US ERA ARCHIVE DOCUMENT

IV. PRIMARY AND SECONDARY COPPER PROCESSING INDUSTRY

IV.A. Characterization of the Industry - Copper

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the Primary and Secondary Copper Industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes.

IV.A.1. <u>Industry Size and Geographic Distribution - Copper</u>

The following discussion is based in part upon the following documents: "U.S. Industrial Outlook 1994 - Metals," U.S. Department of Commerce, and information provided by the U.S. Department of the Interior, Bureau of Mines.

Variation in facility counts occur across data sources due to many factors, including reporting and definitional differences. This document does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

Copper ore is mined in both the Northern and Southern Hemispheres but is primarily processed and consumed by countries in the Northern Hemisphere. The U.S., is both a major producer (second only to Chile) and consumer of copper.

The domestic primary unwrought, or unworked, integrated copper industry consists of mines, concentrators, smelters, refineries, and electrowinning plants (SIC 3331 encompasses facilities engaging in primary smelting and refining, but not mining). The number of operating mines producing copper has decreased from 68 mines in 1989 to 65 mines in 1992. Of the 65 mines actively producing copper in the U.S., 33 list copper as the primary product. The remaining 32 mines produce copper either as a byproduct or co-product of gold, lead, zinc, or silver (U.S. DOI, Bureau of Mines). Nineteen of the 33 active mines that primarily produce copper are located in Arizona, which accounts for 65 percent of domestically mined copper ore. The remaining mines are located throughout New Mexico and Utah, which together account for 28 percent of domestic production, and Michigan, Montana, and Missouri account for the remainder (U.S. DOI, Bureau of Mines). Five integrated producers, Phelps Dodge Corp., Magma Copper Co., ASARCO Incorporated, Kennecott Corp., and Cyprus-AMAX Minerals Co., produce over 90 percent of domestic primary copper.

In 1988, there were 17 copper mines in the U.S. using leaching methods, with total production of approximately 227,000 metric tons of electrowon copper (U.S.

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EPA; U.S. DOI, Bureau of Mines). According to the U.S. Bureau of Mines, in 1991 441,000 metric tons of copper (an increase of 94 percent in three years) were recovered by leaching/electrowinning methods (U.S. DOI, Bureau of Mines). While solution operations are conducted throughout the Southwestern U.S., almost 75 percent of the facilities (14) are located in Arizona. There are two facilities in New Mexico, one in Utah, and one in Nevada.

In 1991, the consumption of refined copper in the U.S. decreased by four percent from 1990 levels. In 1992, refined copper was consumed at approximately 20 wire-rod mills, 41 brass mills, and 750 foundries, chemical plants, and other manufacturers. According to the Bureau of Mines, in 1992 U.S. consumption of copper was about 2.2 million tons. Consumption in 1993 and 1994 rose sharply to almost 2.7 million tons.

Fifty-six percent of recycled, or secondary copper, is derived from new scrap, while 44 percent comes from old scrap. Domestically, the secondary copper smelting industry is led by four producers: Franklin, Southwire Co., Chemetco., and Cerro Copper Co. Like the secondary aluminum industry, these producers buy the scrap they recycle on the open market, in addition to using scrap generated in their own downstream productions. The secondary copper industry is concentrated in Georgia, South Carolina, Illinois, and Missouri.

IV.A.2. <u>Product Characterization - Copper</u>

Because of its superior electrical conductivity, the leading domestic consumer of refined copper is wire mills, accounting for 75 percent of refined copper consumption. Brass mills producing copper and copper alloy semi-fabricated shapes are the other dominant domestic consumers at 23 percent. The dominant end-users of copper and copper alloy are the construction and electronic products industries, accounting for 65 percent of copper end-usage. Transportation equipment such as radiators also account for a fair amount of copper end-usage at 11.6 percent. Copper and copper alloys powders are used for brake linings and bands, bushings, instruments, and filters in the automotive and aerospace industries, for electrical and electronic applications, for anti-fouling paints and coatings, and for various chemical and medical purposes. Copper chemicals, principally copper sulfate and the cupric and cuprous oxides, are widely used as algaecides, fungicides, wood preservatives, copper plating, pigments, electronic applications, and numerous special applications.

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IV.A.3. <u>Economic Trends - Copper</u>

Conditions in the U.S. copper industry continued to improve during 1993, and refined copper production increased approximately seven percent by mid-year as compared to the first half of 1992. U.S. copper consumption is estimated to grow by approximately 1.5 to 7 percent through 2000, while global consumption is expected to increase approximately two percent through the same period. The foreign market, particularly the Asian Pacific region, is expected to be a growing market because of its strong automobile, air conditioning, and consumer electronics industries. China is expected to see the largest increase in demand if economic reforms continue.

IV.B. Industrial Process Description - Copper

This section describes the major industrial processes within the Primary and Secondary Copper Processing industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. This section also describes the potential fate (air, water, land) of these waste products.

IV.B.1. <u>Industrial Processes in the Primary and Secondary Copper Processing Industry</u>

The following discussion is based upon materials provided by the International Copper Association, Ltd., and the following documents: "Copper Technology and Competitiveness," Congress of the United States, Office of Technology Assessment and "Compilation of Air Pollutant Emission Factors (AP42)," the U.S. Environmental Protection Agency.

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Primary Copper Processing

Copper is mined in both open pits and underground mines, depending upon the ore grade and the nature of the ore deposit. Copper ore typically contains less that one percent copper and is in the form of sulfide minerals. Once the ore is delivered above the ground, it is crushed and ground to a powdery fineness, after which it is concentrated for further processing. In the concentration process, ground ore is slurried with water, chemical reagents are added, and air is blown through the slurry. The air bubbles attach themselves to the copper minerals and are then skimmed off of the top of the flotation cells. The concentrate contains between 20 and 30 percent copper. The "tailings," or gangue minerals, from the ore fall to the bottom of the cells and are removed, dewatered by "thickeners," and transported as a slurry to a tailings pond for disposal. All water used in this operation, from dewatering thickeners and the tailings pond, is recovered and recycled back into the process.

Copper can be produced either pyrometallurgically or hydrometallurgically depending upon the ore-type used as a charge. The ore concentrates, which contain copper sulfide and iron sulfide minerals, are treated by pyrometallurgical processes to yield high purity copper products. Oxide ores, that contain copper oxide minerals which may occur in other parts of the mine, together with other oxidized waste materials, are treated by hydrometallurgical processes to yield high purity copper products. Both processes are illustrated in Exhibit 4.

Copper conversion is accomplished by a pyrometallurgical process known as "smelting." During smelting the concentrates are dried and fed into one of several different types of furnaces. There the sulfide minerals are partially oxidized and melted to yield a layer of "matte," a mixed copper-iron sulfide, and "slag," an upper layer of waste.

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Exhibit 4 - Copper Production Process

Source: Office of Technology Assessment.

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The matte is further processed by a process known as "converting." The slag is tapped from the furnace and stored or discarded in slag piles on site. A small amount of slag is sold for railroad ballast and for sand blasting grit. A third product of the smelting process is sulfur dioxide, a gas which is collected, purified, and made into sulfuric acid for sale or for use in hydrometallurgical leaching operations.

Following smelting, the copper matte is fed into a converter. During this process the copper matte is poured into a horizontal cylindrical vessel (approximately 30 x 13 feet) fitted with a row of pipes (See Exhibit 5). The pipes, known as "tuyeres," project into the cylinder and are used to introduce air into the converter. Lime and silica are added to the copper matte to react with the iron oxide produced in the process to form slag. Scrap copper may also be added to the converter. The furnace is rotated so that the tuyeres are submerged, and air is blown into the molten matte causing the remainder of the iron sulfide to react with oxygen to form iron oxide and sulfur dioxide. Following the "blow," the converter is rotated to pour off the iron silicate slag.

Exhibit 5 Cutaway View of a Pierce-Smith Converter for Producing Blister Copper from Matte

Source: Extractive Metallurgy of Copper, A. K. Biswas and W. D. Davenport, Pergamon Press.

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Once all of the iron is removed, the converter is rotated back and given a second blow during which the remainder of the sulfur is oxidized and removed from the copper sulfide. The converter is then rotated to pour off the molten copper, which at this point is called "blister" copper (so named because if allowed to solidify at this point, it will have a bumpy surface due to the presence of gaseous oxygen and sulfur). Sulfur dioxide from the converters is collected and fed into the gas purification system together with that from the smelting furnace and made into sulfuric acid. Due to its residual copper content, slag is recycled back to the smelting furnace.

Blister copper, containing a minimum of 98.5 percent copper, is refined to high purity copper in two steps. The first step is "fire refining," in which the molten blister copper is poured into a cylindrical furnace, similar in appearance to a converter, where first air and then natural gas or propane are blown through the melt to remove the last of the sulfur and any residual oxygen from the copper. The molten copper is then poured into a casting wheel to form anodes pure enough for "electrorefining."

In electrorefining, the copper anodes are loaded into electrolytic cells and interspaced with copper "starting sheets," or cathodes, in a bath of copper sulfate solution. When a DC current is passed through the cell the copper is dissolved from the anode, transported through the electrolyte, and re-deposited on the cathode starting sheets. When the cathodes have built-up to sufficient thickness they are removed from the electrolytic cell and a new set of starting sheets is put in their place. Solid impurities in the anodes fall to the bottom of the cell as a sludge where they are ultimately collected and processed for the recovery of precious metals such as gold and silver. This material is known as "anode slime."

The cathodes removed from the electrolytic cell are the primary product of the copper producer and contain 99.99+ percent copper. These may be sold to wire-rod mills as cathodes or processed further to a product called "rod." In manufacturing rod, cathodes are melted in a shaft furnace and the molten copper is poured onto a casting wheel to form a bar suitable for rolling into a 3/8-inch diameter continuous rod. This rod product is shipped to wire mills where it is extruded into various sizes of copper wire.

In the hydrometallurgical process, the oxidized ores and waste materials are leached with sulfuric acid from the smelting process. Leaching is performed *in situ*, or in specially prepared piles by distributing acid across the top and allowing it to percolate down through the material where it is collected. The ground under the leach pads is lined with an acid proof, impermeable plastic material to prevent leach liquor from contaminating groundwater. Once the

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copper-rich solutions are collected they can be processed by either of two processes - the "cementation" process or the "solvent extraction/electrowinning" process (SXEW). In the cementation process (which is rarely used today), the copper in the acidic solution is deposited on the surface of scrap iron in exchange for the iron. When sufficient copper has been "cemented out" the copper-rich iron is put into the smelter together with the ore concentrates, for copper recovery via the pyrometallurgical route.

In the SXEW process, the pregnant leach solution (PLS) is concentrated by solvent extraction. In solvent extraction, an organic chemical that extracts copper but not impurity metals (iron and other impurities) is mixed with the PLS. The copper-laden organic solution is then separated from the leachate in a settling tank. Sulfuric acid is added to the pregnant organic mixture, which strips the copper into an electrolytic solution. The stripped leachate, containing the iron and other impurities, is returned to the leaching operation where its acid is used for further leaching. The copper-rich strip solution is passed into an electrolytic cell known as an "electrowinning" cell. electrowinning cell differs from an electrorefining cell in that it uses a permanent, insoluble anode. The copper in solution is then plated onto a starting sheet cathode in much the same manner as it is on the cathode in an electrorefining cell. The copper-depleted electrolyte is returned to the solvent extraction process where it is used to strip more copper from the organic. The cathodes produced from the electrowinning process are then sold or made into rod in the same manner as those produced from the electrorefining process.

Electrowinning cells are used also for the preparation of starting sheets for both the electrorefining and electrowinning processes. Here copper is plated onto either stainless steel or titanium cathodes. When sufficient thickness has built-up, the cathodes are removed and the copper plating on both sides of the stainless steel or titanium is stripped off. After straightening and flattening, these copper sheets are fabricated into starting sheet cathodes by mechanically attaching copper strips to be used as hangers when they are in the electrolytic cell. Both the starting sheet and the strips become part of the final product. The same care in achieving and maintaining purity must be maintained with these materials as is practiced for the electrodeposited copper.

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An activity that is carried out concurrently with the primary copper production is sulfur fixation. As mentioned above, in the pyrometallurgical process most of the sulfur in the ore is transformed into sulfur dioxide (though a portion is discarded in the slag). The copper smelting and converting processes typically generate over half a ton of sulfur dioxide per ton of copper concentrate. In order to meet CAA emission standards, sulfur dioxide releases must be controlled. accomplished by elaborate gas collection and filtration systems after which the sulfur dioxide contained in the off-gases is made into sulfuric acid. In general, if the sulfur dioxide concentration exceeds four percent it will be converted into sulfuric acid, an ingredient in fertilizer. Fugitive gases containing less than four percent sulfuric acid are either released to the atmosphere or scrubbed to remove the sulfur dioxide. The sulfur recovery process requires the emissions to flow through a filtering material in the air emissions scrubber to capture the sulfur. A blowdown slurry is formed from the mixture of the filtering material and sulfur emissions. This slurry contains not only sulfur, but cadmium and lead, metals that are present in copper ore. The acid plant blowdown slurry/sludge that results from thickening of blowdown slurry at primary copper facilities is regulated by RCRA as hazardous waste K064.

Secondary Copper Processing

The primary processes involved in secondary copper recovery are scrap metal pretreatment and smelting. Pretreatment includes cleaning and concentration to prepare the material for the smelting furnace. Pretreatment of the feed material can be accomplished using several different procedures, either separately or in combination. Feed scrap is concentrated by manual and mechanical methods such as sorting, stripping, shredding, and magnetic separation. Feed scrap is sometimes briquetted in a hydraulic press. Pyrometallurgical pretreatment may include sweating, burning of insulation (especially from scrap wire), and drying (burning off oil and volatiles) in rotary kilns. Hydrometallurgical methods include flotation and leaching with chemical recovery.

After pretreatment the scrap is ready for smelting. Though the type and quality of the feed material determines the processes the smelter will use, the general fire-refining process is essentially the same as for the primary copper smelting industry.

IV.B.2. Raw Material Inputs and Pollution Outputs

______The material inputs and pollution outputs resulting from primary and secondary copper processing are presented by media in Exhibit 6.

Exhibit 6

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Process Materials Inputs/Pollution Outputs - Copper

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Copper Concentration	Copper ore, water, chemical reagents, thickeners		Flotation wastewaters	Tailings containing waste minerals such as limestone, and quartz
Copper Leaching	Copper concentrate, sulfuric acid		Uncontrolled leachate	Heap leach waste
Copper Smelting	Copper concentrate, siliceous flux,	Sulfur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury, and zinc		Acid plant blowdown slurry/sludge (K064), slag containing iron sulfides, silica
Copper Conversion	Copper matte, scrap copper, siliceous flux	Sulfur dioxide, particulate matter containing arsenic, antimony, cadmium, lead, mercury, and zinc		Acid plant blowdown slurry/sludge (K064), slag containing iron sulfides, silica
Electrolytic Copper Refining	Blister copper		Process wastewater	Slimes containing impurities such as gold, silver, antimony, arsenic, bismuth, iron, lead, nickel, selenium, sulfur, and zinc
Secondary Copper Processing		Particulates	Slag granulation waste	Slag

Primary Copper Processing

Primary copper processing results in air emissions, process wastes, and other solidphase wastes. Particulate matter and sulfur dioxide are the principal air contaminants emitted by primary copper smelters. Copper and iron oxides are the primary constituents of the particulate matter, but other oxides, such as arsenic, antimony, cadmium, lead, mercury and zinc, may also be present, with metallic sulfates and sulfuric acid mist. Single stage electrostatic precipitators are widely used in the primary copper industry to control these particulate emissions. Sulfur oxides contained in the off-gases are collected, filtered, and made into sulfuric acid.

Large amounts of water are used in the copper concentration process though disposal of liquid wastes is rarely a problem because the vast majority of the water

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is recycled back into the process. Once the wastewater exits the flotation process it is sent to a sediment control pond where it is held long enough for most of the sediment to settle.

The seepage and leaking of sulfuric acid solutions used in leaching can also produce liquid wastes, however this potential is off-set by the copper producer's interest to collect as much of the copper-bearing leachate as possible. Older operations generally do not have protective liners under the piles, and experience some loss of leachate. New leaching operations use impermeable membranes to confine leach solutions and channel them to collection ponds.

Electrolytic refining does produce wastewaters that must be treated and discharged, reused, or disposed in some manner. Many facilities use a wastewater treatment operation to treat these wastes.

Primary copper processing primarily generates two solid-phase wastes; slag and blowdown slurry/sludge. Slag is generated during the smelting, converting, fire refining, and electrolytic refining stages. Slag from smelting furnaces is higher in copper content than the original ores taken from the mines. These slags therefore, may be sent to a concentrator and the concentrate returned to the smelter. This slag processing operation results in slag tailings. Slag resulting from converting and fire refining also is normally returned to the process to capture any remaining mineral values. Blowdown slurry/sludge that results from the sulfur recovery process is regulated by RCRA as hazardous waste K064.

Secondary Copper Processing

Secondary copper processing produces the same types of wastes as primary pyrometallurgical copper processing. One type of secondary processing pollutant that differs from primary processing is the air emissions. Air pollutants are generated during the drying of chips and borings to remove excess oils and cuttings fluids and causes discharges of large amounts of dense smoke containing soot and unburned hydrocarbons. These emissions can be controlled by baghouses and/or direct-flame afterburners.

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V. PRIMARY AND SECONDARY LEAD PROCESSING INDUSTRY

V.A. Characterization of the Industry - Lead

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the Primary and Secondary Lead Industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes.

V.A.1. <u>Industry Size and Geographic Distribution - Lead</u>

The following discussion is based upon "U.S. Industrial Outlook 1994 - Metals," U.S. Department of Commerce, and information provided by the U.S. Department of the Interior, Bureau of Mines.

Variation in facility counts occur across data sources due to many factors, including reporting and definitional differences. This document does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

The U.S. is the world's third largest primary lead producer with 1/7 of all production reserves. Over 80 percent of the lead ore mined domestically comes from Missouri. The mines with the largest ore capacity are owned by Asarco Inc., The Doe Run Co., and Cominco American Inc., the first two of which are also integrated producers of refined lead materials. The majority of lead ores mined in the U.S. are smelted in conventional blast furnaces and are refined using pyrometallurgical methods.

In 1993, the lead industry employed 600 workers at primary smelters and refineries, and 1,700 at secondary smelters and refineries. Primary and secondary smelter and refinery employment was not expected to change in 1994 (U.S. DOI, Bureau of Mines, 1995).

The U.S. is the world's largest recycler of lead scrap and is able to meet about 72 percent of its total refined lead production needs from scrap recycling. At the end of 1991, the secondary lead industry consisted of 16 companies that operated 23 battery breakers-smelters with capacities of between 10,000 and 120,000 metric tons a year (mt/y); five smaller operations with capacities between 6,000 and 10,000 mt/y; and 15 smaller plants that produced mainly specialty alloys for solders, brass and bronze ingots, and miscellaneous uses. Sanders Lead Co., East Penn Mfg. Co., and Schuylkill Metals Corp. are some of the larger secondary lead producers in the United States.

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V.A.2. Product Characterization - Lead

Within the U.S., the power storage battery industry is the largest end-user of lead, accounting for 83 percent of the estimated 1.357 Mmt domestically consumed in 1993. Demand for lead by the lead-acid battery industry rose 12 percent to 1.12 Mmt in 1993 due to a significant increase in consumer need for batteries. Industrial demand for batteries rose as well, due both to the growth in demand for stationary batteries used in telecommunications and back-up power systems for computers, lighting, and security systems, as well as an increased need for mobile batteries used in fork lifts and other battery-powered vehicles. Additional lead end-uses and users of consequence are ammunition, consumers of lead oxides used in television glass and computers, construction (including radiation shielding) and protective coatings, and miscellaneous uses such as ballasts, ceramics, and crystal glass.

V.A.3. <u>Economic Trends - Lead</u>

In 1994, domestic consumption of lead is expected to increase seven percent to 1.5 Mmt. This increase is based in part on expected increased demand from the automobile sector for both original and replacement equipment batteries. This increased consumption should continue to be met by the secondary lead industry, which is expected to continue to supply approximately 72 percent of total domestic production. Through 1998, production of unwrought lead is expected to grow 1.4 percent to 1.3 Mmt, while U.S. consumption is estimated to increase 1.4 percent to 1.6 Mmt.

Power storage batteries, both industrial and automotive, will continue to be the largest end-users. Demand for power storage batteries may be greater than initially expected due to several factors. California and nine Northeastern States have recently passed laws requiring the production, but not the consumer use of, electric vehicles. Other innovative uses of lead include lead-acid batteries for load-leveling of electricity. Using batteries for load-leveling reduces the total installed generating capacity needed by charging the battery at times of low demand for electricity, then discharging it to level the power supply at times of peak demand. A pilot facility in Chino, CA has already come on line with a battery which uses 2,000 pounds of lead and has a capacity of 40 megawatt hours. Another potential use for refined lead is the containment of high-level radioactive waste. Argentina and Sweden already employ it for this purpose and this use is being considered elsewhere, including the United States. A final innovative application being tested for lead is its use as a road paving stabilizer. Tests have shown that certain lead compounds can double the life of asphalt while only adding four to five percent to production costs.

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V.B. Industrial Process Description - Lead

This section describes the major industrial processes within the Primary and Secondary Lead Processing industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. This section also describes the potential fate (air, water, land) of these waste products.

V.B.1. <u>Industrial Processes in the Primary and Secondary Lead Processing</u> <u>Industry</u>

The following discussion is based upon the following documents: "Compilation of Air Pollutant Emission Factors (AP42)," "Background Listing Document for K065," "1990 Report to Congress on Special Wastes From Mineral Processing," published by the U.S. Environmental Protection Agency, and "Recycled Metals in The United States, A Sustainable Resource," published by U.S. Department of the Interior, Bureau of Mines.

Primary Lead Processing

The primary lead production process consists of four steps: sintering, smelting, drossing, and pyrometallurgical refining (See Exhibit 7). To begin, a feedstock comprised mainly of lead concentrate is fed into a sintering machine. Other raw materials may be added including iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and particulates gathered from pollution control devices. In the sintering machine the lead feedstock is subjected to blasts of hot air which burn off the sulfur, creating sulfur dioxide. The lead material existing after this process contains about nine percent of its weight in carbon. The sinter is then fed along with coke, various recycled and cleanup materials, limestone, and other fluxing agents into a blast furnace for reducing, where the carbon acts as a fuel

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and smelts or melts the lead material. The molten lead flows to the bottom of the furnace where four layers form: "speiss" (the lightest material, basically arsenic and antimony); "matte" (copper sulfide and other metal sulfides); blast furnace slag (primarily silicates); and lead bullion (98 weight percent lead). All layers are then drained off. The speiss and matte are sold to copper smelters for recovery of copper and precious metals. The blast furnace slag which contains zinc, iron, silica, and lime is stored in piles and partially recycled. Sulfur oxide emissions are generated in blast furnaces from small quantities of residual lead sulfide and lead sulfates in the sinter feed.

Rough lead bullion from the blast furnace usually requires preliminary treatment in kettles before undergoing refining operations. During drossing the bullion is agitated in a drossing kettle and cooled to just above its freezing point (700 to 800 degrees F). A dross, which is composed of lead oxide, along with copper, antimony, and other elements, floats to the top and solidifies above the molten lead.

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Exhibit 7 - Primary Lead Production Process

Source: <u>Air Pollution Engineering Manual</u>, Anthony J. Buonicore and Wayne T. Davis, ed., Air & Waste Management Association, Van Norstrand Reinhold.

The dross is removed and fed into a dross furnace for recovery of the non-lead mineral values. To enhance copper recovery, drossed lead bullion is treated by adding sulfur bearing materials, zinc, and/or aluminum, lowering the copper content to approximately 0.01 percent.

During the fourth step the lead bullion is refined using pyrometallurgical methods to remove any remaining non-lead saleable materials (e.g., gold, silver, bismuth, zinc, and metal oxides such as antimony, arsenic, tin, and copper oxide). The lead is refined in a cast iron kettle during five stages. Antimony, tin, and arsenic are removed first. Then gold and silver are removed by adding zinc. Next, the lead is refined by vacuum removal of zinc. Refining continues with the addition of calcium and magnesium. These two materials combine with bismuth to form an insoluble compound that is skimmed from the kettle. In the final step caustic soda and/or nitrates may be added to the lead to remove any remaining traces of metal impurities. The refined lead will have a purity of 99.90 to 99.99 percent, and may be mixed with other metals to form alloys or it may directly be cast into shapes.

The processes used in the primary production of lead produce several waste streams of concern under different regulatory scenarios. The listed RCRA hazardous wastes include smelting plant wastes that are sent to surface impoundments to settle. The impoundments are used to collect solids from miscellaneous slurries, such as acid plant blowdown, slag granulation water, and plant washings. Acid plant blowdown is generated during the production of lead the same way it is produced at a copper plant; during the recovery of sulfur dioxide emissions. Slag granulation water is produced when hot slag from the process is sprayed with water to be cooled and granulated before transport to a slag pile. Plant washing is a housekeeping process and the washdown normally contains a substantial amount of lead and other process materials. When these materials accumulate in a surface impoundment or are dredged from the surface impoundment they are regulated as hazardous waste K065.

Secondary Lead Processing

The secondary production of lead begins with the recovery of old scrap from worn-out, damaged, or obsolete products and new scrap that is made of product wastes and smelter-refinery drosses, residues, and slags. The chief source of old scrap in the U.S. is lead-acid batteries, though cable coverings, pipe, sheet, and terne bearing metals also serve as a source of scrap. Solder, a tin-based alloy,

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may also be recovered from the processing of circuit boards for use as lead charge.

While some secondary lead is recovered directly for specialty products like babbitt metal, solder, re-melt, and copper-base alloys, about 97 percent of secondary lead is recovered at secondary lead smelters and refineries as either soft (unalloyed) or antimonial lead, most of which is recycled directly back into the manufacture of Unlike copper and zinc, where scrap processing varies new batteries. tremendously by scrap type and ultimate use, the dominance of lead battery scrap allows for a more standard secondary recovery process. Prior to smelting, batteries must be broken by one of several techniques, and classified into their constituent products. The modern battery breaking process classifies the lead into metallics, oxides and sulfate fragments, and organics into separate casing and plate separator fractions. Cleaned polypropylene case fragments are recycled back into battery cases or other products. The dilute sulfuric acid is either neutralized for disposal, or recycled into the local acid market. One of three main smelting processes is then used to reduce the lead fractions to produce lead bullion.

The majority of domestic battery scrap is processed in blast furnaces or rotary reverberatory furnaces. Used to produce a semisoft lead, a reverberatory furnace is more suitable for processing fine particles and may be operated in conjunction with a blast furnace. The reverberatory furnace is a rectangular shell lined with refractory brick, and is fired directly with oil or gas to a temperature of 2300 degrees F. The material is heated by direct contact with combustion gases. The average furnace can process about 50 tons per day. About 47 percent of the charge is recovered as lead product and is periodically tapped into mold or holding pots. Forty-six percent of the charge is removed as slag and later processed in blast furnaces. The remaining seven percent of the furnace charge escapes as dust or fume. Short (batch) or long (continuous) rotary furnaces may be used. Slags from reverberatory furnaces are processed through the blast furnace for recovery of alloying elements.

Blast furnaces produce hard lead from charges containing siliceous slag from previous runs (about 4.5 percent of the charge), scrap iron (about 4.5 percent), limestone (about 3 percent), and coke (about 5.5 percent). The remaining 82.5 percent of the charge is comprised of oxides, pot furnace refining drosses, and reverberatory slag. The proportions of rerun slags, limestone, and coke, respectively vary to as high as eight percent, ten percent, and eight percent of the charge. Processing capacity of the blast furnace ranges from 20 to 80 tons per day. Similar to iron cupolas, the blast furnace is a vertical steel cylinder lined with refractory brick. Combustion air at 0.5 to 0.75 pounds per square inch is introduced through tuyeres (pipes) at the bottom of the furnace. Some of the coke combusts to melt the charge, while the remainder reduces lead oxides to elemental

 lead.

As the lead charge melts, limestone and iron float to the top of the molten bath and form a flux that retards oxidation of the product lead. The molten lead flows from the furnace into a holding pot at a nearly continuous rate. The product lead constitutes roughly 70 percent of the charge. From the holding pot, the lead is usually cast into large ingots, called pigs or sows. About 18 percent of the charge is recovered as slag, with about 60 percent of this being matte. Roughly five percent of the charge is retained for reuse, and the remaining seven percent of the charge escapes as dust or fume.

Refining/casting is the use of kettle type furnaces for re-melting, alloying, refining, and oxidizing processes. Materials charged for re-melting are usually lead alloy ingots that require no further processing before casting. Alloying furnaces simply melt and mix ingots of lead and alloy materials. Antimony, tin, arsenic, copper, and nickel are the most common alloying materials. Refining furnaces, as in primary lead production, are used either to remove copper and antimony to produce soft lead, or to remove arsenic, copper, and nickel for hard lead production.

Newer secondary recovery plants use lead paste desulfurization to reduce sulfur dioxide emissions and waste sludge generation during smelting. At the Doe Run Resource Recycling Facility, battery paste containing lead sulfate and lead oxide is desulfurized with soda ash to produce market grade sodium sulfate solution. The desulfurized paste is processed in a reverberatory furnace. The lead carbonate product may then be treated in a short rotary furnace. The battery grids and posts are processed separately in a rotary smelter.

V.B.2. Raw Material Inputs and Pollution Outputs

The material inputs and pollution outputs resulting from primary and secondary lead processing are presented by media in Exhibit 8.

Exhibit 8
Process Materials Inputs/Pollution Outputs - Lead

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Lead Sintering	Lead ore, iron, silica, limestone flux, coke, soda, ash, pyrite, zinc, caustic, and baghouse dust	Sulfur dioxide, particulate matter containing cadmium and lead		

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Lead Smelting	Lead sinter, coke	Sulfur dioxide, particulate matter containing cadmium and lead	Plant washdown wastewater, slag granulation water	Slag containing impurities such as zinc, iron, silica, and lime, surface impoundment solids (K065)
Lead Drossing	Lead bullion, soda ash, sulfur, baghouse dust, coke			Slag containing such impurities as copper, surface impoundment solids (K065)
Lead Refining	Lead drossing bullion			
Lead-acid Battery Breaking	Lead-acid batteries			Polypropylene case fragments, dilute sulfuric acid
Secondary Lead Smelting	Battery scrap, rerun slag, drosses, oxides, iron, limestone, and coke	Sulfur dioxide, particulate matter containing cadmium and lead		Slag, emission control dust (K069)

Primary Lead Processing

Primary lead processing activities usually result in air emissions, process wastes, and other solid-phase wastes. The primary air emissions from lead processing are substantial quantities of SO₂ and/or particulates. Nearly 85 percent of the sulfur present in the lead ore concentrate is eliminated in the sintering operation. The offgas containing a strong stream of SO₂ (five to seven percent SO₂) is sent to a sulfuric acid plant, while the weak stream (less than 0.5 percent SO₂) is vented to the atmosphere after removal of particulates. Particulate emissions from sinter machines range from five to 20 percent of the concentrated ore feed. Approximately 15 percent of the sulfur in the ore concentrate fed to the sinter machine is eliminated in the blast furnace. However, only half of this amount, about seven percent of the total sulfur in the ore, is emitted as SO₂. Particulate emissions from blast furnaces contain many different kinds of material, including a range of lead oxides, quartz, limestone, iron pyrites, iron-limestone-silicate slag, arsenic, and other metallic compounds associated with lead ores. The emission controls most commonly employed are fabric filters and electrostatic precipitators.

As mentioned above, approximately seven percent of the total sulfur present in lead ore is emitted as SO₂. The remainder is captured by the blast furnace slag. The blast furnace slag is composed primarily of iron and silicon oxides, as well as aluminum and calcium oxides. Other metals may also be present in smaller amounts including antimony, arsenic, beryllium, cadmium, chromium, cobalt, copper, lead, manganese, mercury, molybdenum, silver, and zinc. This blast furnace slag is either recycled back into the process or disposed of in piles on site.

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About 50-60 percent of the recovery furnace output is slag and residual lead that are both returned to the blast furnace. The remainder of this dross furnace output is sold to copper smelters for recovery of the copper and other precious metals.

Slag from the primary processing of lead that is not recycled was retained within the Bevill exemption and addressed in the 1990 Report to Congress. In the subsequent regulatory determination (56 FR 27300), EPA determined that regulation of this waste under Subtitle C was not warranted.

The smelting of primary lead produces a number of wastewaters and slurries, including acid plant blowdown, slag granulation water, and plant washdown water. Slag granulation water is generated when slag is disposed. It can either be sent directly to a slag pile or granulated in a water jet before being transported to the slag pile. The granulation process cools newly generated hot slag with a water spray. Slag granulation water is often transported to surface impoundments for settling. Plant washdown water results from plant housekeeping and normally contains a substantial amount of lead and other process materials. Acid plant blowdown results from the conversion of SO₂ to sulfuric acid. All of these materials are included in the definition of hazardous waste K065.

Secondary Lead Processing

Secondary lead processing results in the generation of air emissions and solidphase wastes. As with primary lead processing, reverberatory and blast furnaces used in smelting account for the vast majority of the total lead emissions. Other emissions from secondary smelting include oxides of sulfur and nitrogen, antimony, arsenic, copper, and tin. Smelting emissions are generally controlled with a settling and cooling chamber, followed by a baghouse. Other air emissions are generated during battery breaking. Emissions from battery breaking are mainly sulfuric acid and dusts containing dirt, battery case material, and lead compounds. Emissions from crushing are also mainly dusts.

The solid-phase wastes generated by secondary processing are emission control dust and slag. Slag is generated from smelting, and the emission control dust, when captured and disposed of, is considered to be hazardous waste K069.

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VI. PRIMARY AND SECONDARY ZINC PROCESSING

VI.A. Characterization of the Industry - Zinc

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the Primary and Secondary Zinc Industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes.

VI.A.1. <u>Industry Size and Geographic Distribution - Zinc</u>

The following discussion is based upon "U.S. Industrial Outlook 1994 - Metals," U.S. Department of Commerce, and information provided by the U.S. Department of the Interior, Bureau of Mines.

Variation in facility counts occur across data sources due to many factors, including reporting and definitional differences. This document does not attempt to reconcile these differences, but rather reports the data as they are maintained by each source.

Zinc is the fourth most widely used metal after iron, aluminum, and copper (lead is fifth). In abundant supply world-wide, zinc is mined and produced mainly in Canada, the former Soviet Union, Australia, Peru, Mexico, and the United States. Historically, in the U.S. recoverable zinc has been mined in 19 States: Alaska, Arizona, Colorado, Idaho, Illinois, Kansas, Missouri, Montana, Nevada, New Jersey, New Mexico, New York, Oklahoma, Pennsylvania, Tennessee, Utah, Virginia, Washington, and Wisconsin. In 1993, nearly 50 percent of all domestic zinc was produced in Alaska. Except for Missouri (eight percent) other exact state production figures were withheld to protect company proprietary data. Other top producing states in order of output were Tennessee, New York, and Missouri.

In 1993, the zinc industry employed 22,250 workers at mines and mills and 1,400 at primary smelters. For 1994, mine and mill employment was expected to stay at 2,200 and employment at zinc smelters was expected to decrease to 1,100 (U.S. DOI, Bureau of Mines, 1995). Employment decreases for primary smelters was attributed to the indefinite closures of a smelter in Oklahoma in later 1993. The four primary zinc smelters in the U.S., are located in Illinois, Oklahoma, Tennessee and Pennsylvania. There are currently 10 secondary zinc recovery plants in the U.S. (U.S. EPA, AP42, 1993).

VI.A.2. Product Characterization - Zinc

The U.S. accounts for almost one-quarter of worldwide slab zinc consumption and is the world's single largest market. About 80 percent of zinc is used in metal form while the rest is used in compound form. Ninety percent of zinc metal is used for galvanizing steel (a form of corrosion protection) and for alloys, and is used in a wide variety of materials in the automotive, construction, electrical, and machinery sectors of the economy. Zinc compound use also varies widely, but is mainly found in the agricultural, chemical, paint, pharmaceutical, and rubber sectors of the economy.

VI.A.3. <u>Economic Trends - Zinc</u>

In 1993, both domestic mine and slab zinc production were down, with slab zinc production down 4.75 percent to .381 Mmt. This production slump was off-set by domestic consumption which increased significantly in 1993, up eight percent, to 1.15 Mmt due to a surge in galvanized steel shipments. Strong growth in automobile demand and continued improvement in the construction industry led to increased consumption along with increased zinc die casting consumption. Consumption of zinc compounds also increased, especially of zinc oxide which increased over 27 percent. More than half of domestic zinc oxide production went to the rubber industry, primarily for use in producing tires (zinc is used in the compounding of rubber before it is cured).

In 1994, domestic refined zinc production is expected to continue its downward trend and drop 3.5 percent from .381 to .370 Mmt. However, domestic demand for zinc is expected to grow 4.2 percent in 1994 to 1.22 Mmt due to increases in all end uses except for nonresidential construction. This increased domestic demand should be met in large part by imports from Canada and Mexico. Imports of slab zinc mainly from these two countries in 1993 made up for almost 65 percent of domestic consumption. Zinc alloy was given preferential status in the Generalized System of Preferences 1990, which allows Mexico and member countries to export zinc alloys to the U.S. duty free. Tariffs on zinc from Canada will be phased out by 1998 due to the U.S.-Canada Free Trade Agreement. Zinc from the former Soviet Union is not expected to be used for U.S. consumption though its production is expected to negatively affect the U.S. market. This situation is similar to that for other metals in that over-production by former eastern bloc countries causes world prices to drop as London Metal Exchange warehouse supplies increase.

Domestically, the long-term demand for zinc is expected to increase, with consumption rising about 2.2 percent a year to reach 1.27 Mmt by 1998. Galvanization using zinc is expected to continue as the largest end-user of zinc,

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and it is predicted that by 1995 virtually all automobiles sold in the U.S. will be made from two-sided steel, enabling these vehicles to last at least ten years without any perforation damage. Zinc die-casting is also expected to increase in use as new applications are put into use.

VI.B. Industrial Process Description

This section describes the major industrial processes within the Primary and Secondary Zinc Processing industry, including the materials and equipment used, and the processes employed. The section is designed for those interested in gaining a general understanding of the industry, and for those interested in the inter-relationship between the industrial process and the topics described in subsequent sections of this profile -- pollutant outputs, pollution prevention opportunities, and Federal regulations. This section does not attempt to replicate published engineering information that is available for this industry. Refer to Section IX for a list of reference documents that are available.

This section specifically contains a description of commonly used production processes, associated raw materials, the byproducts produced or released, and the materials either recycled or transferred off-site. This discussion, coupled with schematic drawings of the identified processes, provide a concise description of where wastes may be produced in the process. This section also describes the potential fate (air, water, land) of these waste products.

VI.B.1. <u>Industrial Processes in the Primary and Secondary Zinc Processing</u> <u>Industry</u>

The following discussion is based upon the following documents: "Compilation of Air Pollutant Emission Factors(AP42), " "Background Listing Document for K065," "1990 Report to Congress on Special Wastes from Mineral Processing," published by the U.S. Environmental Protection Agency, and "Recycled Metals in the United States, A Sustainable Resource," published by U.S. Department of the Interior, Bureau of Mines.

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Primary Zinc Processing

The primary production of zinc begins with the reduction of zinc concentrates to metal (the zinc concentration process consists of separating the ore, which may be as little as two percent zinc, from waste rock by crushing and flotation, a process normally performed at the mining site and discussed in more detail in the Metal Mining Profile). Zinc reduction is accomplished in one of two ways: either pyrometallurgically by distillation (retorting in a furnace) or hydrometallurgically by electrowinning. Because hydrometallurgical refining accounts for approximately 80 percent of total zinc refining, pyrometallurgical zinc refining will not be discussed in detail in this profile.

Four processing stages are generally used in hydrometallurgic zinc refining: calcining, leaching, purification, and electrowinning. Calcining, or roasting, is common to both pyrometallic and electrolytic (a form of hydrometallurgy) zinc refining, and is performed to eliminate sulfur and form leachable zinc oxide. Roasting is a high-temperature process that converts zinc sulfide concentrate to an impure zinc oxide called calcine. Roaster types include multiple-hearth, suspension, or fluidized-bed. In general, calcining begins with the mixing of zinc-containing materials with coal. This mixture is then heated, or roasted, to vaporize the zinc oxide which is then moved out of the reaction chamber with the resulting gas stream. The gas stream is directed to the bag-house (filter) area where the zinc oxide is captured in bag-house dust.

In a multiple-hearth roaster, the concentrate drops through a series of nine or more hearths stacked inside a brick-lined cylindrical column. As the feed concentrate drops through the furnace, it is first dried by the hot gases passing through the hearths and then oxidized to produce calcine. Multiple hearth roasters are unpressurized and operate at approximately 1,300 degrees F.

In a suspension roaster, the concentrates are blown into a combustion chamber. The roaster consists of a refractory-lined cylindrical shell, with a large combustion space at the top and two to four hearths in the lower portion. Additional grinding, beyond that required for a multiple hearth furnace, is normally required to assure that heat transfer to the material is sufficiently rapid for desulfurization and oxidation reaction to occur in the furnace chamber. Suspension roasters are also unpressurized and operate at about 1,800 degrees F.

Fluidized bed roasters require that the sulfide concentrates be finely ground. The concentrates are then suspended and oxidized on a feedstock bed supported on an air column. As in the suspension bed roaster, the reduction rates for desulfurization are more rapid than in the older multiple-hearth processes. Fluidized-bed roasters operate under a pressure slightly lower than atmospheric

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and at temperatures averaging 1,800 degrees F. In the fluidized-bed process, no additional fuel is required after ignition has been achieved. The major advantages of this roaster are greater throughput capacities and greater sulfur removal capabilities. All of the above calcining processes generate sulfur dioxide, which is controlled and converted to sulfuric acid as a marketable process by-product.

Electrolytic processing of desulfurized calcine consists of three basic steps; leaching, purification, and electrolysis. Leaching refers to the dissolving of the captured calcine in a solution of sulfuric acid to form a zinc sulfate solution. The calcine may be leached once or twice. In the double-leach method, the calcine is dissolved in a slightly acidic solution to remove the sulfates. The calcine is then leached a second time in a stronger solution which dissolves the zinc. This second leaching step is actually the beginning of the third step of purification because many of the iron impurities (such as goethite and hematite) drop out of the solution as well as the zinc.

After leaching, the solution is purified in two or more stages by adding zinc dust. The solution is purified as the dust forces deleterious elements to precipitate so that they can be filtered out. Purification is usually conducted in large agitation tanks. The process takes place at temperatures ranging from 104 to 185 degrees F, and pressures ranging from atmospheric to 2.4 atmospheres. The elements recovered during purification include copper as a cake and cadmium as a metal. After purification the solution is ready for the final step; electrowinning.

Zinc electrowinning takes place in an electrolytic cell and involves running an electric current from a lead-silver alloy anode through the aqueous zinc solution. This process charges the suspended zinc and forces it to deposit onto an aluminum cathode (a plate with an opposite charge) which is immersed in the solution. Every 24 to 48 hours, each cell is shut down, the zinc-coated cathodes removed and rinsed, and the zinc mechanically stripped from the aluminum plates. The zinc concentrate is then melted and cast into ingots, and is often as high as 99.995 percent pure.

Electrolytic zinc smelters contain as many as several hundred cells. A portion of the electrical energy is converted into heat, which increases the temperature of the electrolyte. Electrolytic cells operate at temperature ranges from 86 to 95 degrees F at atmospheric temperature. During electrowinning a portion of the electrolyte passes through cooling towers to decrease its temperature and to evaporate the water it collects during the process.

Sulfur dioxide is generated in large quantities during the primary zinc refining process and sulfur fixation is carried out concurrently with the primary production process in order to meet CAA emission standards. Concentrations of sulfur

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dioxide in the off-gas vary with the type of roaster operation. Typical concentrations for multiple hearth, suspension, and fluidized bed roasters are 4.5 to 6.5 percent, 10 to 13 percent, and 7 to 12 percent respectively. This sulfur dioxide is then converted into sulfuric acid.

The sulfur recovery process requires that the emissions from the zinc calcining, or roasting process, where over 90 percent of potential sulfur dioxide is generated during primary zinc refining, flow through a filtering material in the air emissions scrubber to capture the sulfur. A blowdown slurry is formed from the mixture of the filtering material and sulfur emissions. This slurry contains not only sulfur, but cadmium and lead, materials that are always present in zinc ore. The acid plant blowdown slurry/sludge that results from thickening of blowdown slurry at primary zinc facilities is regulated by RCRA as hazardous waste K066.

During the electrolytic refining of zinc, solid materials in the electrolytic solution that are not captured previously during purification may precipitate out in the electrolytic cell. When the cells undergo their periodic shutdown to recover zinc, this precipitated waste (known as anode slimes/sludges) is collected during cell cleaning. Once collected it is sent to a waste water treatment plant and the resulting sludges are also regulated by RCRA as hazardous waste K066.

Secondary Zinc Processing

The secondary zinc industry processes scrap metals for the recovery of zinc in the form of zinc slabs, zinc oxide, or zinc dust. Zinc recovery involves three general operations; pretreatment, melting, and refining (see Exhibit 9). Secondary recovery begins with the separation of zinc-containing metals from other materials, usually by magnetics, sink-float, or hand sorting. In situations where nonferrous metals have been mixed in shredder scrap, zinc can be separated from higher-melting metals such as copper and aluminum, by selective melting in a sweating furnace. A sweating furnace (rotary, reverberatory, or muffle furnace) slowly heats the scrap containing zinc and other metals to approximately 787 degrees F. This temperature is sufficient to melt zinc but is still below the melting point of the remaining metals.

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Exhibit 9 Secondary Zinc Processing

Source: Compilation of Air Pollutant Emission Fasctors, (AP42), U.S. EPA.

Molten zinc collects at the bottom of the sweat furnace and is subsequently recovered. The remaining scrap is cooled and removed to be sold to other secondary processors. In the case of zinc-galvanized steel, the zinc will be recovered largely in furnace dust after the scrap is charged into a steel making furnace and melted. Almost all of the zinc in electric arc furnace (EAF) dust is first recovered in an upgraded, impure zinc oxide product and is then shipped to primary pyrometallurgical zinc smelter for refinement to metal.

Clean new scrap, mainly brass and rolled zinc clippings and reject diecastings, generally require only re-melting before reuse. During melting, the zinccontaining material is heated in kettle, crucible, reverberatory, and electric induction furnaces. Flux is used to trap impurities from the molten zinc. Facilitated by agitation, flux and impurities float to the surface of the melt as dross, and is skimmed from the surface. The remaining molten zinc may be poured into molds or transferred to the refining operation in a molten state. Drosses, fragmentized diecastings, and mixed high-grade scrap are typically remelted, followed by zinc distillation with recovery as metal, dust, or oxide. Sometimes, high-purity drosses are simply melted and reacted with various fluxes to release the metallic content; often the recovered metal can be used directly as a galvanizing brightener or master alloy. Zinc alloys are produced from pretreated scrap during sweating and melting processes. The alloys may contain small amounts of copper, aluminum, magnesium, iron, lead, cadmium, and tin. Alloys containing 0.65 to 1.25 percent copper are significantly stronger than unalloyed zinc.

Medium and low-grade skims, oxidic dust, ash, and residues generally undergo an intermediate reduction-distillation pyrometallurgical step to upgrade the zinc product before further treatment; or, they are leached with acid, alkaline, or ammoniacal solutions to extract zinc. For leaching, the zinc containing material is crushed and washed with water, separating contaminants from zinc-containing material. The contaminated aqueous stream is treated with sodium carbonate to convert zinc chloride into sodium chloride and insoluble zinc hydroxide. The sodium chloride is separated from the insoluble residues by filtration and settling. The precipitate zinc hydroxide is dried and calcined (dehydrated into a powder at high temperature) to convert it into crude zinc oxide. The zinc oxide product is usually refined to zinc at primary zinc smelters. The washed zinc-containing metal portion becomes the raw material for the melting process.

Distillation retorts and furnaces are used either to reclaim zinc from alloys or to refine crude zinc. Bottle retort furnaces consist of a pear-shaped ceramic retort (a long-necked vessel used for distillation). Bottle retorts are filled with zinc alloys and heated until most of the zinc is vaporized, sometimes as long as 24 hours. Distillation involves vaporization of zinc at temperatures from 1800 to

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2280 degrees F, and condensation as zinc dust or liquid zinc. Zinc dust is produced by vaporization and rapid cooling, and liquid zinc results when the vaporous product is condensed slowly at moderate temperatures.

A muffle furnace is a continuously charged retort furnace which can operate for several days at a time. Molten zinc is charged through a feed well that also acts as an airlock. Muffle furnaces generally have a much greater vaporization capacity than bottle retort furnaces.

Air pollution control can be an area of concern when pyrometallurgical processes are employed in the secondary recovery of zinc. When the recovery process used is simply an iron pot re-melt operation to produce zinc metal, fumes will not normally be generated. If slab zinc is needed and a rotary furnace is used, any air emissions are captured directly from the venting system (a rotating furnace sweats, or melts, the zinc separating it from drosses with different melting points, which allows it to be poured off separately). Air emissions become more of a concern when more complicated processes are used to produce zinc powder. Retort and muffle furnaces used to produce zinc powder heat the zinc and other charges to such a high temperature that the zinc vaporizes and is captured in the pollution control equipment. It is this zinc oxide dust that is the process' marketable product. Hoods are employed around the furnace openings used to add additional charge. The fumes collected from the hoods are not normally of high quality and will be used for products like fertilizer and animal feed.

For the most part, the zinc materials recovered from secondary materials such as slab zinc, alloys, dusts, and compounds are comparable in quality to primary products. Zinc in brass is the principal form of secondary recovery, although secondary slab zinc has risen substantially over the last few years because it has been the principal zinc product of EAF dust recycling. Impure zinc oxide products and zinc-bearing slags are sometimes used as trace element additives in fertilizers and animal feeds. Currently about 10 percent of the domestic requirement for zinc is satisfied by old scrap.

Due to environmental concerns, both domestic and world-wide secondary recovery of zinc (versus disposal) is expected to increase. However, the prospect for gains higher than 35 to 40 percent of zinc consumption is relatively poor because of the dissipative nature of zinc vapor.

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VI.B.2. <u>Raw Material Inputs and Pollution Outputs</u>

The material inputs and pollution outputs resulting from primary and secondary zinc processing are presented by media in Exhibit 10.

Exhibit 10
Process Materials Inputs/Pollution Outputs - Zinc

Process	Material Input	Air Emissions	Process Wastes	Other Wastes
Zinc Calcining	Zinc ore, coke	Sulfur dioxide, particulate matter containing zinc and lead		Acid plant blowdown slurry (K066)
Zinc Leaching	Zinc calcine, sulfuric acid, limestone, spent electrolyte		Wastewaters containing sulfuric acid	
Zinc Purification	Zinc-acid solution, zinc dust		Wastewaters containing sulfuric acid, iron	Copper cake, cadmium
Zinc Electrowinning	Zinc in a sulfuric acid/aqueous solution, lead-silver alloy anodes, aluminum cathodes, barium carbonate, or strontium, colloidal additives		Dilute sulfuric acid	Electrolytic cell slimes/sludges (K066)
Secondary Zinc Smelting	Zinc scrap, electric arc furnace dust, drosses, diecastings, fluxes	Particulates		Slags containing copper, aluminum, iron, lead, and other impurities
Secondary Zinc Reduction Distillation	Medium-grade zinc drosses, oxidic dust, acids, alkalines, or ammoniacal solutions	Zinc oxide fumes		Slags containing copper, aluminum, iron, lead, and other impurities

Primary Zinc Processing

Primary zinc processing activities generate air emissions, process wastes, and other solid-phase wastes. Air emissions are generated during roasting, which is responsible for more than 90 percent of the potential SO₂ emissions. Approximately 93 to 97 percent of the sulfur in the feed is emitted as sulfur oxides. Sulfur dioxide emissions from the roasting process at all four primary zinc processing facilities are recovered at on-site sulfuric acid plants. Much of the particulate matter emitted from primary zinc facilities is also attributable to roasters. Though the amount and composition of particulate varies with operating

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parameters, the particulate is likely to contain zinc and lead.

Wastewaters may be generated during the leaching, purification, and electrowinning stages of primary zinc processing when electrolyte and acid solutions become too contaminated to be reused again. This wastewater needs to be treated before discharge.

Solid wastes, some of which are hazardous, are generated at various stages in primary zinc processing. Slurry generated during the operation of sulfuric acid plants is regulated as hazardous waste K066 as is the sludge removed from the bottom of electrolytic cells. The solid copper cake generated during purification is generally sent off-site to recover the copper.

Secondary Zinc Processing

Secondary zinc processing generates air emissions and solid-phase wastes. Air emissions result from sweating and melting and consist of particulate, zinc fumes, other volatile metals, flux fumes, and smoke generated by the incomplete combustion of grease, rubber, and plastics in zinc scrap. Zinc fumes are negligible at low furnace temperatures. Substantial emissions may arise from incomplete combustion of carbonaceous material in the zinc scrap. These contaminants are usually controlled by afterburners, and particulate emissions are most commonly recovered by fabric filters. Emissions from refining operations are mainly metallic fumes. Distillation/oxidations operations emit their entire zinc oxide product in the exhaust dust. Zinc oxide is usually recovered in fabric filters with collection efficiencies of 9 to 99 percent.

The secondary zinc recovery process generates slags that contain metals such as copper, aluminum, iron, and lead. Though slag generated during primary pyrometallurgical processes is exempt from regulation as a hazardous waste under RCRA, slag resulting from secondary processing is not automatically exempt. Therefore if secondary processing slag exhibits a characteristic (e.g., toxicity for lead), it would need to be managed as a hazardous waste.

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VII. MANAGEMENT OF CHEMICALS IN WASTESTREAM

The Pollution Prevention Act of 1990 (EPA) requires facilities to report information about the management of TRI chemicals in waste and efforts made to eliminate or reduce those quantities. These data have been collected annually in Section 8 of the TRI reporting Form R beginning with the 1991 reporting year. The data summarized below cover the years 1992-1995 and is meant to provide a basic understanding of the quantities of waste handled by the industry, the methods typically used to manage this waste, and recent trends in these methods. TRI waste management data can be used to assess trends in source reduction within individual industries and facilities, and for specific TRI chemicals. This information could then be used as a tool in identifying opportunities for pollution prevention compliance assistance activities.

While the quantities reported for 1992 and 1993 are estimates of quantities already managed, the quantities reported for 1994 and 1995 are projections only. The EPA requires these projections to encourage facilities to consider future waste generation and source reduction of those quantities as well as movement up the waste management hierarchy. Future-year estimates are not commitments that facilities reporting under TRI are required to meet.

Exhibit 11 shows that the primary and secondary metals industry managed about 1.9 billion pounds of production-related waste (total quantity of TRI chemicals in the waste from routine production operations) in 1993 (column B). Column C reveals that of this production-related waste, 35 percent was either transferred offsite or released to the environment. Column C is calculated by dividing the total TRI transfers and releases by the total quantity of production-related waste. In other words, about 70 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns D, E and F, respectively. The majority of waste that is released or transferred off-site can be divided into portions that are recycled off-site, recovered for energy off-site, or treated off-site as shown in columns G, H, and I, respectively. The remaining portion of the production-related wastes (12.8 percent), shown in column J, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed off-site.

From the yearly data presented below it is apparent that the portion of TRI wastes reported as recycled on-site has increased and the portions treated or managed through energy recovery on-site have remained steady, but are projected to decrease, between 1992 and 1995.

Exhibit 11 Source Reduction and Recycling Activity for SIC 333-334

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A	В	С	D	E	F	G	H	I	J
1992	1,875	28%	42.98%	1.05%	23.93%	17.38%	0.15%	0.89%	12.68%
1993	1,991	35%	44.77%	0.99%	23.75%	17.17%	0.16%	0.33%	12.85%
1994	2,014	_	46.79%	0.88%	23.12%	16.60%	0.14%	0.35%	12.11%
1995	2,023	_	48.42%	1.01%	21.16%	16.39%	0.18%	0.39%	12.45%

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VIII. CHEMICAL RELEASE AND TRANSFER PROFILE

This section is designed to provide background information on the pollutant releases that are reported by this industry. The best source of comparative pollutant release information is the Toxic Release Inventory System (TRI). Pursuant to the Emergency Planning and Community Right-to-Know Act, TRI includes self-reported facility release and transfer data for over 600 toxic chemicals. Facilities within SIC Codes 20-39 (manufacturing industries) that have more than 10 employees, and that are above weight-based reporting thresholds are required to report TRI on-site releases and off-site transfers. The information presented within the sector notebooks is derived from the most recently available (1993) TRI reporting year (which then included 316 chemicals), and focuses primarily on the on-site releases reported by each sector. Because TRI requires consistent reporting regardless of sector, it is an excellent tool for drawing comparisons across industries.

Although this sector notebook does not present historical information regarding TRI chemical releases over time, please note that in general, toxic chemical releases have been declining. In fact, according to the 1993 Toxic Release Inventory Data Book, reported releases dropped by 42.7% between 1988 and 1993. Although on-site releases have decreased, the total amount of reported toxic waste has not declined because the amount of toxic chemicals transferred off-site has increased. Transfers have increased from 3.7 billion pounds in 1991 to 4.7 billion pounds in 1993. Better management practices have led to increases in off-site transfers of toxic chemicals for recycling. More detailed information can be obtained from EPA's annual Toxics Release Inventory Public Data Release book (which is available through the EPCRA Hotline at 1-800-535-0202), or directly from the Toxic Release Inventory System database (for user support call 202-260-1531).

Wherever possible, the sector notebooks present TRI data as the primary indicator of chemical release within each industrial category. TRI data provide the type, amount, and media receptor of each chemical released or transferred. When other sources of pollutant release data have been obtained, these data have been included to augment the TRI information.

TRI Data Limitations

The reader should keep in mind the following limitations regarding TRI data. Within some sectors, the majority of facilities are not subject to TRI reporting because they are not considered manufacturing industries, or because they are below TRI reporting thresholds. Examples are the mining, dry cleaning, printing, and transportation equipment cleaning sectors. For these sectors, release

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information from other sources has been included.

The reader should also be aware that TRI "pounds released" data presented within the notebooks is not equivalent to a "risk" ranking for each industry. Weighting each pound of release equally does not factor in the relative toxicity of each chemical that is released. The Agency is in the process of developing an approach to assign toxicological weightings to each chemical released so that one can differentiate between pollutants with significant differences in toxicity. As a preliminary indicator of the environmental impact of the industry's most commonly released chemicals, the notebook briefly summarizes the toxicological properties of the top five chemicals (by weight) reported by each industry.

Definitions Associated With Section IV Data Tables

General Definitions

SIC Code -- the Standard Industrial Classification (SIC) is a statistical classification standard used for all establishment-based Federal economic statistics. The SIC codes facilitate comparisons between facility and industry data.

TRI Facilities -- are manufacturing facilities that have 10 or more full-time employees and are above established chemical throughput thresholds. Manufacturing facilities are defined as facilities in Standard Industrial Classification primary codes 20-39. Facilities must submit estimates for all chemicals that are on the EPA's defined list and are above throughput thresholds.

Data Table Column Heading Definitions

The following definitions are based upon standard definitions developed by EPA's Toxic Release Inventory Program. The categories below represent the possible pollutant destinations that can be reported.

RELEASES -- are an on-site discharge of a toxic chemical to the environment. This includes emissions to the air, discharges to bodies of water, releases at the facility to land, as well as contained disposal into underground injection wells.

Releases to Air (Point and Fugitive Air Emissions) -- Include all air emissions from industry activity. Point emissions occur through confined air streams as found in stacks, ducts, or pipes. Fugitive emissions include losses from equipment leaks, or evaporative losses from impoundments, spills, or leaks.

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Releases to Water (Surface Water Discharges) - encompass any releases going directly to streams, rivers, lakes, oceans, or other bodies of water. Any estimates for stormwater runoff and non-point losses must also be included.

Releases to Land -- includes disposal of waste to on-site landfills, waste that is land treated or incorporated into soil, surface impoundments, spills, leaks, or waste piles. These activities must occur within the facility's boundaries for inclusion in this category.

Underground Injection -- is a contained release of a fluid into a subsurface well for the purpose of waste disposal.

TRANSFERS -- is a transfer of toxic chemicals in wastes to a facility that is geographically or physically separate from the facility reporting under TRI. The quantities reported represent a movement of the chemical away from the reporting facility. Except for off-site transfers for disposal, these quantities do not necessarily represent entry of the chemical into the environment.

Transfers to POTWs -- are wastewaters transferred through pipes or sewers to a publicly owned treatments works (POTW). Treatment and chemical removal depend on the chemical's nature and treatment methods used. Chemicals not treated or destroyed by the POTW are generally released to surface waters or landfilled within the sludge.

Transfers to Recycling -- are sent off-site for the purposes of regenerating or recovering still valuable materials. Once these chemicals have been recycled, they may be returned to the originating facility or sold commercially.

Transfers to Energy Recovery -- are wastes combusted off-site in industrial furnaces for energy recovery. Treatment of a chemical by incineration is not considered to be energy recovery.

Transfers to Treatment -- are wastes moved off-site for either neutralization, incineration, biological destruction, or physical separation. In some cases, the chemicals are not destroyed but prepared for further waste management.

Transfers to Disposal -- are wastes taken to another facility for disposal generally as a release to land or as an injection underground.

VIII.A. EPA Toxics Release Inventory for the Nonferrous Metals Industry

TRI release amounts listed below are not associated with non-compliance with

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environmental laws. These facilities appear based on self-reported data submitted to the Toxics Release Inventory program.

Exhibits 11-16 illustrate TRI releases and transfers for the primary nonferrous metals smelting and refining industry (SIC 333). For SIC 333 as a whole, chlorine comprises the largest number of TRI releases. This is reflected in the fact that chlorine is a by-product of the magnesium industry and the largest reporter for SIC 333 is a magnesium facility. The other top SIC 333 releases are copper compounds, zinc compounds, lead compounds, and sulfuric acid, all of which are by-products of the processes discussed previously.

The TRI database contains a detailed compilation of self-reported, facility-specific chemical releases. The top reporting facilities for this sector are listed below. Facilities that have reported only the SIC codes covered under this notebook appear on the first list. The second list contains additional facilities that have reported the SIC code covered within this report, and one or more SIC codes that are not within the scope of this notebook. Therefore, the second list includes facilities that conduct multiple operations — some that are under the scope of this notebook, and some that are not. Currently, the facility-level data do not allow pollutant releases to be broken apart by industrial process.

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Exhibit 12
Top 10 TRI Releasing Primary Metal Industries Facilities (SIC 333)

SIC Codes	Total TRI	Facility Name	City	State
	Releases in			
	Pounds			
3339	73,300,250	Magnesium Corp. of America, Rowley Plant	Rowley	UT
3339	42,728,498	Asarco, Inc., E. Helena Plant	East Helena	MT
3331	14,773,759	Phelps Dodge Mining Co., Hidalgo Smelter	Playas	NM
3331	11,717,315	Kennecott Utah Copper	Magna	UT
3339	8,194,328	DOE Run Co., Herculaneum Smelter	Herculaneum	МО
3331	8,142,539	Chino Mines Co., Hurley Smelter	Hurley	NM
3339	7,085,302	Asarco, Inc., Glover Plant	Annapolis	MD
1021, 3331, 3351	6,223,505	Cyprus Miami Mining Corp.	Claypool	AZ
3331	5,970,420	Asarco, Inc., Amarillo Copper Refinery	Amarillo	TX
3321, 3365	4,496,188	GMC Powertrain Group, Saginaw Grey Iron	Saginaw	MI

Exhibit 13 Top 10 TRI Releasing Primary Smelting and Refining Facilities

Rank	Total TRI	Facility Name	City	State
	Releases in			
	Pounds			
1	73,300,250	Magnesium Corp. of America, Rowley Plant	Rowley	UT
2	42,728,498	Asarco Inc., E. Helena Plant	East Helena	MT
3	14,773,759	Phelps Dodge Mining Co., Hidalgo Smelter	Playas	NM
4	1,1717,315	Kennecott Utah Copper	Magna	UT
5	8,194,328	Doe Run Co., Herculaneum Smelter	Herculaneum	MO
6	8,142,539	Chino Mines Co., Hurley Smelter	Hurley	NM
7	7,085,302	Asarco, Inc., Glover Plant	Annapolis	MD
8	5,970,420	Asarco, Inc., Amarillo Copper Refinery	Amarillo	TX
9	1,123,708	Glenbrook Nickel Co.	Riddle	OR
10	780,927	Alcoa Rockdale Works	Rockdale	TX

Source: U.S. EPA, Toxics Release Inventory Database, 1993..

Note: Being included on these lists does not mean that the release is associated with non-compliance with environmental laws.

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Exhibit 14 TRI Reporting Primary Smelting and Refining Facilities (SIC 333) by State

State	Number of Facilities	State	Number of Facilities
AZ	1	NM	2
CO	1	NY	2
CT	1	ОН	3
IN	1	OR	3
KY	1	PA	2
MD	1	SC	1
MO	3	TX	5
MT	3	UT	3
NC	2	VA	1
NE	1	WA	7
NJ	1		

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Exhibit 15
Releases for Primary Smelting and Refining (SIC 333) in TRI, by Number of Facilities (releases reported in pounds/year)

	# Facilities				Under-			Average
	Reporting	Fugitive		Water	ground	Land	Total	Releases
Chemical Name	Chemical	Air	Point Air	Discharges	Injection	Disposal	Releases	per Facility
Copper	20	9412	248340	508	0	500254	758514	37926
Chlorine	19	153751	67037082	2803	0	11	67193647	3536508
Sulfuric Acid	15	24527	1013009	0	5700000	100920	6838456	455897
Hydrogen Fluoride	14	1565588	1520212	5	0	0	3085805	220415
Manganese	11	15	5130	0	0	5	5150	468
Zinc Compounds	10	47545	102940	8505	5	42345637	42504632	4250463
Chromium	8	10	398	5	0	0	413	52
Copper Compounds	8	559987	408015	1502	65000	27574267	28608771	3576096
Hydrochloric Acid	8	3853	6155294	0	5	5	6159157	769895
Lead Compounds	8	68834	274504	7263	730	7713452	8064783	1008098
Arsenic Compounds	7	7147	30181	3005	52000	2190652	2282985	326141
Antimony Compounds	6	6319	4398	3143	2100	661740	677700	112950
Cadmium Compounds	6	1286	18912	311	0	39734	60243	10041
Nickel Compounds	6	1323	8956	225	4200	1149028	1163732	193955
Nitric Acid	6	15	23670	0	5	15	23705	3951
Aluminum (Fume Or	5	5760	32472	44	0	5	38281	7656
Dust)								
Lead	5	138589	96836	18	0	2352628	2588071	517614
Nickel	5	345	781	4	0	29052	30182	6036
Silver Compounds	5	848	2210	270	100	19633	23061	4612
Barium Compounds	4	5	1850	0	890	456308	459053	114763
Arsenic	3	270	28264	9	0	7114	35657	11886
Cadmium	3	981	6181	11	0	4824	11997	3999
Chromium Compounds	3	250	592	250	0	190005	191097	63699
Manganese Compounds	3	620	823	0	0	2400643	2402086	800695
Selenium Compounds	3	1350	38000	250	2300	120265	162165	54055
Zinc (Fume Or Dust)	3	10190	25682	46	0	4010295	4046213	1348738
1,1,1-Trichloroethane	3	75031	0	0	0	0	75031	25010
Anthracene	2	250	25487	0	0	0	25737	12869
Antimony	2	500	10915	5	0	0	11420	5710
Cobalt	2	250	5	0	0	0	255	128
Cobalt Compounds	2	669	262	255	0	5	1191	596
Cyanide Compounds	2	0	0	500	0	0	500	250
Ethylene Glycol	2	0	0	0	0	0	0	0
Phosphoric Acid	2	0	0	0	0	0	0	0
Thiourea	2	60	0	0	5300	255	5615	2808
Ammonia	1	250	0	0	0	0	250	250
Beryllium Compounds	1	0	0	0	0	0	0	0
Cresol (Mixed Isomers)	1	250	0	250	0	750	1250	1250
Decabromodiphenyl	1	0	250	0	0	0	250	250
Oxide								
Dichlorodifluoromethane	1	18000	0	0	0	0	18000	18000
M-Xylene	1	14000	0	0	0	0	14000	14000
Naphthalene	1	0	467	0	0	0	467	467
Phenol	1	0	0	1	0	0	1	1
Styrene	1	1900	0	0	0	5	1905	1905
Thallium	1	5	250	0	0	755	1010	1010

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Titanium Tetrachloride	1	250	250	0	0	0	500	500
1,2,4-Trimethylbenzene	1	18000	0	0	0	0	18000	18000
Total		2,738,235	77,122,618	29,188	5,832,635	91,868,262	177,590,938	

Exhibit 16
Transfers for Primary Smelting and Refining (SIC 333) in TRI, by Number of Facilities
(Transfers reported in pounds/year)

	# Facilities	POTW				Energy	Total	Average
Chemical Name	Reporting	Discharge	Disposal	Recycling	Treatment	Recovery	Transfers	Transfers
	Chemical	8.		,. 8				per
								Facility
Copper	20	5	17596	124723	0	0	142324	7116
Chlorine	19	0		9991	0	0	9991	526
Sulfuric Acid	15	1	600	6454346	0	0	6454947	430330
Hydrogen Fluoride	14	0	0	0	0	0	0	0
Manganese	11	0	14	46752	0	0	46766	4251
Zinc Compounds	10	760	2692570	750680	833231	0	4277241	427724
Chromium	8	0	0	2361	0	0	2361	295
Copper Compounds	8	459	2900850	3882069	93989	0	6877367	859671
Hydrochloric Acid	8	0	0	0	0	0	0	0
Lead Compounds	8	2401	2253086	2289461	11239	0	4556187	569523
Arsenic Compounds	7	386	1649205	174013	634487	0	2458091	351156
Antimony Compounds	6	1749	345100	29836	15262	0	391947	65325
Cadmium Compounds	6	346	26097	420187	62987	0	509617	84936
Nickel Compounds	6	260	5	237910	3931	0	242106	40351
Nitric Acid	6	0	5	0	11000	0	11005	1834
Aluminum	5	0	317650	3826700	0	0	4144350	828870
(Fume Or Dust)								
Lead	5	5	5	640899	0	0	640909	128182
Nickel	5	5		633	0	0	638	128
Silver Compounds	5	174	5765	8756	255	0	14950	2990
Barium Compounds	4	0	0	0	0	0	0	0
Arsenic	3	5	250	55713	0	0	55968	18656
Cadmium	3	5		212387	0	0	212392	70797
Chromium Compounds	3	0	1200	15000	0	0	16200	5400
Manganese Compounds	3	41	0	5639	0	0	5680	1893
Selenium Compounds	3	0	19005	0	0	0	19005	6335
Zinc (Fume Or Dust)	3	250	0	412568	0	0	412818	137606
1,1,1-Trichloroethane	3	0	0	0	250	0	250	83
Anthracene	2	0	14032	0	0	0	14032	7016
Antimony	2	0	4110	1911550	0	0	1915660	957830
Cobalt	2	0	0	0	0	0	0	0
Cobalt Compounds	2	250	0	77640	0	0	77890	38945
Cyanide Compounds	2	0	53213	0	1813	0	55026	27513
Ethylene Glycol	2	0	0	0	8673	0	8673	4337
Phosphoric Acid	2	0	0	0	160	0	160	80
Thiourea	2	0	0	0	0	0	0	0
Ammonia	1	0	0	0	0	0	0	0
Beryllium Compounds	1	0	0	0	0	0	0	0
Cresol (Mixed Isomers)	1	0	0	0	0	0	0	0

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Decabromodiphenyl Oxide	1	0	4374	0	0	0	4374	4374
Dichlorodifluoromethane	1	0	0	0	0	0	0	0
M-Xylene	1	0	0	0	0	0	0	0
Naphthalene	1	0	0	0	0	0	0	0
Phenol	1	0	0	0	0	0	0	0
Styrene	1	0	0	0	0	0	0	0
Thallium	1	5	0	750	0	0	755	755
Titanium Tetrachloride	1	0	0	0	0	0	0	0
4-Trimethylbenzene	1	0	0	0	0	0	0	0
Total	225	7,107	10,304,732	21,590,56	1,677,277	0	33,579,680	108187.8
				4				2

Exhibits 17-20 illustrate the TRI releases and transfers for the secondary nonferrous metals smelting and refining industry (SIC 334). For the industry as a whole, the largest releases were the various metals: aluminum (fume or dust), zinc compounds, lead compounds, copper and zinc (fume or dust).

Exhibit 17
Top 10 TRI Releasing Secondary Smelting and Refining (SIC 334)

Rank	Total TRI	Facility Name	City	State
	Releases in			
	Pounds			
1	881,970	Gulf Chemical & Metallurgical Corp.	Freeport	TX
2	854,630	Imco Recycling Inc.	Morgantown	KY
3	758,089	Alabama Reclamation Plant	Sheffield	AL
4	329,250	Imco Recycling Inc.	Sapulpa	OK
5	288,070	Alcan Recycling Div.	Berea	KY
6	184,460	Wabash Alloys	Wabash	IN
7	147,455	Chemetco Inc.	Hartford	IL
8	146,852	Schuylkill Metals Corp.	Baton Rouge	LA
9	140,000	Southern Reclamation Co.	Sheffield	AL
10	131,899	North Chicago Refiners & Smelters	North	IL
			Chicago	

Source: U.S. EPA, Toxics Release Inventory Database, 1993.

Note: Being included on these lists does not mean that the release is associated with non-compliance with environmental laws.

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Exhibit 18 TRI Reporting Secondary Smelting and Refining Facilities (SIC 334) by State

_	Number of
State	Facilities
AL	10
AR	3
AZ	1
CA	12
CT	2
FL	1
GA	2
IL	17
IN	13
KS	2
KY	5
LA	1
MA	5
MD	1
MI	7
MN	4
MO	4

	Number of
State	Facilities
MS	1
NC	1
NJ	5
NM	1
NY	8
OH	12
OK	3
PA	13
RI	3
SC	2
TN	9
TX	6
UT	1
VA	1
WI	4
WV	3

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Exhibit 19
Releases for Secondary Smelting and Refining (SIC 334) in TRI, by Number of Facilities (Releases reported in pounds/year)

Chemical Name	# Facilities Reporting Chemical	Fugitive Air	Point Air	Water Discharges	Under- ground Injection	Land Disposal	Total Releases	Average Releases per Facility
Copper	74	17235	56198	2720	0	221287	297440	4019
Nickel	38	5646	5873	262	0	12934	24715	650
Chlorine	32	5103	6304	0	0	0	11407	356
Lead	30	13964	29230	571	0	750	44515	1484
Copper Compounds	29	11921	35205	358	0	1500	48984	1689
Lead Compounds	25	11211	115573	404	0	147930	275118	11005
Manganese	25	7848	3547	10	0	74536	85941	3438
Aluminum (Fume Or Dust)	24	34297	196604	922	11	641760	873594	36400
Zinc Compounds	24	41195	263420	3049	0	0	307664	12819
Sulfuric Acid	21	6917	1730	0	0	0	8647	412
Chromium	19	1465	1937	255	0	2005	5662	298
Zinc (Fume Or Dust)	19	57759	79392	331	0	0	137482	7236
Hydrochloric Acid	14	17116	604670	0	0	0	621786	44413
Nickel Compounds	13	1113	1492	297	0	0	2902	223
Chromium Compounds	10	276	617	0	0	0	893	89
Ammonia	9	1343335	168094	53229	57053	353800	1975511	219501
Antimony	9	364	373	586	0	5	1328	148
Antimony Compounds	9	115	1294	44	0	67760	69213	7690
Silver	9	21	517	251	0	0	789	88
Silver Compounds	9	1033	823	5	0	0	1861	207
Manganese Compounds	8	1074	3426	570	0	0	5070	634
Nitric Acid	8	1008	2628	0	0	0	3636	455
Arsenic	7	310	308	36	0	5	659	94
Arsenic Compounds	7	10	573	16	0	27104	27703	3958
Barium Compounds	6	298	2011	0	0	0	2309	385
Cadmium Compounds	6	545	5409	20	0	0	5974	996
Cobalt	6	905	680	5	0	20	1610	268
Cadmium	3	250	874	281	0	0	1405	468
Hexachloroethane	3	0	11536	0	0	0	11536	3845
Aluminum Oxide (Fibrous Form)	2	0	53	0	0	0	53	27
Barium	2	20	45	0	0	0	65	33
Beryllium	2	0	5	0	0	0	5	3
Methanol	2	1000	0	0	0	0	1000	500
Molybdenum Trioxide	2	500	4205	18750	0	0	23455	11728
Ammonium Sulfate (Solution)	1	250	0	0	0	0	250	250
Cobalt Compounds	1	0	0	0	0	0	0	0
Mercury Compounds	1	250	5	5	0	5	265	265
Phosphoric Acid	1	0	0	0	0	0	0	0

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Phosphorus	1	0	0	0	0	0	0	0
(Yellow Or White)								
Polychlorinated Biphenyls	1	0	0	0	0	0	0	0
Selenium	1	0	1	0	0	0	1	1
Xylene (Mixed Isomers)	1	250	0	0	0	0	250	250
1,1,1-Trichloroethane	1	250	0	0	0	0	250	250
Totals		1,584,854	1,604,652	82,977	57,064	1,551,401	4,880,948	

Exhibit 20
Transfers for Secondary Smelting and Refining (SIC 334) in TRI, by Number of Facilities (Transfers reported in pounds/year)

	# Facilities POTW					Energy	Total	
Chemical Name	Reporting Chemical	Discharge	Disposal	Recycling	Treatment	Recovery	Total Transfers	per Facility
Copper	74	7024	139130	20126255	20233	0	20292642	
								274225
Nickel	38	282	9366	78143	3984	0	91775	2415
Chlorine	32	2545	0	0	0	0	2545	80
Lead	30	1106	675459	1749221	16055	0	2441841	81395
Copper Compounds	29	82	658756	806437	537038	0	2002313	69045
Lead Compounds	25	810	5543943	11216399	1020276	0	17781428	711257
Manganese	25	501	108806	67048	1236	0	177591	7104
Aluminum (Fume Or	24	500	966226	15417	0	0	982143	40923
Dust)								
Zinc Compounds	24	1661	129752	5571000	229930	0	5932343	247181
Sulfuric Acid	21	5	0	7332842	0	0	7332847	
				75525.2		· ·	7552017	349183
Chromium	19	51	11812	43378	83	0	55324	2912
Zinc (Fume Or Dust)	19	5	164242	1048567	8180	0	1220994	64263
Hydrochloric Acid	14	0	750	56965	27557	0	85272	6091
Nickel Compounds	13	23	34996	1531600	4777	0	1571396	
1								120877
Chromium Compounds	10	251	165015	214000	4664	0	383930	38393
Ammonia	9	0	621718	0	0	0	621718	69080
Antimony	9	927	127443	8180	880	0	137430	15270
Antimony Compounds	9	614	935418	641800	10710	0	1588542	
								176505
Silver	9	755	0	8680	0	0	9435	1048
Silver Compounds	9	20	835	485550	186	0	486591	54066
Manganese Compounds	8	75	29005	128500	0	0	157580	19698
Nitric Acid	8	5	1500	11299	750	0	13554	1694
Arsenic	7	67	51353	0	1784	0	53204	7601
Arsenic Compounds	7	110	196876	55734	0	0	252720	36103
Barium Compounds	6	4448	115647	82700	31094	0	233889	38982
Cadmium Compounds	6	257	0	393000	0	0	393257	65543
Cobalt	6	5	905	35045	15	0	35970	5995
Cadmium	3	0	12930	23795	900	0	37625	12542
Hexachloroethane	3	0	0	0	0	0	0	0
Aluminum Oxide	2	0	0	0	0	0	0	0
(Fibrous Form)								
Barium	2	5	62710	0	250	0	62965	31483
Beryllium	2	0	0	7930		0	7930	3965
Methanol	2	0	0	0	0	0	0	0
Molybdenum Trioxide	2	0		165100	17150	0	182250	91125

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Ammonium Sulfate (Solution)	1	0	0	0	0	0	0	0
Cobalt Compounds	1	0	0	0	0	0	0	0
Mercury Compounds	1	0	33200	0	10	0	33210	33210
Phosphoric Acid	1	0	0	0	0	0	0	0
Phosphorus (Yellow Or White)	1	250	0	0	0	0	250	250
Polychlorinated Biphenyls	1	0	255	0	0	0	255	255
Selenium	1	0	2673	0	510	0	3183	3183
Xylene (Mixed Isomers)	1	0	0	0	0	0	0	0
1,1,1-Trichloroethane	1	0	0	0	0	0	0	0
Totals		22,384	10,800,721	51,904,585	1,938,252	0	64,665,942	

VIII.B. Summary of the Selected Pollutants Released

The following is a synopsis of current scientific toxicity and fate information for the top chemicals (by weight) that facilities within this sector self-reported as released to the environment based upon 1993 TRI data. Because this section is based upon self-reported release data, it does not attempt to provide information on management practices employed by the sector to reduce the release of these chemicals. Information regarding pollutant release reductions over time may be available from EPA's TRI and 33/50 programs, or directly from the industrial trade associations that are listed in Section IX of this document. Since these descriptions are cursory, please consult the sources referenced below for a more detailed description of both the chemicals described in this section, and the chemicals that appear on the full list of TRI chemicals appearing in Section IV.A.

The brief descriptions provided below were taken from the 1993 Toxics Release Inventory Public Data Release (EPA, 1994), the Hazardous Substances Data Bank (HSDB), and the Integrated Risk Information System (IRIS), both accessed via TOXNET¹. The information contained below is based upon exposure assumptions that have been conducted using standard scientific procedures. The effects listed below must be taken in context of these exposure assumptions that are more fully explained within the full chemical profiles in HSDB.

Chlorine

<u>Toxicity</u>. Breathing small amounts of chlorine for short periods of time can affect the respiratory tract in humans, causing symptoms such as coughing and chest pain. It is irritating to the skin, eyes, and respiratory tract. Repeated long-term exposure to chlorine can cause adverse effects on the blood and respiratory

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systems.

Ecologically, chlorine is highly toxic to aquatic organisms at low doses.

<u>Carcinogenicity</u>. There is currently no evidence to suggest that this chemical is carcinogenic.

<u>Environmental Fate</u>. Most of the chlorine released to the environment will quickly evaporate.

Physical Properties. Chlorine is a highly reactive gas.

Copper

<u>Toxicity</u>. Metallic copper probably has little or no toxicity, although copper salts are more toxic. Inhalation of copper oxide fumes and dust has been shown to cause metal fume fever: irritation of the upper respiratory tract, nausea, sneezing, coughing, chills, aching muscles, gastric pain, and diarrhea. However, the respiratory symptoms may be due to a non-specific reaction to the inhaled dust as a foreign body in the lung, and the gastrointestinal symptoms may be attributed to the conversion of copper to copper salts in the body.

It is unclear whether long-term copper poisoning exists in humans. Some have related certain central nervous system disorders, such as giddiness, loss of appetite, excessive perspiration, and drowsiness to copper poisoning. Long-term exposure to copper may also cause hair, skin, and teeth discoloration, apparently without other adverse effects.

People at special risk from exposure to copper include those with impaired pulmonary function, especially those with obstructive airway diseases, since the breathing of copper fumes might cause exacerbation of pre-existing symptoms due to its irritant properties.

Ecologically, copper is a trace element essential to many plants and animals. However, high levels of copper in soil can be directly toxic to certain soil microorganisms and can disrupt important microbial processes in soil, such as nitrogen and phosphorus cycling.

<u>Carcinogenicity</u>. There is currently no evidence to suggest that this chemical is carcinogenic.

Environmental Fate. Copper is typically found in the environment as a solid metal

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in soils and soil sediment in surface water. There is no evidence that biotransformation processes have a significant bearing on the fate and transport of copper in water.

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Hydrochloric Acid

<u>Toxicity</u>. Hydrochloric acid is primarily a concern in its aerosol form. Acid aerosols have been implicated in causing and exacerbating a variety of respiratory ailments. Dermal exposure and ingestion of highly concentrated hydrochloric acid can result in corrosivity.

Ecologically, accidental releases of solution forms of hydrochloric acid may adversely affect aquatic life by including a transient lowering of the pH (i.e., increasing the acidity) of surface waters.

<u>Carcinogenicity</u>. There is currently no evidence to suggest that this chemical is carcinogenic.

Environmental Fate. Releases of hydrochloric acid to surface waters and soils will be neutralized to an extent due to the buffering capacities of both systems. The extent of these reactions will depend on the characteristics of the specific environment.

Physical Properties. Concentrated hydrochloric acid is highly corrosive.

Lead

Short-term lead poisoning is relatively infrequent and occurs from ingestion of acid soluble lead compounds or inhalation of lead vapors. Symptoms include nausea, severe abdominal pain, vomiting, diarrhea or constipation, shock, tingling, pain, and muscle weakness, and kidney damage. Death may occur in one to two days. If the patient survives the acute episode, characteristic signs and symptoms of chronic lead poisoning are likely to appear. Chronic lead poisoning affects the gastrointestinal, neuromuscular, blood, kidney, and central nervous Individuals with chronic lead poisoning appear ashen, with an appearance of "premature aging," with stooped posture, poor muscle tone, and emaciation. Neuromuscular syndrome (muscle weakness, easy fatigue, localized paralysis) and central nervous system syndrome (progressive mental deterioration, decreased intelligence, loss of motor skills and speech, hyperkinetic and aggressive behavior disorders, poorly controlled convulsive disorder, severe learning impairment) usually result from intense exposure, while the abdominal syndrome (anorexia, muscle discomfort, malaise, headache, constipation, severe abdominal pain, persistent metallic taste) is a more common manifestation of a very slowly and insidiously developing intoxication.

In the U.S., the central nervous system syndrome is usually more common among

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children, while the gastrointestinal syndrome is more prevalent in adults. Exposure to lead is also linked to decreased fertility in men. Lead is a probable human carcinogen, based on sufficient animal evidence and inadequate human evidence. Populations at increased risk of toxicity from exposure to lead include developing fetuses and young children, individuals with decreased kidney function, and children with sickle-cell anemia.

Environmental Fate. If released or deposited on soil, lead will be retained in the upper two to five centimeters of soil. Leaching is not important under normal conditions, nor generally is the uptake of lead from soil into plants. Lead enters water from atmospheric fallout, runoff or wastewater; it is effectively removed from the water column to the sediment predominantly by adsorption to organic matter and clay minerals. Some lead reenters the water column through methylation by microorganisms. Volatilization is negligible. Lead does not appear to bioconcentrate significantly in fish but does in some shellfish such as mussels. When released to the atmosphere, lead will generally be in dust or adsorbed to particulate matter and subject to gravitational settling.

Zinc and Zinc Compounds

<u>Toxicity</u>. Zinc is a nutritional trace element; toxicity from ingestion is low. Severe exposure to zinc might give rise to gastritis with vomiting due to swallowing of zinc dusts. Short-term exposure to very high levels of zinc is linked to lethargy, dizziness, nausea, fever, diarrhea, and reversible pancreatic and neurological damage. Long-term zinc poisoning causes irritability, muscular stiffness and pain, loss of appetite, and nausea.

Zinc chloride fumes cause injury to mucous membranes and to the skin. Ingestion of soluble zinc salts may cause nausea, vomiting, and purging.

<u>Carcinogenicity</u>. There is currently no evidence to suggest that this chemical is carcinogenic.

<u>Environmental Fate</u>. Significant zinc contamination of soil is only seen in the vicinity of industrial point sources. Zinc is a relatively stable soft metal, though burns in air. Zinc bioconcentrates in aquatic organisms.

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VIII.C. Other Data Sources

The Aerometric Information Retrieval System (AIRS) contains a wide range of information related to stationary sources of air pollution, including the emissions of a number of air pollutants which may be of concern within a particular industry. With the exception of volatile organic compounds (VOCs), there is little overlap with the TRI chemicals reported above. Exhibit 21 summarizes annual releases of carbon monoxide (CO), nitrogen dioxide (NO₂), particulate matter of 10 microns or less (PM10), total particulates (PT), sulfur dioxide (SO₂), and volatile organic compounds (VOCs).

Exhibit 21
Pollutant Releases (Short Tons/Year)

Industry	CO	NO ₂	PM ₁₀	PT	so_2	VOC
U.S. Total	97,208,000	23,402,000	45,489,000	7,836,000	21,888,000	23,312,000
Metal Mining	5,391	28,583	39,359	140,052	84,222	1,283
Nonmetal Mining	4,525	28,804	59,305	167,948	24,129	1,736
Lumber and Wood Products	123,756	42,658	14,135	63,761	9,149	41,423
Wood Furniture and Fixtures	2,069	2,981	2,165	3,178	1,606	59,426
Pulp and Paper	624,291	394,448	35,579	113,571	341,002	96,875
Printing	8,463	4,915	399	1,031	1,728	101,537
Inorganic Chemicals	166,147	108,575	4,107	39,082	182,189	52,091
Organic Chemicals	146,947	236,826	26,493	44,860	132,459	201,888
Petroleum Refining	419,311	380,641	18,787	36,877	648,153	309,058
Rubber and Misc. Plastic Products	2,090	11,914	2,407	5,355	29,364	140,741
Stone, Clay, Glass, and Concrete	58,043	338,482	74,623	171,853	339,216	30,262
Iron and Steel	1,518,642	138,985	42,368	83,017	238,268	82,292
Nonferrous Metals	448,758	55,658	20,074	22,490	373,007	27,375
Fabricated Metals	3,851	16,424	1,185	3,136	4,019	102,186
Electronics	367	1,129	207	293	453	4,854
Motor Vehicles, Bodies, Parts, and Accessories	35,303	23,725	2,406	12,853	25,462	101,275
Dry Cleaning	101	179	3	28	152	7,310

Source U.S. EPA Office of Air and Radiation, AIRS Database, May 1995.

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VIII.D. Comparison of Toxic Release Inventory Between Selected Industries

The following information is presented as a comparison of pollutant release and transfer data across industrial categories. It is provided to give a general sense as to the relative scale of releases and transfers within each sector profiled under this project. Please note that the following table does not contain releases and transfers for industrial categories that are not included in this project, and thus cannot be used to draw conclusions regarding the total release and transfer amounts that are reported to TRI. Similar information is available within the annual TRI Public Data Release book.

Exhibit 22 is a graphical representation of a summary of the 1993 TRI data for the nonferrous metals industry and the other sectors profiled in separate notebooks. The bar graph presents the total TRI releases and total transfers on the left axis and the triangle points show the average releases per facility on the right axis. Industry sectors are presented in the order of increasing total TRI releases. The graph is based on the data shown in Exhibit 23 and is meant to facilitate comparisons between the relative amounts of releases, transfers, and releases per facility both within and between these sectors. The reader should note, however, that differences in the proportion of facilities captured by TRI exist between industry sectors. This can be a factor of poor SIC matching and relative differences in the number of facilities reporting to TRI from the various sectors. In the case of nonferrous metals industry, the 1993 TRI data presented here covers 208 facilities. These facilities listed SIC 333-334 nonferrous metals industry as a primary SIC code.

Exhibit 22 Summary of 1993 TRI Data: Releases and Transfers by Industry

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Exhibit 23 Toxic Release Inventory Data for Selected Industries

			Rele	ases	Trans	fers	Total		
Industry Sector	SIC Range	# TRI Facili ties	Total Releases (10 pounds)	Average Releases per Facility (pounds)	1993 Total (10 pounds)	Average Transfers per Facility (pounds)	Releases + Transfers (10 ⁶ pounds)	Average Release+ Transfers per Facility (pounds)	
Stone, Clay, and Concrete	32	634	26.6	41,895	2.2	3,500	28.2	46,000	
Lumber and Wood Products	24	491	8.4	17,036	3.5	7,228	11.9	24,000	
Furniture and Fixtures	25	313	42.2	134,883	4.2	13,455	46.4	148,000	
Printing	2711- 2789	318	36.5	115,000	10.2	732,000	46.7	147,000	
Electronics/C omputers	36	406	6.7	16,520	47.1	115,917	53.7	133,000	
Rubber and Misc. Plastics	30	1,579	118.4	74,986	45.0	28,537	163.4	104,000	
Motor Vehicle, Bodies, Parts and Accessories	371	609	79.3	130,158	145.5	238,938	224.8	369,000	
Pulp and paper	2611- 2631	309	169.7	549,000	48.4	157,080	218.1	706,000	
Inorganic Chem. Mfg.	2812- 2819	555	179.6	324,000	70.0	126,000	249.7	450,000	
Petroleum Refining	2911	156	64.3	412,000	417.5	2,676,000	481.9	3,088,000	
Fabricated Metals	34	2,363	72.0	30,476	195.7	82,802	267.7	123,000	
Iron and Steel	3312- 3313	381	85.8	225,000	609.5	1,600,000	695.3	1,825,000	
	3321- 3325								
Nonferrous Metals	333, 334	208	182.5	877,269	98.2	472,335	280.7	1,349,000	
Organic Chemical Mfg.	2861- 2869	417	151.6	364,000	286.7	688,000	438.4	1,052,000	
Metal Mining	10	Industry sector not subject to TRI reporting							
Nonmetal Mining	14	Industry sector not subject to TRI reporting							
Dry Cleaning	7215, 7216, 7218	Industry sector not subject to TRI reporting							

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