduction is any onsite activity that reduces the volume or hazard of waste generated at a facility. Source reduction activities include raw materials substitution, product reformulation, process redesign/modernization, and waste segregation (Breton et al., 1988).

Raw materials substitution from a source material that produces a hazardous waste to one that produces a less hazardous or more easily treated waste may be an option in some chemical processes. Use of less hazardous chemicals in final products is also an alternative. For example, efforts are being made to find substitutes for chlorofluorocarbons (CFCs), the chemicals that deplete the earth's ozone layer. CFCs were used as solvents in the metals cleaning industry. A new organization, the Industry Cooperative for Ozone Layer Protection has been formed to work with the U.S. Environmental Protection Agency to reduce and eliminate the use of CFCs as solvents. Substitutes for PCBs are also the focus of some research.

Process changes

Modification in production processes to reduce pollution include good housekeeping to reduce chemical spills, water reuse, optimizing use of raw materials through process control, and modification of production processes to increase efficiency, reduce by-products, and produce more easily treatable pollutants.

Processes can be redesigned for raw materials substitution and recycling. Other changes in process technologies include changing from a wet to a dry process, or substitution of water as a solvent in a reaction or purification step where appropriate.

Toomey and Yu (1989) discuss electrolysis as a method for making specialty organic chemicals. Advantage of electrolysis include low capital costs, low cost redox reagent, broad applicability, and less pollution than most competing processes. Disadvantages include production is usually limited to 10,000 m.t./year, the necessity for new plant, problems in identifying candidate products, electrolyte disposal and reuse, and the fact that the process crosses traditional educational disciplines. The authors outline some of the considerations in identifying candidate products, designing the electrochemical cell, the plant design and scale up problems that may be encountered.

Recycle/Reuse

Segregation of wastes for separate treatment enables some products to be recovered or recycled, as well as the use of separate technologies to remove specific contaminants. If wastes are mixed, they are usually more difficult to treat.

Some waste streams can be recycled after removal of contaminants, and some products can be recovered from wastewaters and sludges, depending on the concentration and other impurities in the waste. Depending on the purity, by-products from chemical processes can sometimes be used as feedstock by the company to make other chemicals, or sold to another company for use in chemical or manufacturing processes.

Waste Exchange

Based on the principle that what is garbage to one person might be valuable to another, a number of public and private waste exchange programs are operating in the United States and Canada, as well as in other industrialized countries. By-product chemicals are among the wastes exchanged through these programs. The waste producer notifies the exchange of by-product chemicals that cannot be used by the company. Other companies notify the exchange of chemicals they are looking for. Products available or wanted are listed in bulletins and circulated to subscribers. The exchange will match up potential sellers with potential buyers. A fee may be involved. In Canada, there is the Canada-Waste Materials Exchange which produces a regular bulletin of waste materials and the Ontario Waste Exchange operated by the Ontario Waste Management Corporation. Exchanges are also in contact with each other for listings of products wanted or available.

Waste Treatment Technologies

Pollutants in the petro/organic chemical industries include reaction by-products, reactor wash water, water used as a medium in surge-pressure emulsions, cooling water, condensates, air purification systems, catalyst regeneration, and drainage water from production, storage and transfer areas.

By-products that cannot be utilized, and contaminated process materials and sludges are treated as wastes and must be disposed of. In the past, much of this waste was put in storage tanks and buried in chemical dumps on the company sites. Chemicals leaching from tanks into the ground and through the groundwater system are the cause of major pollution problems in industrialized countries. In the United States, the Environmental Protection Agency's Superfund Innovative Technology Evaluation (SITE) program was established to develop technologies to clean up these hazardous waste sites. Many of the technologies that have been developed to treat organic chemicals in these sites can also be used to treat wastewater and sludges from organic chemical manufacturing operations.

Over 75 percent of the water in the chemical industry is used for cooling. The remainder in used in production processes, and for cleaning reaction and storage vessels. Water treatment technologies in the petro/organic chemicals industry include pretreatment for sulfide reduction, predigestion, biological oxidation in oxidizing or activated sludge tanks, and sludge treatment.

Best available treatment technologies for metal/cyanide containing wastes (Palmer et al, 1988) are applicable to appropriate waste streams and sludges from petroleum refining and organic chemical operations. Proven, and recovery treatment technologies for halogenated organic containing wastes are outlined in "Halogenated-Organic Containing Wastes: Treatment Technologies" by Surprenant et al. (1988). Treatment for halogenated and non-halogenated organic solvents are discussed in "Treatment Technologies for Solvent Containing Wastes" (Breton et al., 1988).

The United States Environmental Protection Agency Best Demonstrated Treatment Technologies (BDAT) for organic chemical industries include:

> EPA/530/SW-88/031A "Best Demonstrated Available Technology for K015. Final Report", August 1988. K015 waste is specifically generated by the organic chemicals industry and is listed as "still bottoms from the distillation of benzyl chloride". The waste contains high concentrations of organic compounds, low suspended solids, and has a low water content.
>
> EPA/530/SW-89-017D. "BDAT Background Document for K043 Proposed". December 1988. K043 waste is 2,6-dichlorophenol waste from production of 2,4-D and contains volatile organics, semi-volatile organics, dioxan and furan.
>
> EPA/530-SW-89-017E. "BDAT for Phthalate Wastes Vol. 1". 1988. These wastes include distillation light ends from production phthalic anhydride from naphthalene or from ortho-xylene, plus various other phthalate-containing wastes.
>
> EPA/530-SW-89-017F. "Background Document for Organophosphorous Wastes". 1988 These are wastes from the production of phorates which are used in organo-pesticide production.
>
> EPA/530-SW-89-017I. "Proposed BDAT Background Document for F024". 1988. F024 wastes include, but are not limited to, distillation residues, heavy ends, tars and reactor cleanout wastes from production of chlorinated hydrocarbons having

carbon content from 1-5, utilizing free-radical, catalyzed processes.

EPA/530-SW-88-031C. "BDAT Background Document for K048, K050, K051, K052". 1988. K048 is dissolved air-flotation float, K049 is slop oil emulsion solids, K050 is heat exchanger bundle cleaning sludge, K051 is API separation sludge and K052 is tank bottoms (leaded), all from the petroleum refining industry.

EPA/530-SW-88-031B. "Background Document for K016, K018, K019, K020, K030". 1988. K016 is heavy ends or distillation residues from production of carbon tetrachloride, K018 is heavy ends from the fractionation column in ethyl chloride production, K019 is heavy ends from distillation of ethylene dichloride production, K020 is heavy ends from distillation of vinyl chloride in vinyl chloride monomer production, and K030 is column bottom or heavy ends from combined production of trichloroethylene and perchloroethylene production

EPA/530-SW-89-017J. "Proposed BDAT Background Document for Wastes from Production of Dinitrotoluene, Toluenediamine, and Toluene diisocyanate, K027, K11-K116, U221 and U223", December 1988.

EPA/530-SW-88-031G. BDAT Background Document for K103 and K104". K103 is process residues from aniline extraction from production of aniline and K104 is combined wastewater streams generated from nitrobenzene/aniline production.

EPA/530-SW-88-031J. BDAT for K101 and K102 Low Arsenic Subcategory". 1988 K101 is distillation tar residues from the distillation of aniline-based compounds in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds, and K102 is residue from use of activated carbon for decolorization in the production of veterinary pharmaceuticals from arsenic or organo-arsenic compounds.

EPA/530-SW-88-031O. "BDAT for K001". 1988. K001 is bottom sediment sludge from treatment of wastewaters from wood preserving processes that use creosote and/or pentachlorophenol

EPA/530-SW-88-031Q. "BDAT for K022". 1988. K022 is distillation bottom tars from production of phenol/acetone

EPA/530-SW-88-031S. "BDAT for K099". 1988. K099 is untreated wastewater from production of 2,4-D.

Wastewater treatment technologies used for chemical industry wastewaters include aeration, settling tanks, grit collection, oil/water separation, precipitation, biooxidation, digestion, ion exchange, ozonation, reverse osmosis, coagulation, flocculation, oil skimming, ponding, and diffusion.

Petrochemical wastewaters contain a wide range of organics in concentrations ranging from several hundred mg/l to several thousand mg/l, a significant part of which is non-biodegradable in conventional biological wastwater treatment processes (Eckenfelder, 1987). State-of-the-art treatment processes include removal of heavy metals by oxidation/reduction, precipitation and filtration; treatment of organics by chemical oxidation (e.g., hydrogen peroxide); wet air oxidation and granular carbon adsorption; removal of volatile organics by air or steam stripping; and biological treatment by activated sludge process. Eckenfelder suggests that an area for further study is to define the effect of biological treatment on aquatic toxicity and to optimize the biological process for aquatic toxicity removal.

The degree of adsorption of organic compounds on activated carbon is related to the molecular weight, octanol water partition coefficient, or solubility of the organic molecule (Bowers et al., 1988). Powdered activated carbon is generally added to a biological aeration tank (PACT) process. Granular activated carbon can also be used but surface area for adsorption is less. Toxic organics are selectively removed from the wastewater, thereby reducing the toxicity of the sludge, and carbon can be regenerated.

Guarino et al. (1988) discuss the results of a study on use of activated carbon for treating petrochemical wastewaters to reduce COD levels. Pilot tests using powdered activated carbon (PAC) and granular activated carbon (GAC) showed that the GAC system produced far superior results.

In wet air oxidation, organic compounds are oxidized at elevated temperatures and pressures to produce, typically, acetic acid and carbon dioxide. Vorstman and Tels (1987) studied a wet air oxidation process to treat phenol-containing wastewaters. In the wet-air oxidation process, the components are oxidized in a liquid water phase at elevated temperatures by oxygen that is provided by compressed air. The components to be oxidized may be dissolved or present as suspended solids. The authors used a flow through reactor at temperatures between 230 and 280 C. Phenol conversions of between 80% and 99.6%, and COD conversions of 68% to 96% were achieved. The results were comparable to previous work on batch reactors.

Biological Treatment

Experimental studies on the use of a fixed-film reactor to treat petroleum refinery effluents showed that up to 80% of COD was removed and concentrations of oil, sulfides, and ammonia were considerably reduced (Hamoda and Al-Haddad, 1987). Addition of alum at 100 mg/l for coagulation and flocculation prior to biological treatment reduced the levels of some waste constituents resulting in improved COD removal. However, operating costs were higher when alum is used.

Tokuz (1988) studied the use of rotating biological contactors for treating refinery and petrochemical wastewaters containing chlorinated phenols. He found that removal efficiencies were higher when the hydraulic loading (flow rate) was kept as low as possible (most efficient at 0.04 m3/m2.day) and that removal rates declined as hydraulic loading was increased.

The application of rotating biological contactors to industrial and hazardous liquid wastes is discussed by McKim (1987) who notes that substances that cannot be biologically degraded by a single species of microorganism can often be degraded by combinations of microorganisms. Efficiency depends on organic and hydraulic loading, disk rotation, size and configuration, operating temperature, and staging of reactors. Chemical oxygen demand (COD) rates of 54-63%, BOD removal rates of up to 95%, phenol removal rates of 61 to greater than 99%, and formaldehyde removal rates of up to 99% have been achieved for wastewaters from phenol-formaldehyde resin manufacture. COD and BOD removal rates of 94-96% and 97-99% respectively have been achieved for organic chemical manufacturing where reaction by-products were aldehydes, cyanide, formate, ammonia, etc. The author notes that wastewaters must be fully characterized with respect to nutrients and potentially toxic compounds and that pilot studies on specific wastewaters are usually required.

Woodward (1988) also emphasizes the need to characterize wastewaters to assess the feasibility of biodegradation processes to treat wastes and outlines the procedures for biodegradation feasibility studies for hazardous waste mixtures.

Gledhill et al. (1988) discuss experiments using anaerobic technology on a variety of chemical industrial wastewaters at the Monsanto Company to determine whether any waste streams were candidates for anaerobic treatment. The wastes studied were in the "hard to treat" category. The only waste stream tested that showed amenability to anaerobic treatment was an acetic acid process waste. Other waste streams tested were a pesticide waste and a fiber intermediate waste stream with high organic loadings but neither were deemed suitable for treatment. Despite limited success, Monsanto is continuing research into anaerobic treatment as an alternate to aerobic treatment.

Ng et al. (1988) conducted tests on a variety of wastewaters from organic chemical production to determine the feasibility of anaerobic treatment. In bench scale tests, COD removal efficiencies were greater than 85% for some process wastes. Some of the wastes required neutralization and alkalinity supplementation to ensure high rate treatability and process stability.

Speece (1988) discusses some recent advances in anaerobic treatment of industrial wastewaters and predicts that developments in biomass separation/retention and specific trace nutrient supplementation over the next five years will increase process efficiency.

Halogenated Organics

Electrochemical treatment is being studied as a method of treating halogenated organics in wastewaters in the chemical processing industry (Schmal et al., 1988). Laboratory studies of representative organohalogens from the Europen Community list of priority compounds is being conducted to determine their suitability for electrochemical treatment. The process is intended for use on toxic process wastewaters at the source of the process, before mixing with waste waters from other processes. The experiments showed that it is possible to remove all the chlorine atoms from the organic molecules in aqueous solution. Dehalogenation results in decreased toxicity and makes the wastewater amenable to further biological treatment. The method is also considered to be cost effective when compared with carbon adsorption.

Chlorinated organic wastes include polychlorinated biphenyls (PCBs), dioxins, and other carcinogens. Physical treatment technologies for chlorinated organic wastes include distillation, evaporation, steam stripping, liquid-liquid extraction, carbon adsorption, resin adsorption (Surprenant et al., 1988).

These technologies usually do not destroy the waste constituents but provide opportunities for recovery of valuable components.

Chemical treatment processes for halogenated organics include wet air oxidation, supercritical water oxidation, other chemical oxidation processes, and dechlorination processes (Surprenant et al., 1988).

Biological treatment processes include activated sludge, aerated lagoons, aerobic digestion, anaerobic digestion, trickling filters, rotating biological contactors and composting. The efficiency of biological processes for halogenated organics is not high because many halogenated compounds are not readily biodegraded by naturally occurring microorganisms. Research, however, has resulted in the development of some microorganisms that will biodegrade halogenated organics.

Thermal Technologies

Thermal treatment technologies are among the best demonstrated and available technologies for treatment of halogenated and other organic wastes (Surprenant et al., 1988). Various types of incinerators are available for treating different types of liquid, sold and semisolid wastes. In these, the complex organic molecules are broken down into simple hydrocarbons, carbon dioxide and water, and, in the case of halogenated organics, HCl. In general, halogenated organics are difficult to incinerate. A major problem with incineration is the potential of toxic air emissions if degradation is incomplete.

Emerging treatment technologies discussed by Surprenant et al. (1988) include circulating bed combustion which is an innovation in fluidized bed combustion incineration; catalytic fluidized bed incineration where catalysts are used to reduce the operating temperatures of the incinerators; molten glass incinerators which are electric furnace reactors in which molten glass is used to destroy hazardous organic wastes and to encapsulate solid by-products; molten salt incinerators that involve the combustion of waste materials in a bed of molten salt; pyrolysis processes in which organic constituents are decomposed by applying sufficient thermal input to destroy molecular bonds; and in-situ vitrification.

The major problems with chlorinated organics such as PCBs, dioxins, and furans is obtaining a high enough reaction temperature to break the bonds in the complex molecules. Some incinerators cannot achieve high enough temperatures to destroy PCBs. Pyrolysis systems, which can achieve operating temperatures of up to 12,000 C show greater promise for destroying complex organic molecules. A mobile plasma pyrolysis system developed by Pyrolysis Systems Inc. in Kingston, Ontario, is capable of destroying PCBs with a 99.99999% efficiency. The system has been further developed in a joint venture with Westinghouse Electric Corporation and tested at pilot and full-scale with PCB liquid wastes.

Piersol (EPS 3/HA/5, 1989) evaluated mobile and stationary facilities for the destruction of PCBs. He concluded that rotary kiln incineration with flue-gas treatment is preferable for commercial stationary PCB destruction as it can also handle other industrial organic wastes. Rotary kilns are being successfully operated in Europe and the United States. Solvent extraction is being developed by six U.S. companies for application to PCB-contaminated solids and is considered to be a promising technology. Solvent extraction is classed as a BDAT for some of the EPA RCRA list wastes cited earlier. Mobile technologies evaluated include the plasma pyrolysis system discussed earlier and is regarded as a "promising technology".

Various technologies for destruction of solid organic wastes have been developed and tested under the U.S. Environmental Agency's SITE program (see for example EPA, 1989). These include incineration, pyrolysis, and in-situ stabilization techniques. Many of the technologies are or may be applicable to process sludges.

Pancoski et al. (1988) discuss their on-going investigations into stabilization of petrochemical sludges. Alternatives investigated included incineration, bioreclamation, vitrification, and stabilization agents such as clays, cements, silicates, fly-ash, and diatomaceous earth.

Other Technologies

Studies at the U.K. Atomic Energy Authority's Dounreay facility in Scotland indicate that electrochemical oxidation shows promise as a viable alternative to incineration for destroying toxic chemicals (O'Sullivan, 1989). The process has been tested on PCBs, pesticides and other hazardous organics, converting them to carbon dioxide and water.

Swallow et al. (1989) discuss field testing of a pilot scale process to destroy hazardous organic waste materials. The so-called MODAR process, developed by MODAR Inc., utilizes an oxidation reaction to convert organic compounds to carbon dioxide, water and, when heteroatoms are present, inorganic compounds. The reaction is carried out in a flowing aqueous stream heated and pressurized above the critical point of water. A pilot scale field test showed that the process could destroy organic compounds in toxic waste materials with greater than 99.99% efficiency.

Sutton and Hunter (1989) discuss the destruction of hazardous organic wastes by solar energy. The process uses an innovative solar power system design called the Unified Heliostat Array to supply highly concentrated solar energy to a photochemical reactor. The photons of solar radiation bombard the waste at elevated temperatures and reduce it to harmless compounds. The process has been used to decontaminate soil from hazardous waste sites containing PCBs and polychlorinated dibenzo-p-dioxins (PCDDs) with 99.99999% efficiency.

A number of enhanced oxidation systems that use artificially produced ultraviolet light to destroy halogenated organics are also available (Cater and Buckley, 1990; EPA, 1989 p. 59). In the Rayox hydrogen peroxide/uv system, toxic chlorinated and other organic material has been successfully demonstrated to remove PCBs and TCE from groundwater and to treat process effluent from creosote plant wastewater (Stevens, 1989).

Delchad (1988) discusses the application of chemical demulsifiers in treating oily sludges for volume reduction, oil recovery and to render the wastes non-hazardous. Chemical demulsification can be used as a preliminary or adjunct to other sludge handling techniques such as separation or filter processes, and to pretreat sludges prior to biological or solvent extraction processes.

Complex Wastewaters

The U.S. EPA has introduced stringent pretreatment standards for organic chemicals, plastics and synthetic fibers (OCPSF) with the compliance deadline as November 1990. Yen and Abrahams (1989) outline a complex project undertaken at one plant that manufactures over 900 organic chemical products to enable the plant to comply with the regulations.

The plant has over 200 wastewater streams with 75% falling into the OCPSF category. Most of the contaminants are organic solvents but there are a variety of other impurities including surfactants and monomeric organics.

Source control to reduce the volume (by 50%) and strength of the wastewater and to eliminate contaminants that could interfere with downstream treatment processes are being studied. Materials recovery, chemical substitutions, substitution of dry for wet processes, waste segregation, and containment of material transfer stations to reduce contamination in stormwater are all being considered as part of the overall strategy. Treatment technologies that can be used at sources or at end-of-pipe that are being evaluated include air and steam stripping, solvent extraction for phenols and other low volatility materials, foam fractionation for removal of surfactants, UV/peroxide oxidation for polishing waste streams, carbon adsorption as a polishing step rather than primary removal step because of the high concentrations of organics, and resin adsorption, for the same reasons, as a polishing step. Biological oxidation using activated sludge or powdered activated carbon were also considered but biological sludge disposal and space problems have led to consideration of this process being dismissed.

A pilot plant for pretreatment to remove suspended solids, primary treatment for air and steam stripping, and a polishing step has been constructed.

Because of the large number and variety of wastes it was necessary to characterize all the streams and develop the optimum source control and treatment processes.

To find ways of meeting the same OCPSF guidelines, Amend et al. (1988) of Schenectady Chemicals Inc. studied sequencing batch reactors (SBRs) and found them to show promise as a treatment method. Sequencing batch reactors are batch versions of the activated sludge process. In a flow through activated sludge system, the reaction step is physically segregated from final clarification. In the SBR, the reaction and clarification steps are conducted in the same tank on a timed sequential cycle basis. The phases are fill, react, settle, decant and idle. Advantages over continuous flow through systems include flow and organic load equalization, demand controlled energy consumption, ability to handle shock organic and hydraulic loads, and potentially lower operating costs. An extensive pilot scale treatability program showed that conventional flow through and fixed film aerobic treatment could not consistently treat even the least variable of the potential wastewaters to the required limits. The sequencing batch reactor version of activated sludge technology however, consistently produced effluents that met the requirements. The system is capable of treating much higher influent concentrations of phenols and BOD than is normally present in the company's wastewater. A full scale system is currently being installed.

An Integrated Wastewater Treatment System of the South Petrochemical Complex (acronym SITEL in Portuguese) in Brazil started-up in 1983 and was fully operational by 1985 (Goettems et al. 1987; Simon et al. 1987). Organic and inorganic wastes are separated and pretreated before reaching the complex. Primary treatment consists of equalization and physico-chemical unit operations, secondary treatment is by an activated sludge, extended aeration process, and wastwaters are then routed to tertiary stabilization ponds (tertiary treatment is required by law). Many designers of effluent treatment facilities underestimate the problems of managing the by-products of wastewater treatment, consisting of slurries, sludges, scums, etc. Treatment and final disposal of these at SITEL are discussed by Simon et al. (1987). Some of the solids are treated at a centralized facility for solid wastes.

Another centralized treatment facility for petrochemical wastewaters is described by Franceschi and Nicolosi (1987). The Priolo Associated Biological Plant near Siracusa in Italy treats wastewaters from three major petrochemical plants, three smaller chemical plants and two power plants. Treatment consists of screening, pH correction, equalization and homogenization, denitrification, biological oxidation, and final clarification. Sludge is conditioned with lime, dewatered and then placed in controlled waterproof basins.

INORGANIC CHEMICALS INDUSTRY

The inorganic chemicals companies identified as among the major polluters in the St. Lawrence River System manufacture fireworks and explosives, hydrogen, titanium pigments, coloured pigments, sodium chlorate, phosphorous and phosphates, chloralkali, silicates, hydrogen peroxide, and alum (Centre Saint Laurent, 1989b).

Major pollutants include:

- titanium pigments containing acids, sulfates, iron titanium, aluminum and magnesium
- chloralkali containing chlorine, chlorides, mercury
- explosives containing nitrates, nitrites, acids, COD
- phosphorus, phosphate, NH3, cyanides
- sludges

Many of the discharges are also highly acidic.

Some of the discharges from these industries fall under the Fisheries Act in relation to suspended solids, metals and pH.

The Chlor-Alkali Mercury Liquid Effluent Regulations promulgated under the fisheries act limit the discharge of mercury in liquid effluents to 2.5 grams per tonne of chlorine produced.

McBeath (1985) identified the major priority contaminants from chlor-alkali plants as mercury (from mercury-cell plants), asbestos (from diaphragm-cell plants), priority metals and chlorinated organics.

McBeath (1985) reported significant changes in the chlor-alkali industry production technology since the mid-1970s. Major changes that have been implemented at some Canadian plants include:

- conversion from graphite electrodes to dimensionally stable anodes
- development of treatment processes to eliminate nearly all mercury discharges
- conversion from mercury cells to new ion-exchange membrane technology
- elimination or marked reduction in process wastewaters from diaphragm-cell and mercury-cell plants.

Some wastewater treatment sludges from pigment production, waste water treatment sludges from explosives manufacturing, and mercury are on the U.S. EPA RCRA metal/cyanide waste list and must be treated prior to land disposal.

Treatment Technologies

As with other industries, treatment technologies include waste minimization, materials substitution, process changes to cleaner technologies or to technologies that produce more easily treatable wastes, and recycling/reuse where possible.

Waste treatment includes separation of process waste streams to enable specific treatment processes to be applied to more concentrated solutions; metals extraction and recovery where possible from waste waters and sludges; and analysis of all plant waste streams to determine the most appropriate treatment for the concentrations and types of contaminants.

The Environmental Protection Agency's best demonstrated treatment technology reports applicable to inorganic chemicals industries of concern include:

> EPA/530-SW-89-017G. "BDAT Background Document for Inorganic Pigment Wastes." 1988. This document covers wastewater treatment sludges from the production of chrome yellow and orange, molybdate orange, chrome green, chrome oxide green and iron blue pigments.
>
> EPA/530-SW-88-031F. "BDAT Background Document for K071, K073 and K106". 1988. These are chlorine industry wastes. K071 is brine purification muds from the mercury cell process in chlorine production, where separately pre-purified brine is not used; K073 is chlorinated hydrocarbon waste from the purification step of the diaphragm cell process using graphite anodes in chlorine production, and K106 is wastewater treatment sludge from mercury cell process in chlorine production.
>
> EPA/530-SW-88-031J. "BDAT for K046 nonreactive subcategory". 1988. K046 is wastewater treatment sludges from the manufacture, formulation and loading of lead-based initiating compounds.
>
> EPA/530-SW-88-031N. "BDAT for K086" 1988. K086 is solvent wash, solvent sludge, and caustic water treatability groups for cleaning tubs and equipment used in formulation of ink, pigments, driers, soaps and stabilizers containing chromium and lead.
>
> EPA/530-SW-89-017J. "Proposed BDAT Background Document for Wastes from Production of Dinitrotoluene, Toluenediamine, and Toluene Diisocyanate, K027, K111-K116, U221, U223. 1988.

Many of the wastes from inorganic chemicals industries contain acids and are therefore classed as corrosive wastes. Treatment and recovery technologies for corrosive -containing wastes are discussed by Wilk et al. (1988). These include neutralization followed by physico/chemical processes such as evaporation, crystallization, ion exchange, electrodialysis, reverse osmosis, and solvent extraction, and thermal decomposition, for separation and recovery.

Assano and Olper (1989) describe a process for treating sulfuric acid waste liquids with recovery of anhydrous sodium sulfate at a lead recovery and refinery plant in Mississauga. The process is based on neutralization followed by evaporative crystallization. Detergent-grade sodium sulfate is recovered as a by-product and sold.

McBeath (1985) identified the following treatment regime to treat liquid effluents from mercury-cell chloralkali plants:

- filter brine saturator and treatment solids from the brine, wash to remove residual brine containing soluble mercury and recycle filtrate and wash water
- remove mercury from brine saturator and treatment solids prior to landfilling
- segregate contaminated wastewaters and recycle or reuse if possible; sulfide treatment of mercury-containing wastewater and high pressure filtering to remove mercury; recovery of mercury from treatment solids
- filter caustic solutions to remove mercury
- settling system for combined process, cooling and storm wastewaters; pH adjustment and dechlorination using peroxide or sulfur dioxide

Many of the treatment technologies for heavy metals and chlorinated organics are also applicable to appropriate wastes from inorganic chemicals manufacture.

Treatment technologies applicable to pigment production wastes include high temperature metals recovery, reuse/recycle and stabilization.

Demonstrated technologies for chlorine industry wastes are (EPA/530-SW-88-031F):

- acid leaching
- chemical oxidation
- sludge dewatering combined with acid or water washing
- stabilization
- retorting

Berkowitz (1988) reports the use of solvent extraction for the removal of blasting oil (mixture of nitroglycol and nitroglycerine) from wastewater from the production of explosives by nitration of polyalcohols. The solvent used was dinol, a complex mixture of dinitrotoluenes, nitroxylenes and impurities such as phenols, that is also produced from the nitration plant. The extraction is carried out at elevated temperatures. A full scale plant is operating in Norway to treat a flow of 1500L/h of wastewater. The extract solution is recycled to the production process. Dinol and sludge are settled out in a retention tank and the nitrate containing raffinate can be used in production, treated biologically, or purified.

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CHAPTER SEVEN

CONCLUSIONS

Process and waste treatment technologies to reduce or eliminate waste discharges into the St. Lawrence River System, are to a great extent industry and company specific. Both process changes and waste treatment can cost in the millions of dollars and therefore before any changes are made it is necessary to conduct a careful analysis of current production and waste control methods to identify areas where changes can be incorporated.

Separation of waste streams for treatment is generally better than treating waste streams together. The wastes are more concentrated and specific treatment can be determined for each waste stream. It is always necessary to analyse each waste stream over a period of time to determine any changes in contaminants that may occur and to determine the treatment that will be able to handle maximum amounts of contaminant.

In this report we have briefly described the main processes used in the industry sectors and waste treatment technolgies available. Current research on new technolgies is also discussed. However, the applicability of any technology to the operations of a particular company can only be determined after analysis of the company's present operations and waste streams.

New facilities can easily incorporate state-of-the-art process and control technologies that will make efficient use of resources and minimize waste. It is not so easy for older facilities to incorporate such changes.

Waste minimization processes and practices include source reduction, recycling and reuse.

In some industries, for example, the pulp and paper industry, new bleaching processes that do not use chlorine and therefore eliminate chlorinated organics such as PCBs and dioxins from the waste have been installed by some companies. New dry-handling methods for logs reduce water requirements, and changes in pulping processes reduce or eliminate the use of potentially harmful chemicals or result in contaminants that are easier to treat. In metallurgical and metals finishing operations it is possible to incorporate technology to recover metals from waste process solutions so that they can be reused. The treatment costs can be recovered through reduction in quantites of process solutions necessary. Slightly contaminated wastewaters can sometimes be used for some wash cycles by modifications to the process design.

Product substitution includes ceasing manufacture of hazardous chemicals such as CFCs or PCBs and finding other chemicals that will perform the same functions but that do not contribute to environmental pollution, and replacing products containing highly toxic metals such as hexavalent chromium with non-harmful products.

Waste treatment technolgies vary. Generic technologies identified must be adapted to the specific waste streams of the company as many factors such as acidity, alkalinity, presence of other contaminants, etc. can affect the efficiency of a treatment technology.

Sources Of Information

In discussions with persons who know the various industries and their associated waste problems, we were told that the industry people were well aware of new developments in processing and in waste management. Some companies have, over the years, incorporated new technologies into their existing processes a bit at a time and these companies will have fewer problems in complying with new effluent regulations. Other companies that have not invested gradually in new technologies will have more difficulty and much greater expense in complying with regulations. We were told that some companies do not even have primary treatment for their wastes but discharge directly into water systems.

Sources of information on waste treatment technologies in Canada include Environment Canada, Environmental Protection Service which is responsible for developing effluent limits and monitoring compliance. Numerous reports on various aspects of wastewater treatment and on the status of pollution control in various industrial sectors in Canada have been published by the Division.

Organizations such as the Wastewater Technology Centre and the Provincial Research Organizations have been involved in developing process and wastewater treatment technologies with companies across Canada either at the request of the companies or by initiating the projects themselves and finding industrial partners.

In 1986, the Ontario Government released a white paper entitled "Municipal-Industrial Strategy for Abatement (MISA)", a program to reduce the flow of toxic chemicals into Ontario's waterways (Ontario Ministry of the Environment, 1986). Under the MISA program, the Provinical Government is developing pollution control regulations for the following industrial sectors: petroleum, organic chemical, iron and steel, inorganic chemicals, pulp and paper, mining, metal casting, electric power, and industrial minerals.

The stages in the MISA program are:

- Pre-regulation phase consisting of consultation and monitoring to provide data and information for development of practical regulations for each sector
- Monitoring regulations for each sector based on the pre-regulation monitoring data
- Effluent limits regulations based on monitoring data and an assessment of pollution control technology. Limits will be based on best available technology
- Abatement and enforcement through implementation of the monitoring and effluent limit regulations.

Industry is involved in all aspects of the process and draft legislation will be discussed with industry prior to being enacted. Industry sectors are required to monitor their effluents for a year. Draft legislation is then drawn up. Monitoring is complete in the petroleum refining sector and draft legislation is being reviewed. Other sectors are still in the monitoring phases. Best available technology economically achievable (BATEA) will be established by MISA. A spokesperson at MISA indicated that MISA personnel involved in the various industry monitoring programs will be experts in environmental technologies for their industrial sectors in about two years, if they are not already experts.

The procedures used by the U.S. Environmental Protection Agency in determining Best Demonstrated Available Technologies will form the basis for the MISA BATEA determinations.

In the United States, oganizations such as the Risk Reduction Laboratory in Cincinnati and other organizations that work with the EPA are sources of information on waste treatment technologies.

A Waste Reduction Institute for Scientists and Engineers (WRISE) has been created jointly by the EPA and the University of Cinncinnati to conduct reviews of pollution prevention techniques and recommend where and how to demonstrate and evaluate innovative methods of reducing waste.

In Europe, the NETT European Network (Network for Environmental Technology) was set up as an independent non-profit making international body to promote exchanges of know-how on environmental technologies between companies and bodies using clean technologies and producing little waste. It is designed to bring together researchers in universities, research institutes, scientific associations etc. and suppliers and users of goods and services in an effort to stimulate adoption of clean and low-waste technologies in the European Community.

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