

# Factor 2 Analysis: Technology Advances and Process Changes

# Status of Screening Level Review Phase

**U.S. Environmental Protection Agency** 

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#### **EXECUTIVE SUMMARY**

In November, 2002, the Environmental Protection Agency (EPA) announced the draft *Strategy for National Clean Water Industrial Regulations* ("draft *Strategy*). The draft *Strategy* outlines a process that EPA proposes to use to develop Effluent Guidelines Plans. The process will allow EPA to identify existing effluent guidelines the Agency should consider revising or industrial categories for which the Agency should consider developing new effluent guidelines. EPA used this draft *Strategy* to develop the preliminary Effluent Guidelines Program Plan for 2004/2005. The draft *Strategy* and preliminary Effluent Guidelines Program Plan for 2004/2005 described four factors that the Agency would consider during its process.

This report discusses the status of the EPA's initial screening level review phase for Factor 2, Technology Advances and Process Changes. This factor considers applicable and demonstrated technologies, process changes, or pollution prevention alternatives that can effectively reduce the pollutants remaining in an industry category's wastewater and thereby substantially reduce any identified risk to human health or the environment associated with those pollutants.

The screening level review phase for this factor intended to focus on readily available information to assess technology advances and process changes. EPA surveyed industryspecific literature to identify technology and process changes or pollution prevention approaches that could reduce wastewater pollutant discharges. EPA is pursuing additional data collection activities to obtain further information about technological advances. EPA is also collecting information through a series of national technology conferences.

A few of the tools and resources discussed here provide information that EPA may not be able to consider in the current cycle of planning. These other tools and resources are discussed here in preliminary terms. They may, however, prove useful for future planning cycles. During the current planning cycle, EPA plans to evaluate all of these tools to determine whether they are appropriate for use in this or future planning cycles.

The initial screening of industrial categories relied primarily on information gathered under Factor 1: Human Health and the Environment (addressing discharge amounts, toxicity and effects) and Factor 4: Efficiency and Implementation (addressing efficiency of the guidelines and NPDES permitting programs, multi-media issues, etc.). Using these two factors EPA identified twenty industrial categories for additional data collection. EPA also set its priorities for additional analyses supporting the final Effluent Guidelines Program Plan for 2004/2005. Specifically, EPA intends to complete a detailed review of the following industries to support the final Effluent Guidelines Program Plan for 2004/2005: Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF); and Petroleum Refining. After considering all available data, EPA may decide to identify one or both of these industries in the final Effluent Guidelines Program Plan for 2004/2005 for effluent guidelines revisions. To the extent possible in the limited time remaining in this planning cycle, EPA will continue to address data gaps and uncertainties affecting EPA's estimates of the potential risks and hazards posed by the remaining industries.

EPA found that gathering the data needed to perform a meaningful screening-level analysis for Factor 2 was much more resource-intensive than anticipated. Data sources in this area are widely scattered and often lack sufficient detail and process specificity to be useful at a screening level. They are better suited to in-depth analysis of specific industries. Factor 2 was considered, to the extent possible, during an additional screening-level step EPA applied to a limited set of industries with relatively high estimates of potential risk to human health or the environment. As discussed in the draft *Strategy* and in the preliminary Effluent Guidelines Program Plan for 2004/2005 this factor will also be considered more extensively in the forthcoming detailed investigations.

#### **1.0 INTRODUCTION**

In November, 2002, the Environmental Protection Agency (EPA) announced the draft *Strategy for National Clean Water Industrial Regulations* ("draft *Strategy*).<sup>1</sup> The draft *Strategy* outlines a process that EPA proposes to use to develop Effluent Guidelines Program Plans. Under the Clean Water Act (CWA), EPA establishes technology-based national regulations, termed "effluent guidelines," to reduce pollutant discharges from industrial facilities to waters of the United States. Section 304(m) of the CWA requires EPA to publish an Effluent Guidelines Program Plan every two years. CWA Section 304(m)(1)(A) also requires EPA to establish a schedule for the annual review and revision of all existing effluent guidelines. Additionally, CWA Section 304(m)(1)(B) requires EPA to identify categories of point sources discharging toxic or non-conventional pollutants for which EPA has not published effluent guidelines.

The preliminary Effluent Guidelines Program Plan for 2004/2005<sup>2</sup> described the four factors EPA considered during its screening-level analyses. Factor 2 (Technology Advances and Process Changes) considers applicable and demonstrated technologies, process changes, or pollution prevention alternatives that can effectively reduce the pollutants remaining in an industry category's wastewater and thereby substantially reduce any identified risk to human health or the environment associated with those pollutants. This memo summarizes the Factor 2 screening level information gathered on some of the twenty industries identified for further data collection. Table 1 lists these twenty industries. See "Description and Results of EPA Methodology to Synthesize Screening Level Results for the Effluent Guidelines Program Plan for 2004/2005," DCN 548, Section 3.0, on how these industries were identified.

<sup>&</sup>lt;sup>1</sup>U.S. EPA, "Draft Strategy for National Clean Water Industrial Regulations," EPA-821-R-02-025, http://epa.gov/guide/strategy/, November 2002.

<sup>&</sup>lt;sup>2</sup>This preliminary Plan was signed by EPA's Assistant Administrator for Water on December 23, 2003. It is expected to be published in the Federal Register on December 31, 2003.

No.	Factor Identifying Industry for Additional Data Collection		Industry	CFR Part
	Factor 1	Factor 4		
1		Х	Canned and Preserved Fruits and Vegetable Processing	407
2		Х	Canned and Preserved Seafood Processing	408
3		Х	Coal Mining	434
4		Х	Coil Coating	465
5		Х	Dairy Products Processing	405
6		Х	Electrical and Electronic Components	469
7	Х		Fertilizer Manufacturing	418
8	Х	Х	Inorganic Chemical Manufacturing	415
9		Х	Metal Molding and Casting	464
10		Х	Mineral Mining and Processing	436
11	Х		Nonferrous Metals Manufacturing	421
12		Х	Oil and Gas Extraction (including coal bed methane development as a potential new subcategory) †	435
13	Х	Х	Ore Mining and Dressing	440
14	Х	Х	Organic Chemicals, Plastics, & Synthetic Fibers (including CFPR operations as a potential new subcategory)	414
15	Х	Х	Petroleum Refining (including petroleum bulk stations and terminals as a potential new subcategory)	419
16	Х		Phosphate Manufacturing	422
17	Х	Х	Pulp, Paper, and Paperboard (Phase II)	430
18	Х	Х	Steam Electric	423
19	Х		Textile Mills	410
20	Х	Х	Timber Products Processing	429

 Table 1: Industries Identified For Further Data Collection

<sup>†</sup> Note: The oil and gas extraction industry (SIC 1311) does not report discharges to TRI and there is very little information in PCS about discharges from these point sources. EPA was able to make order of magnitude estimates of toxic and non-conventional pollutant discharges from coalbed methane extraction operations based on an on-going study with EPA's Denver Office (Region 8).

EPA was able to compile Factor 2 information on the following industries identified in Table 1: (1) Aluminum Manufacturing and Forming; (2) Construction Products; (3) Industrial Organic Chemicals; (4) Oil and Gas Field Services; and (5) Semiconductor Manufacturing. EPA was unable to identify technology advances and process changes for all twenty industries identified in Table 1. EPA anticipates completing these summaries before publication of the final Effluent Guidelines Program Plan for 2004/2005.

The initial screening of industrial categories relied primarily on information gathered under Factor 1: Human Health and the Environment (addressing discharge amounts, toxicity and effects) and Factor 4: Efficiency and Implementation (addressing efficiency of the guidelines and NPDES permitting programs, multi-media issues, etc.). Using these two factors EPA identified the twenty industrial categories for additional data collection (see Table 1). EPA also set its priorities for additional analyses supporting the final Effluent Guidelines Program Plan for 2004/2005. Specifically, EPA intends to complete a detailed review of the following industries to support the final Effluent Guidelines Program Plan for 2004/2005: Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF); and Petroleum Refining. After considering all available data, EPA may decide to identify one or both of these industries in the final Effluent Guidelines Program Plan for 2004/2005 for effluent guidelines revisions. To the extent possible in the limited time remaining in this planning cycle, EPA will continue to address data gaps and uncertainties affecting EPA's estimates of the potential risks and hazards posed by the remaining industries.

EPA found that gathering the data needed to perform a meaningful screening-level analysis for Factor 2 was much more resource-intensive than anticipated. Data sources in this area are widely scattered and often lack sufficient detail and process specificity to be useful at a screening level. They are better suited to in-depth analysis of specific industries. Factor 2 was considered, to the extent possible, during an additional screening-level step EPA applied to a limited set of industries with relatively high estimates of potential risk to human health or the environment.<sup>3</sup> As discussed in the draft *Strategy* and in the preliminary Effluent Guidelines Program Plan for 2004/2005 this factor will also be considered more extensively in the forthcoming detailed investigations.

This report contains information readily available from government sources and industry and other publications. No new data (e.g. from effluent sampling or environmental monitoring) has been generated for this report. Thus, no statements regarding the accuracy, precision, representativeness, completeness, or comparability of the data presented in this report are included.

<sup>&</sup>lt;sup>3</sup>See "Description and Results of EPA Methodology to Synthesize Screening Level Results for the Effluent Guidelines Program Plan for 2004/2005," DCN 548, Section 3.0.

#### 2.0 Factor 2 Information Resources

EPA reviewed several industry- or technology-focused resources to identify additional industrial categories likely to have technology advances or process changes. These three resources are EPA's Office of Compliance Sector Notebooks, industry journals, and industry association publications and web sites, and are discussed in the following sections.

#### 2.1 Office of Compliance Sector Notebooks

The Sector Notebook series is produced by the EPA's Office of Enforcement and Compliance Assurance (OECA) to provide users with a consolidated source of compliancerelated information for specific industry sectors. It is a set of industry profiles containing detailed sector-specific environmental information. Unlike many resource materials, which are organized by air, water, and land pollutants, the Notebooks provide a holistic, "whole facility" approach by integrating manufacturing process, applicable regulations, and other relevant environmental information. Sector Notebooks are available for a total of 23 industry sectors. Each Notebook includes the following information:

- Overview of the industry, including size, geographic distribution, organizational structure, products, economic trends, and financial analysis;
- Description of manufacturing processes, including inputs of raw materials and pollution outputs;
- Summary of chemical releases to the environment;
- Summary of applicable federal statutes and regulations;
- Compliance and enforcement history;
- Review of major legal actions;
- Pollution prevention opportunities;
- Government and industry initiatives for compliance assurance; and
- Resource materials and contacts.

Sector Notebooks may be useful references for a more detailed look at specific industries identified for second-level screening.

#### 2.2 Office of Wastewater Management's Clean Water Act Recognition Awards

The Office of Wastewater Management in EPA's Office of Water runs a program called "Clean Water Act Recognition Awards. This program was formerly National Wastewater Management Excellence Awards Programs. Through this program, EPA recognizes municipalities, wastewater treatment programs, facilities, and individuals on a national level as examples of an outstanding commitment to protect and improve the quality of the nation's waters. The national winners have demonstrated exceptional technological achievements of innovative processes in their waste treatment and pollution abatement programs. National awards are presented for prominent accomplishments in innovative operations and maintenance; exemplary biosolids management; outstanding local pretreatment programs; and creative and cost-effective storm water and combined sewer overflow control programs and projects.

A compilation of winners for the period of 1986 through 2002 is available online at <u>http://www.epa.gov/owm/pdfs/prevwinn86-02.pdf</u>. Although these awards are plant specific, they may provide a starting place for identifying innovative technological advances in wastewater treatment. EPA intends to review the supporting documentation to determine whether this resource can be used in the detailed investigation phase of the current planning process.

#### 2.3 Industry Journals

An important source of information on technology advances and process changes is industry journals and industry-focused literature. The scope of available information made it difficult to utilize this resource in the screening level review phase. However, journals and other literature will be included in the detailed investigation phase of the current planning cycle.

#### 2.4 Industry Association Publications and Web Sites

Another important source of information on technology advances and process changes is industry trade association publications and their web sites. The scope of available information made it difficult to utilize this resource in the screening level review phase. However, trade association resources will be included in the detailed investigation phase of the current planning cycle.

## 2.5 Industrial Wastewater and Best Available Treatment (BAT) Technologies Conference

EPA recently co-sponsored a technical conference with Vanderbilt University entitled *Industrial Wastewater and Best Available Treatment (BAT) Technologies: Performance, Reliability, and Economics.* Over the last 30 years, industries have accumulated much expertise and experience in wastewater treatment process design and operation to comply with effluent limitations guidelines and standards. This meeting provided a forum to share these experiences and lessons learned. Representatives of academia, government, and industry shared information on water pollution control, including improvements to traditional wastewater treatment processes, process changes, and best management practices that lead to reductions in pollution.

Industries seek to meet effluent limitations guidelines and standards (and reduce production and treatment costs) by designing treatment systems appropriate for specific process wastewater characteristics and managing process water flow (including recycle-reuse). Although the types and quantities of pollutants generated varies from industry to industry, their treatment and pollution goals are similar: use waste minimization processes and the best treatment technologies available to minimize pollutant discharge. This section presents a brief overview of these technology advances, including biological treatment, filtration and membrane technologies, control of metals, and pollution prevention approaches.

#### 2.5.1 Biological Treatment Processes

Advances in biological treatment are a result of regulatory initiatives to control nutrients (nitrogen and phosphorous), multimedia approaches to control volatile organic pollutant emissions, and the need for treatment systems to handle higher organic pollutant loadings. Although new operating techniques and equipment have been developed to meet these challenges, basic biological treatment principals including pretreatment and equalization are a necessity for optimum performance. Pretreatment of biological system influent (including sedimentation, flotation, precipitation, stripping, and ion exchange) lessens the amount of non-degradable solids entering the system, removes toxic constituents which can slow bacterial metabolic activity, and prevents the introduction of constituents that impede solid-liquid separation. Equalization dampens both flow and organic loads to the biological treatment system, creating consistent feed to microorganisms (F/M) ratios and preventing solids wash-out from clarification systems.

Improvements to typical treatment technologies may occur due to site-specific issues such as water quality-based effluent limitations, local water concerns, land availability, materials recycle, and economics. For example, a chemicals manufacturing company implements anaerobic technologies in Europe and Asia because energy and sludge disposal costs are more significant there than in the US. A pulp and paper mill that does not have large amount of level land in proximity to the manufacturing area cannot use the common practice of treating wastewater in large aerated stabilization basins. Instead, the mill has developed methods to achieve maximum BOD and TSS reduction with only hours of detention in the biological reactor.

The remainder of this section presents a summary of the operational or equipment changes that have been made to full-scale biological treatment systems to enhance nutrient removal, control air emissions, and allow for stable treatment of high-strength organic wastewater. **Biological Nutrient Removal (BNR).** Conventional activated sludge wastewater treatment systems can be modified to remove ammonia, nitrate and organic nitrogen, and total phosphorus, while continuing to remove BOD and other organic pollutants. To remove total nitrogen, an anoxic zone is created in the system by either adding a new tank prior to the aeration basin or by isolating a portion of the aeration tank using a constructed barrier. Nitrate, formed in the aerobic portion of the system from conversion of both free ammonia and organically bound nitrogen, is recycled with a portion of the system effluent to the anoxic tank where it is converted to nitrogen gas.

Phosphorus can be removed using conventional activated sludge systems by installing an anaerobic tank prior to the anoxic denitrification tank and the aerated activated sludge tank In the anaerobic tank, in-coming raw wastewater is mixed with biomass in the absence of oxygen, causing the biomass to rapidly uptake BOD and release phosphate. Phosphate from the anaerobic tank enters the aerobic portion of the treatment system where it is incorporated back into the biomass during cell synthesis. Phosphate is removed from the treatment system via sludge wasteage.

Some facilities have also implemented sustainable development projects utilizing BNR for the control of nutrients. Organic chemicals manufacturing operations have wastewaters with high levels of nitrate and carbonaceous content. Treatment operations comprised of BNR, a constructed wetland, and land application (for beneficial reuse of biosolids) has resulted in removals of COD above 99 percent, and virtually complete removal of nitrate and nitrite.

BNR may also be applicable for treatment of wastewater generated by hospitals and at industrial organic chemicals manufacturing facilities. Hospital waste contains nitrogen compounds found in pharmaceutical and personnel care products, while industrial organic chemicals manufacturing facilities use a variety of raw materials including phosphoric acid, ammonia, and nitric acid.

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**Control of Volatile Organic Compound (VOC) Emissions from Activated Sludge Treatment Systems.** As a result of the Clean Air Act (CAA), many industries are now required to control emissions of VOCs from wastewater treatment systems. One method of controlling VOC emissions from the activated sludge process is to cover the tanks and collect and treat the off-gas. Covering the tanks prevents the uncontrolled emission of VOCs; however, the temperature inside the activated sludge system increases to levels that inhibit biological activity by the mesophilic bacteria. To overcome the stripping problems caused by diffused aeration systems (course and fine bubble diffusers), and the temperature problems associated with covering the tanks, a number of industries began to install high purity oxygen (HPO) systems.

HPO systems inject pure oxygen into the aeration tank rather than bubbling air through the wastewater. Because of the high driving force caused by pure oxygen systems compared to conventional aeration, dissolved oxygen (DO) levels of 50 to 100 mg/L can be achieved, negating the need for large volumes of air to achieve DO levels of only 2 mg/L. HPO also opens up the possibility of hydrogen sulfide elimination in gravity and force sewer mains. Oxygen supplementation of combined sewer overflow basins, rivers, and reservoirs using HPO offers practical solutions not possible or economical using conventional aeration techniques. HPO systems may be applicable to water generated from oil and gas field services both to control sulfides and to provide dissolved oxygen prior to discharge.

**Treatment of High-Strength Wastewater.** One new technique currently being used to handle easily degradable, high organic-strength wastewater is the aerobic selector. Selectors are low residence time tanks placed ahead of aeration basins that accept the influent stream and return activated sludge (RAS) thus creating a high organic loading rate condition in the selector. This condition favors floc formation over filamentous bulking organisms, resulting in mixed liquor with good settling properties. If filamentous organisms are not controlled, operational problems and deterioration in effluent quality will result.

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Another new piece of equipment used to control biological treatment systems is on-line respirometers. On-line respirometers produce a continuous record of factors that influence treatment process performance. Common applications include monitoring oxygen uptake, monitoring the effect of changes in wastewater composition common in a number of industrial facilities, and identifying the presence of toxics that can adversely affect wastewater treatment.

Both the addition of a biological selector and an on-line respirometer may be applicable to wastewater generated from the industrial organic chemicals and plastic product manufacturing industries. Each of these industries generate high organic-strength wastewater with varying composition. The selector will prevent bulking caused by the easily degradable organics and the on-line respirometer may help prevent process upsets resulting from process changes or periodic releases of toxics.

#### 2.5.2 Filtration and Membrane

Advances in filtration and membrane systems have occurred to better control the presence of oils and solids in treated effluent, as well as to increase the ability to reuse water in manufacturing operations. Membranes have also been used in conjunction with biological treatment systems for the control of oily wastewaters and high-strength organic wastewaters.

**Oils Control.** Improvements to conventional solids filtration at off-shore oil and gas extraction operations includes the addition of oil-adsorbent media of resin, polymer, and clay to treat the effluent. Conventional treatment typically produces effluent with free oil. However, upsets caused by production surges can produce non-compliant effluent concentrations. During these times, the oil-adsorbent media system can be activated to polish the final effluent within effluent standards. The system has typically achieved oil and grease effluent concentrations less than 10 ppm. The system is also effective at reducing water soluble organics.

**Solids Control.** Ultrafiltration and reverse osmosis systems are used for the control of suspended solids in recycled waters and treated effluent. In addition, reverse osmosis is becoming a preferred method for producing demineralized process water. Increased operating pressures and cross-flow velocities make this technology tolerant of influent feed conditions. These systems have been used at oil refineries, plasticizer plants, and auto manufacturing plants.

Control of effluent solids is also a key issue for biological treatment systems. Loss of solids in the effluent can result in permit violations plus difficulties controlling sludge age. Common causes for solids loss from the clarifier include filamentous bulking, increased salinity of the wastewater, or changes in the ionic characteristics of the floc particles. At one pulp and paper mill, changes in the ionic characteristics of the floc particles was caused by the addition of strong negatively charged dispersants in the paper coating process. To overcome the problems caused by the dispersants, new coagulating agents and polymers were evaluated. Results of the evaluation indicated simple treatment chemical changes can have a major impact on effluent quality and biological treatment system performance.

**Membrane Bioreactors.** Membrane bioreactors (MBRs) have been used to pretreat high-strength wastewater at pharmaceutical facilities, and to treat oily wastewater from an automotive engine plant (following pretreatment with ultrafiltration). MBRs consist of a suspended growth biological reactor and an ultrafiltration or microfiltration membrane for biological solids retention. The membrane serves to keep the microbial solids in the reactor to provide a highly clarified effluent stream without the need for a separate clarification step. MBRs use less space than conventional biotreatment systems, increase the removal of suspended solids, reduce wasting and sludge production, and improve biodegradation. For oily wastes, oil-water emulsions can be pretreated in an ultrafiltration unit with the permeate feeding the MBR system. The oily wastes can be recovered for reuse. The MBR operates with higher mixed liquor suspended solids levels (10,000 mg/L and higher) than conventional activated sludge and produces a large biomass with longer solids retention times.

#### 2.5.3 Metals Removal

Environmental regulations necessitate the development of technologically and economically feasible processes for the removal (and potential recovery) of metals from industrial wastewater prior to discharge. Many laboratory-scale, pilot-scale, and commercial-scale projects have been conducted to improve conventional metals removal and recovery processes. Several different improvements are being attempted, or have already been accomplished, including: less area required for the treatment system (smaller footprint), removal of difficult compounds, production of a recyclable product rather than a hazardous sludge, and the reduction of downstream pollutant loadings.

**Smaller Footprint.** The conventional treatment for removing TSS, oil and grease, and metals from wastewater generated at a steelmaking facility is iron or alum coagulation followed by conventional solids-liquid separation. This design often results in a large system footprint, and these systems may have difficulty managing sudden increases in hydraulic loading. The pilot-scale operation of the ActiFlo system, however, achieved the desired reductions of TSS, oil and grease, lead, nickel, zinc, and copper (with the use of additional sulfide treatment) using less than 15 percent of the space needed for a conventional system. ActiFlo uses microsand as a seed for floc formation with iron coprecipitation , allowing for high overflow rates and short detention times. The use of microsand in the pilot-scale operation results in the development of a denser floc with a higher settling velocity, and allows a higher overflow rate. This design translates into a potentially reduced system footprint and capital costs if expanded to the commercial scale.

**Removal of Difficult Compounds.** Several pilot tests investigated the removal of compounds from wastewater such as methylated arsenic compounds, phosphite, and hypophosphite. These removal processes are still under investigation. Methylated arsenic compounds do not respond to conventional arsenic removal methods such as iron coprecipitation, alum, sulfide, and activated alumina treatments. Post-precipitation advanced oxidation tests were

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conducted to attempt to liberate arsenic which could then be precipitated by traditional methods. Further removal of the remaining arsenic was attempted through absorption. Although both oxidation and absorption improved upon traditional precipitation, neither method proved truly successful for removal of methylated arsenic compounds.

Pilot tests were also run to remove phosphite and hypophosphite from phosphorus plant wastewater, which is difficult to remove using conventional lime precipitation, solids separation, and neutralization processes used to remove ortho-phosphate. The test was based on the use of chemical oxidation of phosphite and hypophosphite to ortho-phosphate; however, efficient chemical oxidation was not achieved.

**Production of a Recyclable or Nonhazardous Product.** Hexavalent chromium is used within industry to meet critical high erosion control and other metal surface finishing. The two conventional treatment methods to control discharges are: hexavalent chromium reduction followed by precipitation, settling, flocculation, thickening, dewatering, and disposal of the resultant sludge in a hazardous waste landfill; and the use of anionic exchange resins, which are non-specific for chromium. Both of these processes can be expensive due to capital costs and disposal issues. Two ideas are proposed for the production of a recyclable or nonhazardous product: 1) the anion liquid ion exchange (A-LIX<sup>TM</sup>) technology and 2) the use of granular ferric hydroxide (GFH).

The A-LIX<sup>TM</sup> extraction/stripping process has been tested at the commercial scale. The hexavalent chromium is captured as part of an oil-soluble salt, then sent to a mixer where sodium hydroxide neutralizes the extractant and releases the captured chromate. The aqueous chromium concentrate can then be withdrawn for reuse or recycle.

A column study was conducted to establish the effectiveness of using GFH for the removal of both hexavalent chromium and antimony from wastewater. The spent GFH media can

be disposed as a non-hazardous material, which is an improvement upon the traditional anionic exchange resin. GFH removal has yet to be demonstrated at the commercial scale.

#### 2.5.4 Pollution Prevention Approaches

Biological and physical/chemical treatment technologies and upstream waste minimization projects are the building blocks in the development of industrial pollution control strategies. Waste minimization projects often reduce or eliminate the need for "end of the pipe" treatment systems. For example, a chemicals manufacturing company was able to reduce BOD<sub>5</sub>, methylene chloride, chloroform, and toluene at a combined organic chemicals, plastics, and synthetic fibers (OCPSF) and pesticides plant by implementing several small source reduction programs along with minor waste treatment modifications. Another chemicals company identified three waste streams to recycle and reuse within their plant: 1) the low strength organic wastewater from the PVC process; 2) cooling tower cycle increase; and 3) evaporator process condensate recycle. Basic steelmaking, hot rolling, and steel finishing processes in the iron and steel industry also employ the best available technologies for flow management and waste minimization.

Conventional metal hydroxide precipitation wastewater treatment systems consume large amounts of alkaline and coagulant/flocculant chemicals to cause settling in the clarifier and dewatering for sludge cake disposal. However, waste minimization processes such as electrowinning (EW) can be used to recover metals and reduce downstream pollutant loadings. EW works similarly to the electroplating process, and can potentially be used to reduce the loading of zinc, copper, lead, cyanide, nickel, cadmium, silver, and gold. EW has potential for becoming an economically feasible option at the commercial scale, especially for precious metals.

#### 2.6 Industrial Wastewater Technology Websites

EPA reviewed information from two other websites for information on applicable and demonstrated technologies, process changes, or pollution prevention alternatives that can effectively reduce the pollutants remaining in an industry category's wastewater and thereby substantially reduce any identified risk to human health or the environment associated with those pollutants. These websites include the European Integrated Pollution Prevention and Control Bureau and the Canadian Wastewater Technology Centre.

#### 2.6.1 European Integrated Pollution Prevention and Control Bureau

The European Union has a set of common rules on permitting for industrial installations. These rules are set out in the so-called IPPC Directive of 1996. IPPC stands for Integrated Pollution Prevention and Control. In essence, the IPPC Directive is about minimizing pollution from various point sources throughout the European Union. All installations covered by Annex I of the Directive are required to obtain a permit from the authorities in the EU countries. Unless they have a permit, they are not allowed to operate. The permits must be based on the concept of Best Available Techniques (or BAT), which is defined in Article 2 of the Directive. These BAT reports are listed at: http://www.jrc.es/pub/english.cgi/0/733169.

#### 2.6.2 Canadian Wastewater Technology Centre

The Environmental Technology Advancement Directorate's Wastewater Technology Centre (WTC) located in Burlington, Ontario, has been in operation since 1972. It provides specialized science and technical, research and development support as well as demonstration and validation for Environment Canada (EC). Among other specialties, the WTC develops and assesses novel industrial and municipal wastewater treatment technologies. This work supports EC's efforts in pollution prevention, management of existing toxic substances, identification of new toxic substances and treatment technologies. Reports from the WTC can be downloaded from: http://www.ec.gc.ca/etad/en/wtc\_e.htm.

#### 3.0 Industry-Specific Technology Advances Reviews

EPA was able to compile Factor 2 information on the following industries identified in Table 1: (1) Aluminum Manufacturing and Forming; (2) Construction Products; (3) Industrial Organic Chemicals; (4) Oil and Gas Field Services; and (5) Semiconductor Manufacturing. EPA was unable to identify technology advances and process changes for all twenty industries identified in Table 1. EPA anticipates completing these summaries before publication of the final Effluent Guidelines Program Plan for 2004/2005.

#### 3.1 Aluminum Manufacturing and Forming Industry

The aluminum manufacturing and forming industry has exhibited above average growth and was identified as a discharger of sediment contaminants by the National Sediment Contaminant Point Source Inventory. It was also listed as an "Industry of the Future." The industry is currently subject to the requirements of the ELGs for the Nonferrous Metals Manufacturing Point Source Category (40 CFR 421) and the Aluminum Forming Point Source Category (40 CFR 467).

#### 3.1.1 Technology Advances

The production of aluminum can be divided into primary aluminum manufacturing (Standard Industrial Classification (SIC) Code 3334) and secondary aluminum manufacturing or aluminum recycling (SIC 3341). The first step in primary aluminum manufacturing involves extracting alumina from bauxite. Aluminum is then produced by the electrolysis of the extracted alumina through a carbon anode. The anodes used in this process are consumed and must be replaced frequently. Consequently, most aluminum reduction plants include anode production facilities. The production of anodes generates wastewater containing suspended solids, fluorides, and polycyclic aromatic hydrocarbons. OIT is currently conducting research on the use of ceramic anodes, which are inert and would not be consumed in the reaction. While the carbon

anodes that are currently used in aluminum production are replaced every several weeks, ceramic anodes would only need to be replaced once a year or less. The commercial application of ceramic anodes in the aluminum industry would reduce the production of anodes thus reducing the wastewater generated by anode manufacturing. Another OIT project proposes an "aluminum production cell" to replace the Hall-Heroult process currently used to produce aluminum from alumina. The aluminum production cell process does not use anodes and would therefore reduce wastewater generation associated with anode production.

Aluminum recycling requires only 5 to 8 percent of the energy required to produce aluminum from ore. Due to the energy saved by recycling aluminum and the high quality of the metal recovered, aluminum recycling has almost doubled in the last ten years. In 2000, recycled aluminum accounted for a third of the U.S. aluminum supply. In addition, OIT is working to develop new aluminum scrap sorting technologies such as Laser Induced Breakdown Spectroscopy, that will further increase aluminum recycling and the volume of wastewater associated with this process.

New technologies will also expand opportunities for aluminum packaging. Aluminum beverage cans are being developed that can be resealed, chill themselves, and indicate the temperature of their contents via color. Aluminum cylinders that can be used to store gas under pressure are also being developed. New vehicle systems may require high-pressure gas which will increase the demand for strong, light weight cylinders. The increased use of aluminum in packaging will increase aluminum manufacturing and the associated wastewater production.

#### **3.1.2** Wastewater Generation and Treatment

Primary aluminum smelting (from bauxite) generally produces wastewaters containing metals plus polycyclic aromatic hydrocarbons (PAHs) and cyanide. Wastewater is generated from wet air pollution control equipment, contact cooling, cathode reprocessing, and pot repair and soaking. Regulated pollutants for all subcategories include antimony, nickel, aluminum, fluoride, and benzo(a)pyrene. Cyanide is also included in the list of regulated pollutants for cathode reprocessing operations. Other pollutants include ammonia-nitrogen, arsenic, cadmium, chromium, lead, silver, zinc, and PAHs.

Treatment of wastewater from primary aluminum smelting includes preliminary treatment of cyanide by iron precipitation followed by chemical precipitation, gravity clarification, and media filtration. EPA determined through pilot-scale treatability testing that more than 99 percent of the PAHs can be removed by chemical precipitation and solids removal. Therefore, pretreatment of wastewater using activated carbon was not required to remove small amounts of PAHs.

Secondary aluminum smelting (from scrap) generally produces wastewaters containing metals, ammonia, and phenolics. Wastewater is generated from wet air pollution control equipment, contact cooling, scrap screening and milling, and dross washing. Regulated pollutants for all subcategories include lead, zinc, aluminum, and ammonia nitrogen. Total phenolics is also included in the list of regulated pollutants for wet air pollution control equipment associated with delacquering operations.

Treatment of wastewater from secondary ammonia smelting consists of ammonia stripping pretreatment of the dross washing effluent, activated carbon pretreatment for removal of phenol from wet air pollution control wastewater streams, and pretreatment of casting cooling water for removal of oil and grease. All wastewater is treated by an end-of-pipe chemical precipitation and gravity settling system for metals removal.

Aluminum forming operations generate wastewaters containing metals, cyanide, solids, and oil and grease. Current regulations (40 CFR Part 467) have subcategorized aluminum forming operations into rolling, extrusion, forging, and drawing. Unit operations generating wastewaters include:

- Contact cooling water from casting and heat treatment;
- Wet air pollution control equipment (scrubbers) associated with annealing furnaces, forges, degassing systems, and cleaning and etching tanks;
- Rolling and drawing lubrication systems;
- Casting lubrication systems; and
- Cleaning and etching solutions and rinses.

Regulated pollutants for all subcategories include chromium, cyanide, zinc, aluminum, oil and grease, total suspended solids, and pH. Other metals listed in the PCS database for aluminum forming include cadmium, lead, nickel, selenium, tin, and mercury. Nutrients and VOCs listed in the PCS database under aluminum forming include ammonia nitrogen, phosphorus, chloroethane, 1,1,1-trichloroethane, dichloroethane, and dichloroethylene.

Treatment of aluminum forming wastewater is a combination of end-of-pipe treatment and in-plant controls for pollution prevention. End of pipe treatment includes oil skimming for oil removal, chemical precipitation, pH adjustment, cyanide oxidation, hexavalent chromium reduction, and chemical emulsion breaking. In-process pollution prevention includes recycling of heat treatment contact cooling water, recycle of rod casting contact cooling water, recycle of air pollution control scrubber liquor, and countercurrent cascade rinsing applied to cleaning or etching and extrusion die cleaning rinses.

For both primary and secondary aluminum smelting and aluminum forming, replacing the gravity clarifiers with membrane filters (microfilters) will improve long-term effluent quality and may allow additional water to be recycled. Membrane filtration following chemical precipitation is becoming more common due to its ability to achieve consistently low effluent metals concentrations. In the metal finishing industry, membrane filters have shown the ability to consistently remove nearly all precipitated metal hydroxides. Although gravity clarification systems can remove metals to these levels under ideal conditions, changes in solids characteristics and rapid increases in flows (slug loadings) will result in a deterioration in effluent quality.

#### **3.2 Construction Products Industry**

The economic census indicates strong growth in the construction products industry, and both Table 1 and Table 2 include several entries representing the industry. The growth of the construction productions industry is a result of the demand for residential and nonresidential construction. The production of construction products can be divided into two steps: 1) the mining and quarrying of the minerals (non-metal, non-fuel mining, SIC 14), and 2) the physical modification of the mined minerals to produce a manufactured product (stone, clay, and glass products, SIC 32). The mining and quarrying of minerals for construction products is subject to the requirements of the Effluent Limitations Guideline (ELG) for the Mineral Mining and Processing Point Source Category (40 CFR 436). The manufacture of stone, clay, glass, and concrete construction products is subject to the following ELGs: Cement Manufacturing (40 CFR 411), Glass Manufacturing, Insulation Fiberglass Subcategory (40 CFR 426), and Asbestos Manufacturing (40 CFR 427).

#### 3.2.1 Technology Advances

The mining industry was selected as one of OIT's "Industries of the Future" and emphasis has been placed on the development of technologies for mining and processing minerals and materials. Through its participation in the Industries of the Future program, the U.S. mining industry has developed a research plan, known as the Crosscutting Technology Roadmap, which encompasses metallic minerals, nonmetallic minerals, and coal mining. Research and development work in some areas specified by Crosscutting Technology Roadmap could result in the development of new technologies that would impact wastewater production and composition. For example, the roadmap has identified the development of a method for high pressure water extraction as a research priority and estimates that a commercially available method will become available in the next three years. The commercial use of high pressure water extraction would potentially increase the amount of wastewater generated by the industry and necessitate the development of new wastewater handling procedures.

The Industries of the Future program has also recently funded research and development projects aimed at the development of improved separation and dewatering technologies, dust emission control technologies, and by-product recovery. Improvements in the efficiency of separation and by-product recovery technologies could reduce wastewater generation while improvements in dust emission control could potentially increase wastewater generation. The use of advanced technologies such as satellite communication, computer modeling, and smart sensors are already widespread in the industry and have resulted in more efficient mining and processing which reduces the amount of waste generated.

Wastewater from processing facilities can contains chemicals such as sulfuric acid, chromium, phenols, zinc, ammonia, hydrochloric acid, and phosphoric acid, that are currently used to remove mineral impurities. However, there have been efforts made to develop safe, efficient, and economically and environmentally beneficial separation processes. For example, the Idaho National Engineering and Environmental Laboratory (INEEL) has been "experimenting with environmentally friendly catalysts that can replace current noxious chemicals" and has also been working on "developing new processing methods that minimize waste generation."

Pollution prevention techniques available to stone, clay, and glass product manufacturing facilities can be classified into three categories: 1) source reduction, 2) recycling and reuse, and 3) improved operating practices. Many new "ready-mix" concrete plants have greatly reduced water use in recent years due to wastewater disposal issues and drought conditions in some parts of the country. An increasing number of companies are choosing to use completely closed-loop systems.

#### **3.2.2.** Wastewater Generation and Treatment

The primary toxic pollutants associated with mining and quarrying of minerals are metals and nutrients. Discharge monitoring data for SIC codes 1422 and 1442 show facilities monitor effluent for arsenic, barium, beryllium, cadmium, chromium, cobalt, lead, mercury, molybdenum, nickel, selenium, and vanadium. Nutrients include ammonia, nitrate, and phosphorus. EPA regulates pH and TSS for processes that do not recycle all water. Certain discharges in the industrial sand and gravel category are also regulated for fluoride. In general, the mineral mining industry uses gravity settling (with or without flocculants) to removed suspended solids. Some operations require pH adjustment before recycle or discharge of treated water.

Pollutants from cement manufacturing include pH, total dissolved solids (TDS), TSS, alkalinity and acidity, potassium, sulfate, and temperature. Facilities in SIC codes 3241 and 3273 monitor their effluent for a number of metals including arsenic, beryllium, cadmium, chromium, manganese, nickel, lead, selenium, vanadium, and zinc as potential pollutants in the cement manufacturing industry. Nutrients include ammonia and nitrate/nitrite. Facilities in the non-leaching subcategory must recycle and reuse wastewater and contain runoff from coal piles and discarded kiln dust. Facilities is the leaching subcategory must segregate leaching streams from non-leaching streams, install suitable facilities to neutralize the leachate streams with stack gas to a pH of 9, and install a secondary clarifier or settling basin to reduce suspended solids to not more than 0.8 lbs per ton of dust leached. For material piles and kiln dust piles, facilities install dikes to control runoff and neutralization and sedimentation facilities for treatment of runoff that cannot be controlled.

For the insulation fiberglass segment of the glass manufacturing industry, the following chemical, physical, and biological properties characterize the process wastewater effluent:

Phenols Oil and Grease (O&G)

BOD	Ammonia
COD	pH
TDS	Color
TSS	Turbidity
Temperature	Specific conductance

The control technologies for the insulation fiberglass segment consists of recycle and reuse of process waters and non-contact cooling water within the operation. Complete recycle should have been implemented by July, 1977.

The chemical, physical and biological parameters that define the pollutant constituents in wastewater from the asbestos manufacturing industry include:

TSS	BOD
COD	pН
Temperature	TDS
Nitrogen	Phosphorus
Phenols	Metals

Asbestos itself is not included in the list of pollutants because suspended solids present in the wastewater are to a large extent asbestos fibers. Removal of suspended solids by sedimentation will also remove asbestos fibers. For the asbestos-cement pipe, asbestos-cement sheet, and asbestos paper manufacturing segments, the control technology is sedimentation, with coagulation if necessary, for removal of suspended solids. The asbestos millboard subcategory is zero discharge, and the asbestos roofing and floor tile subcategories include sedimentation with skimming, if necessary. With the exception of asbestos millboard subcategory, BAT is zero discharge.

#### 3.3 Industrial Organic Chemicals Industry

The industrial organic chemicals was identified by the National Sediment Contaminant Point Source Inventory as one of the three major industrial dischargers of sediment contaminants (EPA, 1997). In addition, the chemical industry as a whole is one of OIT's "Industries of the Future." The organic chemicals industry (SIC 286) is divided into three categories: 1) gum and wood chemicals, 2) cyclic organic crudes and intermediates, and 3) industrial organic chemicals not elsewhere classified. The manufacture of cyclic crudes and intermediates and industrial organic chemicals not elsewhere classified is subject to the requirements of the Effluent Limitations Guideline (ELG) for Organic Chemicals, Plastics, and Synthetic Fibers (OCPSF) (40 CFR 414), established in 1987 and revised in 1993. The manufacture of gum and wood chemicals is subject to the requirements of the ELG for the Gum and Wood Chemicals Manufacturing Point Source Category (40 CFR 454), established in 1976 and reviewed in 1976 and 1995.

#### 3.3.1 Technology Advances

Due to the variety in the chemical reactions and processes used to produce organic chemicals, many chemical process advancements and developments apply only to the production of a particular chemical. For example, in January 2002, scientists at the National Institute of Advanced Industrial Science & Technology reported that they had developed a one-step catalytic process to convert benzene to phenol. This new technique is higher yielding than current industrial routes to phenol.

However, advances in separation techniques can be applied to a much broader segment of the industry. Although many of the separation techniques used in the chemical industry are already highly developed, these separation techniques could be improved in terms of energy efficiency, raw materials use, or cost effectiveness. Increased efficiency of separation processes could result in decreased water use and wastewater production by the organic chemicals industry. Additional decreases in wastewater generation at organic chemical manufacturing facilities can be achieved through improvements in equipment such as vacuum pumps, seal pumps, and stream jets and implementation of waste reduction practices.

Through the Industries of the Future program, OIT and the U.S. chemical industry have defined goals for the future, developed a portfolio of research and development projects, and accelerated progress towards major technology breakthroughs in areas such as chemical synthesis, bioprocesses and biotechnology, and materials technology.

#### **3.3.2** Wastewater Generation and Treatment

As a result of the variety in the processes used and products produced, a wide range of pollutants is found in the wastewaters of the organic chemicals industry, including a variety of conventional pollutants, toxic priority pollutants, and nonconventional pollutants. Many of the toxic and nonconventional pollutants found in the wastewaters of this industry are organic compounds produced by the industry for sale, while others are by-products of the production processes. Since there is generally more than one reaction pathway available to the reactants of chemical reactions, undesirable by-products are often produced resulting in a mixture of unreacted raw materials, products, and by-products. The processes used to separate the desired product from this mixture generate additional residues, with little or no commercial value, that end up in process wastewater, in air emissions, and as chemical wastes. The combination of raw materials and production processes used at a facility determine the characteristics of the wastewater generated.

The gum and wood chemicals manufacturing point source category generally generates wastewater containing conventional pollutants. Regulated pollutants include BOD<sub>5</sub>, TSS, and pH. Review of discharge monitoring data for SIC code 2861 shows facilities monitor effluent for metals, phenol, toxaphene, ammonia, and phosphorus. The metals include aluminum, copper, cadmium, lead, nickel, selenium, and zinc.

Biological treatment is BAT for the gum and wood chemicals industry.

Pretreatment of individual waste streams is performed to remove toxic metals, volatile organics, and oil and grease. Volatile and semi-volatile organic compounds can be removed by air/steam stripping, and oil and grease can be removed by oil skimming, and chemical emulsion breaking followed gravity flotation or dissolved air flotation. Chemical precipitation followed by gravity clarification is the typical metals treatment system used by the industry. Both biological treatment and metals precipitation is expected to remove the majority of easily degradable organic pollutants and metals. Nutrients (ammonia and phosphorus) can be removed by the biological treatment system; however, modifications to promote nitrification/denitrification and phosphorus uptake would likely be required by most systems.

The OCPSF industry generates wastewater containing organic compounds, nutrients, metals, and cyanide. Pollutants of concern include volatile organic compounds, semivolatile organic compounds, alcohols, PAHs, nitrate and ammonia nitrogen, and metals. Metals include chromium, cobalt, copper, lead, nickel, zinc, and total cyanide.

Because of the complexity of the industry and the number of different manufacturing processes, pretreatment requirements vary considerably. Amenable cyanide is typically removed by chemical oxidation. Volatile and semi-volatile organic compounds are treated by air/steam stripping, carbon adsorption, and distillation. Oil and grease is removed by oil skimming and ultrafiltration. Hexavalent chromium is reduced by chrome reduction, and heavy metals are removed by chemical precipitation and ion exchange.

End-of-pipe treatment systems consist of primary and secondary technologies. Primary technologies include equalization, neutralization, oil separation, primary clarification, coagulation and flocculation, and dissolved air flotation. Secondary technologies include biological treatment processes. The majority of facilities use activated sludge or aerated lagoons. Other, less prevalent biological treatment technologies at chemical manufacturing facilities include aerobic lagoons, anaerobic lagoons, rotating biological contactors, trickling filters, and oxidation ditches.

At EPA's recent Industrial Wastewater and Best Available Treatment Technology conference, DuPont Corporation provided an overview of their new integrated wastewater management facility in Victoria, Texas. The facility, a Nylon Intermediates manufacturing plant, is currently regulated under the OCPSF ELG. The new wastewater management facility features an innovative anoxic/oxic biological treatment plant, a constructed wetland, and land application pilot area for demonstrating beneficial reuse of the biosolids. The treatment system is working well with Chemical Oxygen Demand (COD) removal above 99 percent, virtually complete removal of nitrate and nitrite, and 100 percent permit compliance.

Since startup three years ago, the DuPont-Victoria biological treatment system and constructed wetlands have returned more than 1.6 billion gallons of water to the Guadalupe River for downstream reuse, including drinking water. The plant has also removed approximately 8.4 and 1.7 million pounds of nitrate-nitrogen and nitrite-nitrogen respectively from the wastewater and about 112 million pounds of organics. The constructed wetlands and land application areas are providing treated wastewater and biosolids with a quality sufficient for both flora and fauna to survive and reproduce.

#### **3.4** Oil and Gas Field Services Industry

Oil and gas field services (SIC code 138) includes the identification of hydrocarbon reserves through surveying activities, exploratory drilling to verify the presence or absence of hydrocarbon reserves and to determine the quantity of the reserves, and development of drilling operations. Oil and gas field services have increased dramatically since 2000. Rising oil and gas prices are creating more demand for products, which causes more exploration and development. Oil and gas field services wastewater discharges are subject to the requirement of the Effluent

Limitations Guideline (ELG) for the Oil and Gas Extraction Point Source Category (40 CFR 435), promulgated in 1979 and most recently reviewed in 2001.

#### 3.4.1 Technology Advances

Technology advances in the industry have increased the efficiency of both exploration and development. For example, exploration has long relied on 3-dimensional (3-D) seismic techniques to determine where oil wells are located. Advances in 3-D seismic surveys have enabled producers to evaluate prospects more accurately. Because 3-D seismic technology improves the accuracy of the drilling, less drilling waste is generated, less water is extracted relative to the oil and gas, and there are fewer impacts of exploration because fewer wells are drilled to extract the reserves. In 1996, 80 percent of off-shore surveys and 75 percent of onshore surveys used 3-D seismic technology. Recently, 4-D seismic surveys are being developed which allow 3-D surveys to be observed over time. 4-D surveys provide information about the flow of the hydrocarbon reserves and further increase the efficiency of oil and gas extraction. 4-D surveys are not yet widely used; only about 60 4-D surveys had been performed by 1999.

Seismic surveys are disrupted by the presence of salt because large amounts of sound energy are lost when passed through salt. Oil and gas contained in salt can be modeled by a combination of advanced seismic technology, complex mathematical modeling, and improved data processing and imaging. This new technology, called subsalt imaging, allows for better reservoir characterization and, therefore, more efficient recovery of hydrocarbons. Subsalt imaging is currently limited in use; however, testing and development continue to improve this technology.

Advanced drilling techniques have reduced the impacts of drilling on water quality. These techniques include measurement-while-drilling systems and horizontal, multilateral, and slimhole drilling. Measurement-while-drilling systems measure downhole parameters to allow for more accurate drilling, which reduces drilling waste. Modern drill bits improve drilling performance while decreasing waste. Horizontal drilling permits drilling in areas inaccessible by vertical drilling. Multilateral drilling utilizes horizontal and vertical drilling to create a network of interconnected wellbores surrounding a single major wellbore, which allows for more effective hydrocarbon extraction. Slimhole drilling is a drilling technique that requires less drilling fluid and produces less cuttings and wastewater; slimhole rigs occupy far less space than conventional rigs, the footprint can be 75 percent smaller.

Alternative drilling methods are being researched which decrease the amount of drilling fluids or muds used. Pneumatic drilling substitutes air for drilling fluid; however, this technology is only suitable for certain formation types and can create potentially explosive situations. Synthetic drilling muds are also being investigated. They are more effective than water-based muds, and lack the toxicity of oil-based muds.

Advanced off-shore platform technology allows for the recovery of deep water resources. An estimated 90 percent of reserves are under 3,000 feet or more of water. New technology reduces construction and production times and operational footprints. Off-shore drilling technology has enabled deepwater oil and gas reserves to be accessed with decreased environmental impacts. Also, voluntary Safety and Environmental Management Programs (SEMPs) are in place for almost all off-shore wells. The goals of SEMPs are to reduce human error and increase worker safety and environmental protection by identifying and correcting potential hazards.

#### **3.4.2 Wastewater Generation and Treatment**

Oil and gas extraction includes on-shore, off-shore, and coastal extraction operations. On-shore oil and gas extraction operations are required to meet zero discharge of process wastewater pollutants. Coastal and off-shore extraction operations are regulated for oil and grease, free oil, diesel oil, mercury, cadmium, PAHs, biodegradation rate, and toxicity from produced water, deck drainage, water-based drilling and cutting fluids, non-aqueous drilling and cutting fluids, and well treatment fluids. Discharge monitoring data for SIC code 1389 shows facilities also monitor for ammonia nitrogen, total cyanide, arsenic, beryllium, total and hexavalent chromium, lead, manganese, thallium, nickel, silver, selenium, toluene, benzene, ethylbenzene, and phenol.

In 2000, EPA investigated the technological aspects of four drilling waste management technologies, including product substitution, solids control equipment, land-based treatment and disposal, and onsite subsurface injection. Since 1990, the oil and gas industry developed synthetic-based drilling fluids (SBFs) to provide the drilling performance of traditional oil-based fluids (OBFs) but with lower environmental impact and greater worker safety. EPA looked at the use of SBFs as a pollution prevention technology while allowing the discharge of waste solids (cuttings) containing less toxic and persistent materials. In addition, EPA evaluated the use of advanced solids control equipment in conjunction with SBFs to allow for controlled discharges.

Land-based treatment and disposal consists primarily of subsurface injection of drilling wastes. Drilling wastes are received in vacuum trucks, dump trucks, cuttings boxes, or barges from both on-shore and off-shore drilling operations. Most of these treatment and disposal facilities employ a landfarming technique whereby the wastes are spread over small areas and are allowed to biodegrade until they become clay-like substances that can be stockpiled outside the landfarming area. Another common practice at centralized commercial facilities is the processing of drilling waste into a reuseable construction material. This process consists of dewatering the drilling waste and mixing the solids with binding and solidification agents. The oil and metals are stabilized within the solids matrix and cannot leach from the solids. The resulting solids are then used as daily cover at a Class I municipal landfill. Other potential uses for the stabilized material include use as a base for road construction and levee maintenance.

Research is also being conducted on advanced water treatment technologies. Freeze-thaw evaporation purifies wastewater generated from oil and gas development operations (produced water) by separating out dissolved solids, metals, and chemicals. In this process, produced water is placed in a holding pond. When temperatures are below freezing, the produced water is sprayed on a freezing pad where the brine and dissolved solids separate from the ice due to varying densities. The brine is disposed of. As the ice melts, purified water drains from the freezing pad. During warm temperatures, evaporation from the pond is substituted for freezing cycles. The produced water volume requiring disposal was reduced by 80 percent in preliminary tests.

The volume of water brought to the surface during oil and gas exploration and development may also be reduced. Downhole oil/water separation uses mechanical or natural methods to separate the oil and water. The oil is brought to the surface and the water is pumped into a subsurface injection zone. This technology can reduce produced water volumes by 95 percent and increase oil production by 50 percent.

#### 3.5 Semiconductor Manufacturing Industry

The semiconductor manufacturing industry (SIC 3674) is one of the fastest growing industries in the United States. It had a 144 percent increase in the value of shipments between 1992 and 1997, the second highest percent increase in the manufacturing sector. (See Table 2 above.) The semiconductor manufacturing industry is currently subject to the requirements of the Effluent Limitations Guideline (ELG) for the Electrical and Electronic Components Point Source Category (40 CFR 469), established in 1983 and revised in 1985. Electroplating operations in the semiconductor manufacturing are also subject to the requirements of the ELG for the Metal Finishing Point Source Category (40 CFR 433), established in 1983.

#### 3.5.1 Technology Advances

Currently, the production of semiconductors uses a multitude of chemicals and large volumes of deionized water. However, new technology decreases the amount of water

needed in semiconductor production by using an alternative method to wash the chips. One method uses carbon dioxide at high temperatures and pressures. Using this "supercritical carbon dioxide" is inexpensive and cleans the chips without generating large quantities of wastewater.

In addition, emerging technology can improve the treatment of wastewater from semiconductor production, to allow for recycling and reuse. Membrane distillation evaporates water across a polymer membrane. Contaminants remain on the heated side of the membrane and the water vapor condenses to water on the clean side of the membrane. This process cleans water so thoroughly that nearly all water is expected to be able to be reused in the semiconductor plant.

Certain semiconductor manufacturers have recently begun performing a Controlled Collapse Chip Connection (C4) electroplating process to add selective thin metal deposits to the surface of the wafer to act as connection points. According to industry personnel, this process is required to allow for increased connection points caused by decreased circuit size (hence an increase in the number of devices per semiconductor).

Several semiconductor manufacturers recently began performing a new process for using copper to replace aluminum in microprocessors, enhancing electron migration and reducing the width of the circuitry. These sites use a copper metallization process, in which copper is applied with an electroplating operation followed by a rinse. This process is part of a sequence of photolithography, etching, and copper deposition processes performed in a clean room environment. The process deposits a microscopic layer of copper on selected (i.e., circuitry) portions of the wafer. Historically, electroplating operations were performed only in the assembly and packaging step of the semiconductor manufacturing process. However, the recent development of the copper metallization and lead bump processes results in electroplating operations that are also performed in the fabrication process, with electroplating operations generating less than 1 percent of the discharge rates from the semiconductor fabrication operations.

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#### **3.5.2** Wastewater Generation and Treatment

Semiconductor manufacturing processes generate a wide variety of wastestreams, including spent solutions (e.g., solvents, acids, cleaning solutions, resist material, etchant solution, electroplating solutions, and developing solutions), wafer rinse waters following processing steps, and other wastewater sources such as wet air pollution control and machine cooling and lubrication. Accordingly, discharge monitoring data for SIC 3674 shows a wide variety of pollutants monitored, including nutrients, cyanide, fluoride, metals, solvents, residual chlorine, and hydrogen peroxide.

40 CFR part 469 applies to discharges from all processes associated with semiconductor manufacturing, except electroplating, vapor deposition, and sputtering which are covered by 40 CFR part 433. Regulated pollutants for part 469 include total toxic organics, fluoride, arsenic, total suspended solids (TSS), and pH. Toxic organics are associated with the use of solvents and other solutions in cleaning, degreasing, and other processing steps. Fluoride is generated by the use of hydrofluoric acid as an etchant or cleaning agent. Arsenic is generated at only those facilities that manufacture gallium or indium arsenide crystals. (Most semiconductor facilities do not perform crystal growth, preferring to instead obtain single crystal silicon ingots from other firms.) Regulated pollutants for part 433 include total toxic organics, cadmium, chromium, copper, lead, nickel, silver, zinc, cyanide (total), oil and grease, TSS, and pH.

The pollutant control technology basis for 40 CFR 469 includes neutralization for pH control, solvent management for control of toxic organics, and precipitation and clarification of the concentrated fluoride wastestream. The pollutant control technology basis for 40 CFR 433 includes solvent management, segregation of waste streams, and end-of-pipe treatment consisting of pretreatment of segregated wastestreams (e.g., cyanide destruction, hexavalent chromium reduction, chemical emulsion breaking, and chemical reduction to break chelated metals) followed by neutralization, chemical precipitation, and gravity clarification.

However, based on site visits conducted by EPA in 1997, semiconductor manufacturing facilities are able to achieve the existing effluent limitations with spent solutions management and minimal end-of-pipe treatment (e.g., fluoride precipitation of fluoride-bearing wastewaters and neutralization) due to water purity requirements of production processes. Because of product specification, processes require ultrapure water, and opportunities for water conservation may be limited. Many facilities use counter-flow rinses where possible, but do not allow much impurity build-up in the water. In addition, parts 469 and 433 wastewaters are commonly commingled prior to treatment and discharge, which can result in metals levels below treatability and, in some cases, below detection.

Note that at facilities performing (C4) electroplating processes (see Section 3.7.1), monitoring at the source would require dedicated equipment installed in clean rooms to demonstrate compliance. For this reason, EPA has provided guidance to permitting authorities that electroplating operations conducted in a clean room should not be covered under part 433.