

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.1 PRODUCTION

The demand for hydrogen cyanide in the United States during 2000 was 1.615 billion pounds, up slightly from 1.605 billion pounds in 1999 (ChemProfiles 2001). The demand for hydrogen cyanide is projected to increase to 1.838 billion pounds in 2004 (ChemProfiles 2001). Major producers of hydrogen cyanide are Adisseo USA, Inc. (Institute, West Virginia); BP Chemicals (Green Lake, Texas and Lima, Ohio); Cyanco Co. (Winnemucca, Nevada); Cytec Industries (Waggoman, Louisiana); Degussa Corp. (Theodora, Alabama); Dow Chemical (Freeport, Texas); DuPont (Memphis, Tennessee; Beaumont, Texas; Orange, Texas; and Victoria, Texas); Rhom and Haas Texas Inc. (Deer Park, Texas); Solutia, Inc. (Alvin, Texas); and Syngenta Crop Protection (St. Garbiel, Louisiana) (SRI 2003). The combined annual production capacity of these plants is approximately 2.019 billion pounds (SRI 2003).

As of July 2003, the following companies produced other cyanide compounds in the United States (HSDB 2004; SRI 2003):

ammonium thiocyanate:	Akzo America, Inc., Jamesville, Wisconsin; The Proctor and Gamble Company, Phillipsburg, New Jersey; and Witco Corporation, Taft, Louisiana
cyanamide:	Cyanamid Canada, Inc., Niagara Falls, Ontario
cyanogen:	Matheson Gas Products, Inc., Gloucester, Massachusetts
potassium cyanide:	DuPont Chemical Company, Memphis, Tennessee; and Hampshire Chemical Corporation, Nashua, New Hampshire
potassium silver cyanide:	Engelhard Corporation, Union, New Jersey; and Metalor Technologies USA

Facilities in the United States producing sodium cyanide and their annual capacity (in millions of pounds) in 2004 include: Cyanco Co., Winnemucca, Nevada (86); and Du Pont Chemical Company, Memphis, Tennessee (200) (SRI 2004). The combined annual capacity from these facilities of 286 million pounds is down from 346 million pounds in 2003 due to the idling of the CyPlus (formerly Degussa Corporation) plant in Theodore, Alabama (SRI 2003, 2004).

Facilities in each state that manufactured or processed hydrogen cyanide or cyanide compounds in 2002, the range of the maximum amounts stored on site, and the types of production or use activities (e.g., production for sale or on-site use in processing) are shown in Tables 5-1 and 5-2, respectively (TRI02

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-1. Facilities that Produce, Process, or Use Hydrogen Cyanide

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AK	1	0	99	1, 5
AL	2	0	999,999	1, 3, 4, 5, 6, 14
CA	4	0	9,999	1, 5, 13
CO	1	100	999	1, 5
DE	1	1,000	9,999	1, 3, 5, 12
ID	1	0	99	1, 5
IL	1	10,000	99,999	1, 6, 13, 14
IN	2	1,000	999,999	1, 5
KY	1	100	999	1, 5
LA	7	0	9,999,999	1, 3, 4, 5, 6, 12, 13, 14
MA	1	100	999	1, 5
MS	1	1,000	9,999	1, 5
MT	2	0	999	1, 5
NH	1	100,000	999,999	2, 3, 6
NV	6	0	9,999,999	1, 3, 5, 6, 13
OH	2	1,000	9,999,999	1, 4, 5, 6
OK	1	0	99	1, 5
PA	1	1,000,000	9,999,999	1, 5, 13
SC	2	0	999,999	1, 3, 5, 6
TN	3	0	49,999,999	1, 3, 4, 5, 6
TX	16	0	499,999,999	1, 3, 4, 5, 6, 12, 13, 14
UT	1	0	99	1, 5
WA	1	100	999	1, 5
WV	2	0	9,999	1, 3, 5, 6

Source: TRI02 2004 (Data are from 2002)

^aPost office state abbreviations used

^bAmounts on site reported by facilities in each state

^cActivities/Uses:

- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. Produce | 6. Impurity | 11. Chemical Processing Aid |
| 2. Import | 7. Reactant | 12. Manufacturing Aid |
| 3. Onsite use/processing | 8. Formulation Component | 13. Ancillary/Other Uses |
| 4. Sale/Distribution | 9. Article Component | 14. Process Impurity |
| 5. Byproduct | 10. Repackaging | |

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-2. Facilities that Produce, Process, or Use Cyanide Compounds

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
AK	1	100,000	999,999	1, 5
AL	6	100	9,999,999	1, 3, 4, 5, 6, 12, 13
AR	4	0	99,999	2, 3, 6, 12
AZ	2	1,000	99,999	6, 11, 12
CA	13	1,000	9,999,999	1, 2, 3, 5, 6, 7, 9, 11, 12
CO	1	10,000	99,999	1, 3, 5, 9, 13, 14
CT	6	1,000	99,999	1, 3, 6, 11, 12
DE	1	1,000	9,999	1, 3, 5, 12
FL	1	10,000	99,999	12
GA	1	1,000	9,999	12
ID	1	10,000	99,999	1, 3, 7
IL	18	0	99,999	1, 3, 5, 6, 7, 11, 12, 13
IN	11	100	49,999,999	1, 2, 3, 4, 5, 6, 7, 9, 11, 12
KY	6	100	99,999	1, 6, 7, 8, 12, 13
LA	4	0	99,999	1, 3, 5, 6, 12, 14
MA	5	0	99,999	1, 3, 4, 6, 11, 12
MD	2	1,000	99,999	1, 2, 3, 5, 6, 12
ME	2	1,000	99,999	11
MI	14	0	9,999,999	1, 2, 3, 5, 6, 7, 8, 12
MN	5	100	999,999	1, 3, 5, 8, 11, 12
MO	4	1,000	99,999	1, 5, 6
MS	1	10,000	99,999	1, 5
MT	1	1,000	9,999	1, 5
NC	2	1,000	99,999	8
NE	1	10,000	99,999	12
NH	1	10,000	99,999	1, 3, 5, 6
NJ	3	100	99,999	1, 7, 12, 13
NV	14	1,000	9,999,999	1, 3, 4, 5, 6, 7, 8, 9, 13, 14
NY	8	100	99,999	1, 2, 3, 4, 5, 6, 7, 9, 11, 12
OH	17	0	999,999	1, 3, 5, 6, 7, 8, 11, 12, 13, 14
OK	2	1,000	99,999	1, 3, 6
OR	3	1,000	99,999	1, 2, 3, 7, 13
PA	10	100	99,999	1, 6, 7, 11, 12, 13
PR	2	1,000	9,999	12
RI	7	100	99,999	1, 2, 3, 4, 5, 6, 7, 8, 9, 11
SC	4	1,000	999,999	11, 12
SD	3	1,000	999,999	1, 2, 3, 5, 6, 7
TN	5	1,000	9,999,999	1, 2, 3, 4, 5, 6, 7
TX	11	0	49,999,999	1, 3, 4, 5, 6, 12, 13

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-2. Facilities that Produce, Process, or Use Cyanide Compounds

State ^a	Number of facilities	Minimum amount on site in pounds ^b	Maximum amount on site in pounds ^b	Activities and uses ^c
UT	2	10,000	999,999	1, 3, 5, 6, 12
VA	3	100	99,999	1, 5, 6, 8
WA	2	100	99,999	1, 2, 3, 5
WI	6	0	99,999	1, 3, 5, 6, 7, 11
WV	2	1,000	9,999,999	1, 5

Source: TRI02 2004 (Data are from 2002)

^aPost office state abbreviations used

^bAmounts on site reported by facilities in each state

^cActivities/Uses:

- | | | |
|--------------------------|--------------------------|-----------------------------|
| 1. Produce | 6. Impurity | 11. Chemical Processing Aid |
| 2. Import | 7. Reactant | 12. Manufacturing Aid |
| 3. Onsite use/processing | 8. Formulation Component | 13. Ancillary/Other Uses |
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5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

2004). The information in Tables 5-1 and 5-2 is derived from the Toxics Release Inventory (TRI). The TRI data should be used with caution since only certain types of facilities are required to report. This is not an exhaustive list. No information is available in the TRI database for thiocyanate compounds in this profile because these compounds are not included under SARA, Title III and, therefore, are not among the chemicals that facilities are required to report (EPA 2003q).

There are two common methods of manufacturing hydrogen cyanide. The first consists of the formation of hydrogen cyanide as a byproduct during the synthesis of acrylonitrile from the reaction of propylene and ammonia with air. The second method involves direct synthesis by the reaction of methane and ammonia with air over platinum catalysts (CMR 1993; Curry 1992; Homan 1987). Another less common manufacturing method is being applied in Spain and Australia that involves the reaction of ammonia with propane or butane in a fluidized bed of coke particles (Shine 1971). Other methods of production include the dehydration of formamide and the reaction of sodium carbonate with coke-oven gas (Curry 1992; Sittig 1980). The formamide method of production has now been replaced by direct synthesis from methane and ammonia (Homan 1987). Of the total production capacity in the United States, direct synthesis and other routes of primary production accounts for 77% of the hydrogen cyanide produced; byproduct of acrylonitrile production accounts for the remaining 23% (CMR 1993; SRI 1995). The methods of commercial production of potassium and sodium cyanide include reacting potassium or sodium carbonate with carbon and ammonia, and reacting hydrogen cyanide with potassium or sodium hydroxide (Curry 1992; HSDB 2004). Sodium cyanide can also be prepared by heating sodium amide with carbon or by melting sodium chloride and calcium cyanamide together in an electric furnace (Hartung 1982). Potassium silver cyanide is manufactured by adding silver chloride to a solution of potassium cyanide (Sax and Lewis 1987). Calcium cyanide is manufactured by heating calcium cyanamide with a source of carbon in electric furnaces at temperatures $>1,000\text{ }^{\circ}\text{C}$ (Curry 1992; Homan 1987). It may also be produced by neutralization of lime with hydrogen cyanide (Homan 1987).

Cyanogen is usually prepared by adding an aqueous solution of sodium or potassium cyanide to an aqueous solution of copper(II) sulfate or chloride (Homan 1987; Windholz 1983). It may also be produced by heating mercury cyanide, or by heating hydrogen cyanide in the presence of a catalyst (Homan 1987). Cyanogen chloride is produced by the action of chlorine on hydrogen cyanide or by the action of chlorine on moist sodium cyanide suspended in carbon tetrachloride and kept cooled to $-3\text{ }^{\circ}\text{C}$ (Homan 1987; Windholz 1983). Ammonium thiocyanate is produced by boiling an aqueous solution of ammonium cyanide with sulfur or polysulfides or by reaction of ammonia and carbon disulfide (Homan 1987; Sax and Lewis 1987).

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

5.2 IMPORT/EXPORT

The imports and exports of hydrogen cyanide through principal U.S. customs districts are negligible (CMR 2001). Recent import and export data for some of the cyanide compounds included in this profile are summarized in Table 5-3 for 2003 (USDOC 2003). Import volumes were greatest for thiocyanates, cyanates, and fulminates at 9.92 millions pounds followed closely by cyanides and cyanide oxides of sodium at 8.54 million pounds. Cyanides and cyanide oxides of sodium comprise the majority of exports for cyanide compounds with a volume of 104.6 million pounds. The second largest export item among the cyanide compounds was potassium cyanide at 3.41 million pounds. Germany, Japan, South Korea, and the Czech Republic were the primary exporters of these cyanide chemicals to the United States in 2003 (USDOC 2003). The most recent import data that could be found for copper (I) cyanide indicate that 0.52 and 0.26 million pounds of this compound were imported into the United States in 1984 and 1986, respectively (HSDB 2004). Recent import data could not be found in the available literature for potassium silver cyanide, cyanogen, or cyanogen chloride.

Export volumes of cyanide compounds (foreign and domestic volumes combined) shown in Table 5-3 fluctuated widely over the period January 1989 and April 1994. No obvious trends were evident except for potassium cyanide, where export volumes decreased from 3.13 million pounds in 1989 to 0.46 million pounds in 1994. However, export volumes for potassium cyanide have risen to 3.41 million pounds in 2003. Export volumes of sodium cyanide varied between 104.6 and 150.2 million pounds between 1989 and 1994 and have decreased to 104.6 million from a high of 150.2 million pounds in 1994. Export data could not be found in the available literature for calcium cyanide, potassium silver cyanide, cyanogen, or cyanogen chloride.

5.3 USE

The predominant users of cyanides are the steel, electroplating, mining, and chemical industries. The principal cyanide compounds used in industrial operations are potassium and sodium cyanide and calcium cyanide, particularly in metal leaching operations (Curry 1992; EPA 1993g). Cyanides have been well established in uses as insecticides and fumigants; in the extraction of gold and silver ores; in metal cleaning; in the manufacture of synthetic fibers, various plastics, dyes, pigments, and nylon; and as reagents in analytical chemistry (EPA 1978c, 1993g; HSDB 2004). Cyanides are present in some foods, but this presence is due mainly to the production of hydrogen cyanide from naturally-occurring

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Table 5-3. Import and Export Volumes of Cyanide Compounds^a

Compounds	2003 Imports (million pounds)
Imports:	
Potassium cyanide	0.571
Calcium cyanide	0.007
Cyanides and cyanide oxides of sodium	8.54
Other cyanides and cyanide oxides	0.632
Thiocyanates, cyanates, and fulminates	9.92
Nonaromatic thiocyanates used for pesticides	No data
Exports:	
Potassium cyanide	3.41
Calcium cyanide	No data
Cyanides and cyanide oxides of sodium	104.6
Other cyanides and cyanide oxides	0.966
Thiocyanates, cyanates, and fulminates	1.29
Nonaromatic thiocyanates used for pesticides	No data

^aUSDOC (2003)

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

cyanogenic compounds in foods (see Sections 6.4.4 and 6.5). Cyanogen has been used as a high-energy fuel in the chemical industry and as a rocket or missile propellant; cyanogen and its halides are used in organic syntheses, as pesticides and fumigants, and in gold-extraction processes (EPA 1978c; HSDB 2004). When used in pesticidal applications and in accordance with the product label, cyanide compounds are registered and regulated by the EPA under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (EPA 1998, 2004u).

As a commercially available product, hydrogen cyanide is sold as a gas and is also available as a technical grade liquid in concentrations of 5, 10, and 96–99.5%. Almost all grades of hydrogen cyanide contain a stabilizer such as phosphoric acid to prevent decomposition and explosion (Curry 1992). In recent years, the use of hydrogen cyanide in the nylon and methyl methacrylate production processes has produced a strong demand. The use pattern for hydrogen cyanide is the following: adiponitrile (for nylon 6/6), 47%; methyl methacrylate, 27%; sodium cyanide, 8%; methionine, 6%; chelating agent, 2%; cyanuric chloride, 2%; and miscellaneous uses, including nitriloacetic acid and salts, 8% (CMR 2001). Miscellaneous applications also include the use of hydrogen cyanide as an insecticide and rodenticide for fumigating enclosed spaces (grain storage, etc.) (Worthing 1987) and its use in the manufacture of ferrocyanides, acrylates, lactic acid, pharmaceutical, and specialty chemicals (Worthing 1987).

Cyanide salts have various uses. The most significant applications of compounds included in this profile are uses in electroplating and metal treatment, as an anti-caking agent in road salts, and in gold and silver extraction from ores. Minor applications include use as insecticides and rodenticides, as chelating agents, and in the manufacture of dyes and pigments (EPA 1978c; Pesce 1993; Sax and Lewis 1987; Worthing 1987). Calcium cyanide is used as a cement stabilizer (Curry 1992; Windholz 1983) and has had limited use in rodent control and as a beehive fumigant (Lowe and Sullivan 1992). Formerly used as a polymerization catalyst and as an antifouling agent in marine paints, copper (I) cyanide continues to be used in plating baths for silver, brass, and copper-tin alloy plating. Many metal polishes contain potassium or sodium cyanide. Potassium cyanide has a primary use in silver plating and is also used as a reagent in analytical chemistry. Potassium and sodium cyanide are used in combination for nitriding steel (HSDB 2004). One method of achieving hardened, weather-resistant metal surfaces uses a process known as cyaniding, which involves heating the metal in a liquid solution of sodium cyanide, sodium chloride, and sodium carbonate in the presence of atmospheric oxygen (Curry 1992). Fumigation of fruit trees, railway cars, and warehouses, and treatment of rabbit and rat burrows and termite nests are included among the former uses for sodium cyanide (HSDB 2004).

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

Cyanogen, a colorless gas with an almond-like odor, is used in organic syntheses, as a fumigant, as a fuel gas for welding and cutting heat-resistant metals, and as a rocket and missile propellant with ozone or fluorine (Sax and Lewis 1987; HSDB 2004). Applications of cyanogen chloride include use in chemical syntheses, as a military poison gas, as a metal cleaner, in ore refining, and in the production of triazine herbicides, optical brighteners, dyestuffs, and synthetic rubber (Hartung 1982; Homan 1987; HSDB 2004; Sine 1994; Windholz 1983). Cyanogen chloride has also been used a warning agent in fumigant gases due to the fact that at low concentrations, it has strong lacrimatory effects (Homan 1987).

Ammonium thiocyanate is used as an ingredient in antibiotic fermentations, pesticides, liquid rocket propellants, adhesives, and matches; in photographic processes; to improve the strength of silks; in the manufacture of transparent artificial resins; and as a weed killer and defoliant (Sax and Lewis 1987; Weil and Sandler 1997; Windholz 1983).

5.4 DISPOSAL

It has been estimated that 4.7 billion gallons of cyanide-containing wastes and 0.8 billion gallons of reactive wastes containing cyanide compounds were generated in the United States in 1983 (Grosse 1986). Regulations governing the treatment and disposal of cyanide-containing wastes are detailed in Chapter 8. Cyanide is listed among the 65 toxic pollutants regulated by the Effluent Guidelines and Standards given in Title 40, Sections 400–475, of the Code of Federal Regulations. The pretreatment standards established for point source categories such as hydrogen peroxide manufacturing, electroplating, metal finishing, and ferroalloy manufacturing, regulate emissions of cyanides based on either total amount of cyanide or as cyanide that is amenable to chlorination in waste streams. Under the Resource Conservation and Recovery Act (RCRA), cyanide is listed as a hazardous waste when it is discarded as a commercial chemical product, off-specification species, container residue, or spill residue; a waste from non-specific sources; or a waste from specific sources (EPA 1980a). Cyanide salts and complexes are the basis for listing 11 solid waste streams as hazardous wastes under RCRA (EPA 1986b). According to RCRA, cyanide-containing wastes are required to be treated by the best available technology before the wastes are disposed of in land. Cyanogen- and cyanogen chloride-containing waste, for example, are assigned the hazardous waste codes P031 and P033, respectively, and must be treated by chemical or electrolytic oxidation employing specific oxidizing reagents (e.g., hypochlorite, peroxides, ozone, or ultraviolet light assisted ozone) or other reagents of equivalent efficiency; wet air oxidation incorporating a surrogate or indicator parameter; or treatment by incineration in units operated in compliance with RCRA standards (EPA 1986b). The concentration of cyanide permissible in wastes

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

for land disposal is described in the Land Disposal Restriction in Title 40 Section 268, of the Code of Federal Regulations and varies according to the nature of wastes. The maximum concentration in treated waste (i.e., non-waste water) should not exceed 590 mg/kg for total cyanides and 30 mg/kg for cyanides amenable to chlorination (EPA 1988c). While liquids are prohibited from land disposal, the maximum concentrations allowable in most treated waste waters, with the exception of the bottom streams from the acetonitrile column and the waste water stripper used in the production of acrylonitrile, are 1.9 mg/L for total cyanides and 0.86 mg/kg for cyanides amenable to chlorination (EPA 1988c).

Conducted in the presence of sodium hydroxide and sodium hypochlorite, the chemical oxidation method commonly referred to as alkaline chlorination is the most widely used commercial method for treating cyanide-containing wastes. This method results in the conversion of the cyanide solution to the less toxic cyanate. Depending on the cyanides present, the product will be a sludge or solution, which when sufficient reaction time has been allowed, will largely be devoid of free cyanide (IRPTC 1985).

The alkaline chlorination process has been applied to the removal of cyanide from waste waters and slurries generated as a consequence of cyanide heap leaching gold and other precious metals from low grade ores (EPA 1994c). However, few mining sites currently use this technology. Instead, cyanide in waste water or spent ore heaps is converted to cyanate through reactions with sulfur dioxide, ferrous sulfate, or hydrogen peroxide. These processes have been shown to effectively lower cyanide concentrations to levels that are within federal and state limits for discharge from the mining site (EPA 1994c). A limitation of the technique is that it does not remove free chlorine, chloramines, or iron cyanides, which are toxic to fish. Other approaches that have demonstrated good efficiencies for removing cyanide from spent ore heaps and waste water include precipitate from leachate through reaction with cuprous ions, reaction of cyanide ion with sulfur dioxide, or biodegradation of cyanide (Akcil and Mudder 2003; EPA 1994c). The sulfur dioxide method is limited by an inability to remove thiocyanate, cyanate, and ammonia, which are toxic to fish, and may not provide sufficient removal efficiencies to meet local permit requirements (EPA 1994c). Biodegradation of cyanide in waste water and leachate is effective on soluble forms of cyanide, but may not be effective on degrading cyanide bound in metal complexes (EPA 1994c).

Cyanide salts should not be treated with acid in preparation for disposal or flushed into drains that may contain or subsequently receive acid waste. Acidification is not a recommended method of treatment prior to disposal because of the liberation of hydrogen cyanide. Similarly, incineration of cyanides must proceed with caution and is not recommended unless extensive equipment capable of safely handling

5. PRODUCTION, IMPORT/EXPORT, USE, AND DISPOSAL

liberated hydrogen cyanide is available (IRPTC 1985). Of the cyanide compounds included in this profile, only hydrogen cyanide and cyanogen chloride are listed as potential candidates for rotary kiln incineration or fluidized bed incineration (HSDB 2004).

The biodegradation of cyanides has been investigated, with varying results, for several industrial processes, and additional research in this area would be valuable. While investigations of the potential for microbial species found in mineral processing waste waters demonstrate effective removal of cyanide, metal complexed cyanide, and thiocyanate (Boucabeille 1994b; EPA 1994c), complex cyanides did not appear amenable to biodegradation at gasworks sites (Thomas and Lester 1993). Application of formaldehyde to electroplating waste under basic conditions can convert the cyanide anion to substituted acetates in addition to recovering copper and silver as free metals with formaldehyde reduction (Tucker and Carson 1985). Calcium or sodium polysulfide treatment converts some cyanide wastes into less toxic thiocyanate (Higgins and Desher 1988). These examples suggest that typical treatments involve the decomposition of cyanides to less toxic compounds by physical or chemical processes. More than 97% of cyanide is typically removed from waste waters by alkaline chlorination, electrolysis, or ozonation process. Cyanide from some wastes can be removed by ion-exchange resins. After using an appropriate treatment method such as those described above, cyanide wastes may be disposed of in a secured sanitary landfill (Grosse 1986; Higgins and Desher 1988; Tucker and Carson 1985). Disposal by injection of high-pH cyanide wastes into sandstone was investigated by Scrivner et al. (1986). Currently, the injection of waste water containing hydrogen cyanide and cyanide compounds through underground injection is a major method for disposal of these wastes. The available data indicate that in 2002, 1.44 million pounds of hydrogen cyanide and 5.10 million pounds of cyanide compounds were disposed of by underground injection (see Section 6.2) (TRI02 2004).