

EPA/310-R-95-004

EPA Office of Compliance Sector Notebook Project

Profile of the Inorganic Chemical Industry

September 1995

Office of Compliance
Office of Enforcement and Compliance Assurance
U.S. Environmental Protection Agency
401 M St., SW (MC 2221-A)
Washington, DC 20460

This report is one in a series of volumes published by the U.S. Environmental Protection Agency (EPA) to provide information of general interest regarding environmental issues associated with specific industrial sectors. The documents were developed under contract by Abt Associates (Cambridge, MA), and Booz-Allen & Hamilton, Inc. (McLean, VA). This publication may be **purchased** from the Superintendent of Documents, U.S. Government Printing Office. A listing of available Sector Notebooks and document numbers is included at the end of this document.

All telephone orders should be directed to:

Superintendent of Documents
U.S. Government Printing Office
Washington, DC 20402
(202) 512-1800
FAX (202) 512-2250
8:00 a.m. to 4:30 p.m., ET, M-F

Using the form provided at the end of this document, all mail orders should be directed to:

U.S. Government Printing Office
P.O. Box 371954
Pittsburgh, PA 15250-7954

Complimentary volumes are available to certain groups or subscribers, such as public and academic libraries, Federal, State, local, and foreign governments, and the media. For further information, and for answers to questions pertaining to these documents, please refer to the contact names and numbers provided within this volume.

Electronic versions of all Sector Notebooks are available on the EPA Enviro\$en\$e Bulletin Board and via the Internet on the Enviro\$en\$e World Wide Web. Downloading procedures are described in Appendix A of this document.

Cover photograph by Steve Delaney, EPA. Photograph courtesy of Vista Chemicals, Baltimore, Maryland. Special thanks to Dave Mahler.

Contacts for Available Sector Notebooks

The Sector Notebooks were developed by the EPA Office of Compliance. General questions regarding the Sector Notebook Project can be directed to the EPA Work Assignment Managers:

Michael Barrette

US EPA Office of Compliance
401 M St., SW (2223-A)
Washington, DC 20460
(202) 564-7019

Gregory Waldrip

US EPA Office of Compliance
401 M St., SW (2223-A)
Washington, DC 20460
(202) 564-7024

Questions and comments regarding the individual documents can be directed to the appropriate specialists listed below.

<u>Document Number</u>	<u>Industry</u>	<u>Contact</u>	<u>Phone (202)</u>
EPA/310-R-95-001.	Dry Cleaning Industry	Joyce Chandler	564-7073
EPA/310-R-95-002.	Electronics and Computer Industry	Steve Hoover	564-7007
EPA/310-R-95-003.	Wood Furniture and Fixtures Industry 564-7021		Bob Marshall
EPA/310-R-95-004.	Inorganic Chemical Industry	Walter DeRieux	564-7067
EPA/310-R-95-005.	Iron and Steel Industry	Maria Malave	564-7027
EPA/310-R-95-006.	Lumber and Wood Products Industry	Seth Heminway	564-7017
EPA/310-R-95-007.	Fabricated Metal Products Industry	Greg Waldrip	564-7024
EPA/310-R-95-008.	Metal Mining Industry	Keith Brown	564-7124
EPA/310-R-95-009.	Motor Vehicle Assembly Industry	Suzanne Childress	564-7018
EPA/310-R-95-010.	Nonferrous Metals Industry	Jane Engert	564-5021
EPA/310-R-95-011.	Non-Fuel, Non-Metal Mining Ind.	Keith Brown	564-7124
EPA/310-R-95-012.	Organic Chemical Industry	Walter DeRieux	564-7067
EPA/310-R-95-013.	Petroleum Refining Industry	Tom Ripp	564-7003
EPA/310-R-95-014.	Printing and Publishing Industry	Ginger Gotliffe	564-7072
EPA/310-R-95-015.	Pulp and Paper Industry	Maria Eisemann	564-7016
EPA/310-R-95-016.	Rubber and Plastic Industry	Maria Malave	564-7027
EPA/310-R-95-017.	Stone, Clay, Glass and Concrete Ind.	Scott Throwe	564-7013

EPA/310-R-95-018. Transportation Equip. Cleaning Ind. Virginia Lathrop 564-7057

Industry Sector Notebook Contents: Inorganic Chemicals Manufacturing

Exhibits Index	iii
List of Acronyms	v
I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT	1
A. Summary of the Sector Notebook Project	1
B. Additional Information	2
II. INTRODUCTION TO THE INORGANIC CHEMICALS INDUSTRY	3
A. Introduction, Background, and Scope of the Notebook	3
B. Characterization of the Inorganic Chemical Industry	4
1. Product Characterization	4
2. Industry Size and Geographic Distribution	5
3. Economic Trends	10
III. INDUSTRIAL PROCESS DESCRIPTION	13
A. Industrial Processes in the Inorganic Chemical Industry	13
1. Mercury Cell	16
2. Diaphragm Cell	18
3. Membrane Cell	20
4. Auxiliary Processes	22
B. Raw Material Inputs and Pollution Outputs in the Production Line	24
1. Mercury Cell	25
2. Diaphragm Cell	25
3. Membrane Cell	26
4. Auxiliary Processes	27
C. Management of Chemicals In Wastestream	29
IV. CHEMICAL RELEASE AND TRANSFER PROFILE	31
A. EPA Toxic Release Inventory for the Inorganic Chemical Industry	34
B. Summary of Selected Chemicals Released	43
C. Other Data Sources	48
D. Comparison of Toxic Release Inventory Between Selected Industries	50

V. POLLUTION PREVENTION OPPORTUNITIES	53
VI. SUMMARY OF APPLICABLE FEDERAL STATUTES AND REGULATIONS	73
A. General Description of Major Statutes	73
B. Industry Specific Requirements	84
C. Pending and Proposed Regulatory Requirements	87
VII. COMPLIANCE AND ENFORCEMENT HISTORY	89
A. Inorganic Chemical Industry Compliance History	93
B. Comparison of Enforcement Activity Between Selected Industries	95
C. Review of Major Legal Actions	100
1. Review of Major Cases	100
2. Supplementary Environmental Projects	100
VIII. COMPLIANCE ASSURANCE ACTIVITIES AND INITIATIVES	103
A. Sector-related Environmental Programs and Activities	103
B. EPA Voluntary Programs	103
C. Trade Association/Industry Sponsored Activity	108
1. Environmental Programs	108
2. Summary of Trade Associations	111
IX. CONTACTS/ACKNOWLEDGMENTS/RESOURCE MATERIALS/BIBLIOGRAPHY	113
ENDNOTES	115

Exhibits Index

Exhibit 1: Inorganic Chemicals Industry Dominated by a Large Number of Small Facilities . . .	6
Exhibit 2: Inorganic Chemicals Facilities Distribution	6
Exhibit 3: Chlorine Capacity Located Primarily Along Gulf Coast, Southeast, Northwest, and Great Lakes Region	8
Exhibit 4: Top U.S. Companies with Inorganic Chemical Manufacturing Operations	9
Exhibit 5: Chlorine Electrolysis Cells	15
Exhibit 6: Main Characteristics of the Different Electrolysis Processes	16
Exhibit 7: Mercury Electrolysis Cell and Flow Diagram	17
Exhibit 8: Typical Diaphragm Electrolysis Cell and Flow Diagram	19
Exhibit 9: Typical Membrane Electrolysis Cell	21
Exhibit 10: Source Reduction and Recycling Activity for Inorganic Chemicals Industry (SIC 281) as Reported within TRI	30
Exhibit 11: 1993 Releases for Inorganic Chemical Manufacturing Facilities (SIC 281) in TRI, by Number of Facilities Reporting	36
Exhibit 12: 1993 Transfers for Inorganic Chemical Manufacturing Facilities (SIC 281) in TRI, by Number of Facilities Reporting	39
Exhibit 13: Top 10 TRI Releasing Inorganic Chemicals Facilities	42
Exhibit 14: Top 10 TRI Releasing Facilities Reporting Inorganic Chemical SIC Codes to TRI	43
Exhibit 15: Pollutant Releases (short tons/year)	48
Exhibit 16: Summary of 1993 TRI Data: Releases and Transfers by Industry	51
Exhibit 17: Toxics Release Inventory Data for Selected Industries	52
Exhibit 18: Process/Product Modifications Create Pollution Prevention Opportunities	57
Exhibit 19: Modifications to Equipment Can Also Prevent Pollution	66
Exhibit 20: Five-Year Enforcement and Compliance Summary for Inorganic Chemicals Manufacturing	94
Exhibit 21: Five-Year Enforcement and Compliance Summary for Selected Industries	96
Exhibit 22: One-Year Inspection and Enforcement Summary for Selected Industries	97
Exhibit 23: Five-Year Inspection and Enforcement Summary by Statute for Selected Industries	98
Exhibit 24: One-Year Inspection and Enforcement Summary by Statute for Selected Industries	99
Exhibit 25: FY-1993-1994 Supplemental Environmental Projects Overview: Inorganic Chemical Manufacture	102
Exhibit 26: 33/50 Program Participants Reporting SIC 281 (Inorganic Chemicals)	104
Exhibit 27: Contacts for State and Local Pollution Prevention Programs	109

List of Acronyms

AFS -	AIRS Facility Subsystem (CAA database)
AIRS -	Aerometric Information Retrieval System (CAA database)
BIFs -	Boilers and Industrial Furnaces (RCRA)
BOD -	Biochemical Oxygen Demand
CAA -	Clean Air Act
CAAA -	Clean Air Act Amendments of 1990
CERCLA -	Comprehensive Environmental Response, Compensation and Liability Act
CERCLIS -	CERCLA Information System
CFCs -	Chlorofluorocarbons
CO -	Carbon Monoxide
COD -	Chemical Oxygen Demand
CSI -	Common Sense Initiative
CWA -	Clean Water Act
D&B -	Dun and Bradstreet Marketing Index
DSA -	Dimensionally stable
ELP -	Environmental Leadership Program
EPA -	United States Environmental Protection Agency
EPCRA -	Emergency Planning and Community Right-to-Know Act
FIFRA -	Federal Insecticide, Fungicide, and Rodenticide Act
FINDS -	Facility Indexing System
HAPs -	Hazardous Air Pollutants (CAA)
HSDB -	Hazardous Substances Data Bank
IDEA -	Integrated Data for Enforcement Analysis
LDR -	Land Disposal Restrictions (RCRA)
LEPCs -	Local Emergency Planning Committees
MACT -	Maximum Achievable Control Technology (CAA)
MCLGs -	Maximum Contaminant Level Goals
MCLs -	Maximum Contaminant Levels
MEK -	Methyl Ethyl Ketone
MSDSs -	Material Safety Data Sheets
NAAQS -	National Ambient Air Quality Standards (CAA)
NAFTA -	North American Free Trade Agreement
NCDB -	National Compliance Database (for TSCA, FIFRA, EPCRA)
NCP -	National Oil and Hazardous Substances Pollution Contingency Plan
NEIC -	National Enforcement Investigation Center
NESHAP -	National Emission Standards for Hazardous Air Pollutants
NO ₂ -	Nitrogen Dioxide
NOV -	Notice of Violation
NO _x -	Nitrogen Oxide

NPDES -	National Pollution Discharge Elimination System (CWA)
NPL -	National Priorities List
NRC -	National Response Center
NSPS -	New Source Performance Standards (CAA)
OAR -	Office of Air and Radiation
OECA -	Office of Enforcement and Compliance Assurance
OPA -	Oil Pollution Act
OPPTS -	Office of Prevention, Pesticides, and Toxic Substances
OSHA -	Occupational Safety and Health Administration
OSW -	Office of Solid Waste
OSWER -	Office of Solid Waste and Emergency Response
OW -	Office of Water
P2 -	Pollution Prevention
PCS -	Permit Compliance System (CWA Database)
POTW -	Publicly Owned Treatments Works
RCRA -	Resource Conservation and Recovery Act
RCRIS -	RCRA Information System
SARA -	Superfund Amendments and Reauthorization Act
SDWA -	Safe Drinking Water Act
SEPs -	Supplementary Environmental Projects
SERCs -	State Emergency Response Commissions
SIC -	Standard Industrial Classification
SO ₂ -	Sulfur Dioxide
SO _x -	Sulfur Oxides
TOC -	Total Organic Carbon
TRI -	Toxic Release Inventory
TRIS -	Toxic Release Inventory System
TCRIS -	Toxic Chemical Release Inventory System
TSCA -	Toxic Substances Control Act
TSS -	Total Suspended Solids
UIC -	Underground Injection Control (SDWA)
UST -	Underground Storage Tanks (RCRA)
VOCs -	Volatile Organic Compounds

I. INTRODUCTION TO THE SECTOR NOTEBOOK PROJECT

I.A. Summary of the Sector Notebook Project

Environmental policies based upon comprehensive analysis of air, water and land pollution are an inevitable and logical supplement to traditional single-media approaches to environmental protection. Environmental regulatory agencies are beginning to embrace comprehensive, multi-statute solutions to facility permitting, enforcement and compliance assurance, education/ outreach, research, and regulatory development issues. The central concepts driving the new policy direction are that pollutant releases to each environmental medium (air, water and land) affect each other, and that environmental strategies must actively identify and address these inter-relationships by designing policies for the "whole" facility. One way to achieve a whole facility focus is to design environmental policies for similar industrial facilities. By doing so, environmental concerns that are common to the manufacturing of similar products can be addressed in a comprehensive manner. Recognition of the need to develop the industrial "sector-based" approach within the EPA Office of Compliance led to the creation of this document.

The Sector Notebook Project was initiated by the Office of Compliance within the Office of Enforcement and Compliance Assurance (OECA) to provide its staff and managers with summary information for eighteen specific industrial sectors. As other EPA offices, states, the regulated community, environmental groups, and the public became interested in this project, the scope of the original project was expanded. The ability to design comprehensive, common sense environmental protection measures for specific industries is dependent on knowledge of several inter-related topics. For the purposes of this project, the key elements chosen for inclusion are: general industry information (economic and geographic); a description of industrial processes; pollution outputs; pollution prevention opportunities; Federal statutory and regulatory framework; compliance history; and a description of partnerships that have been formed between regulatory agencies, the regulated community and the public.

For any given industry, each topic listed above could alone be the subject of a lengthy volume. However, in order to produce a manageable document, this project focuses on providing summary information for each topic. This format provides the reader with a synopsis of each issue, and references where more in-depth information is available. Text within each profile was researched from a variety of sources, and was usually condensed from more detailed sources pertaining to specific topics. This approach allows for a wide coverage of activities that can be further

explored based upon the citations and references listed at the end of this profile. As a check on the information included, each notebook went through an external review process. The Office of Compliance appreciates the efforts of all those that participated in this process and enabled us to develop more complete, accurate and up-to-date summaries.

I.B. Additional Information

Providing Comments

OECA's Office of Compliance plans to periodically review and update the notebooks and will make these updates available both in hard copy and electronically. If you have any comments on the existing notebook, or if you would like to provide additional information, please send a hard copy and computer disk to the EPA Office of Compliance, Sector Notebook Project, 401 M St., SW (2223-A), Washington, DC 20460. Comments can also be uploaded to the Enviro\$en\$e Bulletin Board or the Enviro\$en\$e World Wide Web for general access to all users of the system. Follow instructions in Appendix A for accessing these data systems. Once you have logged in, procedures for uploading text are available from the on-line Enviro\$en\$e Help System.

Adapting Notebooks to Particular Needs

The scope of the existing notebooks reflect an approximation of the relative national occurrence of facility types that occur within each sector. In many instances, industries within specific geographic regions or states may have unique characteristics that are not fully captured in these profiles. For this reason, the Office of Compliance encourages state and local environmental agencies and other groups to supplement or re-package the information included in this notebook to include more specific industrial and regulatory information that may be available. Additionally, interested states may want to supplement the "Summary of Applicable Federal Statutes and Regulations" section with state and local requirements. Compliance or technical assistance providers may also want to develop the "Pollution Prevention" section in more detail. Please contact the appropriate specialist listed on the opening page of this notebook if your office is interested in assisting us in the further development of the information or policies addressed within this volume.

If you are interested in assisting in the development of new notebooks for sectors not covered in the original eighteen, please contact the Office of Compliance at 202-564-2395.

II. INTRODUCTION TO THE INORGANIC CHEMICALS INDUSTRY

This section provides background information on the size, geographic distribution, employment, production, sales, and economic condition of the inorganic chemicals industry. The type of facilities described within the document are also described in terms of their Standard Industrial Classification (SIC) codes. Additionally, this section contains a list of the largest companies in terms of sales.

II.A. Introduction, Background, and Scope of the Notebook

The inorganic chemical industry manufactures over 300 different chemicals accounting for about 10 percent of the total value of chemical shipments in the U.S.¹ This industry categorization corresponds to Standard Industrial Classification (SIC) code 281 Industrial Inorganic Chemicals established by the Bureau of Census to track the flow of goods and services within the economy. The 281 category includes alkalis and chlorine (SIC 2812), industrial gases (SIC 2813) (e.g., hydrogen, helium, oxygen, nitrogen, etc.), inorganic pigments (SIC 2816), and industrial inorganic chemicals, not elsewhere classified (SIC 2819). Approximately two-thirds of the value of shipments for the inorganic chemical industry, including over 200 different chemicals, are classified under industrial inorganic chemicals, not elsewhere classified (SIC 2819). The industry does not include those establishments primarily manufacturing organic chemicals, agricultural pesticides, drugs, soaps, or cosmetics. However, the 281 industry group does include a significant number of integrated firms that are engaged in the manufacture of other types of chemicals at the same site. Conversely, many manufacturing facilities not categorized under SIC 281, especially organic chemicals facilities (SIC 286), fertilizer plants (SIC 287), pulp and paper mills (SIC 26), and iron and steel mills (SIC 331), produce and use inorganic chemicals in their processes at the same facility.² For example, a significant number of inorganic chemical manufacturing processes are part of very large chemical manufacturing or pulp manufacturing facilities, making characterization strictly by SIC code difficult.

Whenever possible, this notebook describes the entire inorganic chemical industry. In many cases, however, specific details relating to some of the topics covered by the notebook (facility size, economic trends, geographic distribution, pollutant releases, pollution prevention issues, and applicable regulations) vary depending on the type of inorganic chemical manufacturing process. The large number of different industrial processes used in the inorganics industry could not all be covered in this notebook. As a result, most sections of this notebook describe the entire inorganic

chemical industry as a whole. These sections are usually augmented with information specific to the largest single industrial process within the industry: chlorine and caustic soda production (SIC 2812). Section III, Industrial Process Description, rather than attempting to describe every inorganic chemical manufacturing process, deals solely with the production of chlorine and caustic soda.

II.B. Characterization of the Inorganic Chemical Industry

II.B.1. Product Characterization

Inorganic Chemicals Industry

The inorganic chemical industry manufactures chemicals which are often of a mineral origin, but not of a basic carbon molecular. Inorganic chemicals are used at some stage in the manufacture of a great variety of other products. The industry's products are used as basic chemicals for industrial processes (i.e., acids, alkalis, salts, oxidizing agents, industrial gases, and halogens); chemical products to be used in manufacturing products (i.e., pigments, dry colors, and alkali metals); and finished products for ultimate consumption (i.e., mineral fertilizers, glass, and construction materials). The largest use of inorganic chemicals is as processing aids in the manufacture of chemical and nonchemical products. Consequently, inorganic chemicals often do not appear in the final products.³

Chlor-alkali Sector

The chlor-alkali industry produces mainly chlorine, caustic soda (sodium hydroxide), soda ash (sodium carbonate), sodium bicarbonate, potassium hydroxide, and potassium carbonate. In 1992, chlorine and caustic soda production accounted for about 80 percent of the chlor-alkali industry's value of shipments and, in terms of weight, were the eighth and ninth largest chemicals produced in the U.S., respectively. Chlorine and caustic soda are co-products produced in about equal amounts primarily through the electrolysis of salt (brine).⁴

The majority of domestic chlorine production (70 percent) is used in the manufacturing of organic chemicals including: vinyl chloride monomer, ethylene dichloride, glycerine, glycols, chlorinated solvents, and chlorinated methanes. Vinyl chloride, which is used in the production of polyvinyl chloride (PVC) and many other organic chemicals, accounts for about 38 percent of the total domestic chlorine production. The pulp and paper industry consumes approximately 15 percent of U.S. chlorine

production, and about eight percent is used in the manufacturing of other inorganic chemicals. Other major uses are disinfection treatment of water, and the production of hypochlorites. More than two-thirds of all chlorine is consumed in the same manufacturing plant in the production of chemical intermediates.⁵

The largest users of caustic soda are the organic chemicals industry (30 percent) and the inorganic chemicals industry (20 percent). The primary uses of caustic soda are in industrial processes, neutralization, and off-gas scrubbing; as a catalyst; and in the production of alumina, propylene oxide, polycarbonate resin, epoxies, synthetic fibers, soaps, detergents, rayon, and cellophane. The pulp and paper industry uses about 20 percent of total domestic caustic soda production for pulping wood chips, and other processes. Caustic soda is also used in the production of soaps and cleaning products, and in the petroleum and natural gas extraction industry as a drilling fluid.⁶

II.B.2. Industry Size and Geographic Distribution

Inorganic Chemical Industry

The inorganic chemical industry is characterized by a relatively large number of small facilities. The Bureau of the Census identified 665 companies operating 1,429 facilities within SIC 281 in 1992.^a Most of these facilities were classified under SIC 2819 -- industrial inorganic chemicals, not elsewhere classified -- which are typically smaller facilities producing specialty inorganic chemicals. The Bureau of Census employment data for 1992 (Exhibit 1) indicated that about 63 percent of inorganic chemical facilities employed fewer than 20 people. A significant portion of inorganic chemicals are produced and used within the same plant in the manufacturing of organic chemicals. The number of these facilities and the number of people employed in the inorganic chemical production portion of the industrial processes is not included in this data.

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

Exhibit 1: Inorganic Chemicals Industry Dominated by a Large Number of Small Facilities				
	Inorganic Chemicals		Chlor-alkali	
Employees per Facility	Number of Facilities	Percentage of Facilities	Number of Facilities	Percentage of Facilities
1-9	682	48%	12	24%
10-19	212	15%	6	12%
20-49	253	18%	3	6%
50-249	221	15%	23	44%
250-999	51	3%	6	12%
1,000->2,500	10	1%	1	2%
Total	1,429	100%	51	100%
Source: Bureau of the Census, 1992 Census of Manufacturers.				

Inorganic chemical facilities are typically located near consumers and to a lesser extent raw materials. The largest use of inorganic chemicals is in industrial processes for the manufacture of chemicals and nonchemical products; therefore, facilities are concentrated in the heavy industrial regions along the Gulf Coast, both east and west coasts, and the Great Lakes region. Since a large portion of inorganic chemicals produced are used by the organic chemicals manufacturing industry, the geographical distribution of inorganic facilities is very similar to that of organic chemicals facilities (Exhibit 2).

(Source: U.S. EPA Toxic Release Inventory Database, 1993)

Chlor-alkali Sector

The alkali and chlorine industry, however, consists of a relatively small number of medium to large facilities. The Bureau of the Census identified 34 companies operating 51 facilities within the SIC 2812 in 1992. According to The Chlorine Institute (an industry trade group), there were 25 companies operating 52 chlorine production plants in 1989. The Bureau of Census employment data for 1992 indicated that about 60 percent of those employed in the chlor-alkali industry worked at facilities with over 50 employees (Exhibit 1).^{7,8}

The distribution of the chlor-alkali sector differs from that of the inorganic chemicals industry as a whole. Since chlorine and caustic soda are co-products produced in almost equal amounts, the distribution of the caustic soda manufacturing industry is essentially the same as the chlorine manufacturing industry. Chlorine is difficult to store and transport economically; therefore, chlorine and caustic soda are produced near the chlorine consumers which are primarily chemical manufacturers and

pulping operations. Consequently, chlor-alkali facilities are concentrated near the chemical industries along the Gulf Coast, followed by the Great Lakes region as shown in the table below. Other important areas are in the vicinity of the pulp mills of the Southeast and Northwest (Exhibit 3). In 1989, almost half of the chlorine plants in the U.S. (72 percent of domestic chlorine production) were located along the Gulf Coast. Two states, Louisiana and Texas, accounted for two-thirds of the domestic chlorine production.⁹

Exhibit 3: Chlorine Capacity Located Primarily Along Gulf Coast, Southeast, Northwest, and Great Lakes Region

State	Number of Chlorine Plants	Annual Capacity (thousand tons per year)	Percent of Total U.S. Operating Capacity
Louisiana	9	4,068	37%
Texas	5	3,314	30%
New York	4	652	6%
Alabama	5	592	5%
Washington	4	503	5%
West Virginia	2	392	3%
Georgia	3	246	2%
Tennessee	1	230	2%
Other States (14)	19	1,139	10%
U.S. Total	52	11,136	100%

Source: *Kirk-Othmer Encyclopedia of Chemical Technology, 4th ed. Vol. 1, 1993* .

Ward's Business Directory of U.S. Private Companies, produced by Gale Research Inc., compiles financial data on U.S. companies including those operating within the inorganic chemicals manufacturing industry. Ward's ranks U.S. companies, whether they are a parent company, subsidiary or division, by sales volume within the 4-digit SIC codes that they have been assigned as their primary activity. Exhibit 4 lists the top ten inorganic chemical manufacturing companies in the U.S. Readers should note that: 1) Companies are assigned a 4-digit SIC that most closely resembles their principal industry; and 2) Sales figures include total company sales, including sales derived from subsidiaries and operations not related to the manufacture of inorganic chemicals. Additional sources of company specific financial information include Standard & Poor's *Stock Report Services*, Dunn & Bradstreet's *Million Dollar Directory*, Moody's Manuals, and annual reports.

Exhibit 4: Top U.S. Companies with Inorganic Chemical Manufacturing Operations		
Rank^a	Company^b	1993 Sales (millions of dollars)
1	Dow Chemical Co. - Midland, MI	18,800
2	Hanson Industries, Inc. - Iselin, NJ	6,092
3	WR Grace and Co. - Boca Raton, FL	6,049
4	Occidental Chemical Corp. - Dallas, TX	4,600
5	BOC Group, Inc. - Murray Hill, NJ	4,500
6	FMC Corp. - Chicago, IL	3,899
7	Eastman Kodak Co. - Kingsport, TN	3,740
8	Air Products and Chemicals, Inc. - Allentown, PA	2,931
9	ARCO Chemical Co. - Newtown Square, PA	2,837
10	Ethyl Corp. - Richmond, VA	2,575

Note: ^a When *Ward's Business Directory* listed both a parent and subsidiary in the top ten, only the parent company is presented above to avoid double counting sales volumes. Not all sales can be attributed to the companies' inorganic chemical manufacturing operations.
^b Companies shown listed SICs 2812, 2813, 2816 and 2819 as primary activities.

Source: *Ward's Business Directory of U.S. Private and Public Companies* - 1993.

II.B.3. Economic Trends

Inorganic Chemicals Industry

The Bureau of the Census estimated that there were 1,429 facilities in the inorganic chemical industry in 1992. The industry employed 103,000 people and had a total value of shipments of \$27.4 billion. The total value of shipments for the inorganic chemicals industry increased about one percent per year between 1992 and 1994. These values do not include inorganic chemicals manufactured for captive use within a facility nor the value of other non-industrial inorganic chemical products manufactured by the same facility. It does, however, include intra-company transfers which are significant in this industry. The inorganic chemical industry's growth rate is expected to continue to increase with the growth of the economy. The U.S. is a net exporter of inorganic chemicals with most exports shipped to the European Community (EC) followed by Canada and Mexico. This positive trade balance increased significantly in 1993 to \$1.7 billion and is expected to continue as the European economy improves. By comparison, the 1992 Census of Manufactures for Industrial Organic Chemicals reports a 1992 value of shipments for organic chemicals of \$64.5 billion and a total employment of 125,100 people. The 1992 value of shipments for the entire chemical industry (SIC 28) totaled \$292.3 billion with an employment of 850,000 people.¹⁰

Because inorganic chemicals are used in the manufacturing of many products, the industry tends to grow at the same rate as overall industrial production. In the late 1980s, the industry experienced high growth rates and, in the early 1990s, the industry saw little real growth in output, as a reflection of the U.S. economy's recession. The industry has historically had low profit margins which, in recent years, have decreased further with increasing pollution abatement costs.¹¹

Chlor-alkali Sector

The Bureau of the Census data for 1992 shows that there were 51 facilities within the inorganic chemicals industry that manufactured alkalies and chlorine. These chlor-alkali facilities employed 8,000 people and had a total value of shipments of \$2.8 billion. This was an increase of 1.7 percent from 1991. The chlor-alkali industry as a whole is expected to grow at its past rate of 1.5 times gross domestic product (GDP) growth through the 1990s. Because chlorine and caustic soda are electrolysis co-products, the production of one product can depend on the demand of the other product. The market pull has switched several times between caustic soda and chlorine in the past few decades. Presently, chlorine demand is

controlling production; consequently, there is a current excess availability of caustic soda in the U.S. This excess material is typically exported to fill a significant demand outside the U.S. The consumption of caustic soda is growing faster than the consumption of chlorine, however, and domestic caustic soda demand is expected to control production in the coming years.¹²

After reaching record high levels in the late 1970s, chlorine production declined in the early 1980s due in part to the economic recession between 1980 and 1982. Chlorine production increased slowly through the 1980s and, as of 1992, had not reached the record high levels and growth rates of the 1970s. This is due in part to the relative maturity of the chlorine usage industries and more recent environmental pressures aimed at curtailing chlorine use. Regulatory restrictions on the production or disposal of some products which require large amounts of chlorine to manufacture (i.e., chlorofluorocarbons, PVC, and chlorinated solvents) have adversely affected the market. Chlorine's commercial appeal has been further reduced by initiatives such as the International Joint Commission of Great Lakes Water Quality (a Canada-U.S. environmental oversight group) and a number of environmental groups which call for a gradual phaseout or an immediate ban of chlorine and chlorinated compounds as industrial feedstocks.¹³

The production of caustic soda is very dependent on the short term and long term chlorine demand and production because chlorine cannot be stored economically. Increased demand for chlorine must be met immediately by increased chlorine production via electrolysis of brine and, consequently, caustic soda production. Domestic and export demand for caustic soda was very strong in the 1980s with the pick up of the world economy and an increase in pulp and paper production. In the late 1980s, there was a worldwide shortage of caustic soda due to increased demand and lower U.S. chlorine production. The demand for caustic soda is expected to continue to grow in the coming years; however, there are a number of uncertainties that may limit the growth rate. Some industries have begun switching from caustic soda to soda ash where possible to avoid caustic soda shortages. Soda ash, which is extremely plentiful in the U.S., is obtained almost entirely from natural sources of trona ore. Demand for caustic soda may also decrease as pulp mills increase their reclamation of caustic soda from spent pulping liquor.¹⁴

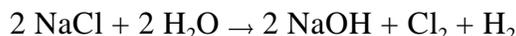
III. INDUSTRIAL PROCESS DESCRIPTION

This section describes the major industrial processes within the inorganic chemical 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 (via air, water, and soil pathways) of these waste products.

III.A. Industrial Processes in the Inorganic Chemical Industry

Chlorine and caustic soda are co-products of electrolysis of saturated aqueous solutions of sodium chloride, NaCl (salt water or brine). In addition, relatively small amounts (by weight) of hydrogen gas are produced in the process. The overall chemical reaction is as follows:



Energy, in the form of direct current (d-c) electricity, is supplied to drive the reaction. The amount of electrical energy required depends on the design of the electrolytic cell, the voltage used, and the concentration of brine used. For each ton of chlorine produced, 1.1 tons of sodium hydroxide and 28 kilograms of hydrogen are produced.

Three types of electrolysis processes are used for the manufacture of chlorine, caustic soda, and hydrogen from brine:

- Mercury Cell Process
- Diaphragm Cell Process
- Membrane Cell Process

Virtually all chlorine produced in the U.S. is manufactured by one of these three electrolysis processes. Each electrolytic cell consists of an anode and cathode in contact with the brine solution. Exhibit 5 shows the basic elements, inputs and outputs of each type of electrolytic cell. The distinguishing feature of each cell type is the method employed to separate and prevent the mixing of the chlorine gas and sodium hydroxide. Consequently, each process produces a different purity of chlorine gas and a different concentration of caustic soda. Exhibit 6 is a summary of the major differences between each cell type. In 1988, diaphragm cells accounted for 76 percent of all domestic chlorine production, followed by mercury cells with 17 percent, and membrane cells with five percent. The industry is moving away from mercury and diaphragm cells and is moving towards the use of membrane cells. Membrane cells are a relatively recent development which have fewer adverse effects on the environment and produce a higher quality product at a lower cost than the other methods.^{15,16}

(Source: Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, 1994.)

Exhibit 6: Main Characteristics of the Different Electrolysis Processes			
Component	Mercury Cell	Diaphragm Cell	Membrane Cell
Cathode	Mercury flowing over steel	Steel or steel coated with activated nickel	Steel or nickel with a nickel based catalytic coating
Diaphragm / Membrane	None	Asbestos or polymer modified asbestos	Ion-exchange membrane
Anode	Titanium with RuO ₂ or TiO ₂ coating (DSA anode)	Titanium with RuO ₂ or TiO ₂ coating (DSA anode)	Titanium with RuO ₂ or TiO ₂ coating (DSA anode)
Cathode Product	Sodium amalgam	10-12% NaOH with 15-17% NaCl and H ₂	30-33% NaOH and H ₂
Decomposer / Evaporator Product	50% NaOH and H ₂ from decomposer	50% NaOH with 1% NaCl and solid salt from evaporator	50% NaOH with very little salt
Electricity Consumption	3,300 kWh per ton Cl ₂	2,750 kWh per ton Cl ₂	2,100-2,450 kWh per ton NaOH
Source: Kirk-Othmer Encyclopedia of Chemical Technology, 4th Edition, 1994.			

III.A.1. Mercury Cell

The mercury cell process consists of slightly inclined steel troughs through which a thin layer of mercury (about three mm) flows over the bottom (Exhibit 7). The cells are operated at 75 to 85 °C and atmospheric pressure. The mercury layer serves as the cathode for the process and the saturated brine solution (25.5 percent NaCl by weight) flows through the troughs above the mercury. The anodes are usually incorporated into the cell covers and are suspended horizontally in the brine solution.

The height of the anodes within the brine is adjusted to the optimal height either manually or through an automatic computer controlled system.¹⁷

Electrolytic cell anodes were made of graphite until the late 1960s when anodes of titanium coated with ruthenium oxide (RuO_2) and titanium oxide (TiO_2) were developed. The RuO_2 and TiO_2 anodes, termed DSA (dimensionally stable) anodes, are more stable than the graphite anodes (i.e., they do not need to be replaced as frequently) and are more energy efficient.¹⁸

(Source: Industrial Inorganic Chemistry, Büchner, et al., 1989.)

The chlorine gas is produced at the anodes where it moves upward through gas extraction slits in the cell covers. Sodium ions are absorbed by the mercury layer and the resulting sodium and mercury mixture, called the amalgam, is processed in "decomposer" cells to generate sodium hydroxide and reusable mercury. The amalgam entering the decomposer cell has a sodium concentration of approximately 0.2 to 0.5 percent by weight. The decomposer consists of a short-circuited electrical cell where graphite serves as the anode and the amalgam serves as the cathode. The amalgam and water flowing through the cell come into direct contact with the graphite. The hydrolysis of the water on the graphite in the presence of the amalgam results in a strong exothermic reaction generating mercury to be reused in the electrolytic cell, a 50 percent caustic soda solution, and hydrogen gas. Mercury cells are operated to maintain a 21 to 22 percent by weight NaCl concentration in the depleted brine leaving the cell. The dissolved chlorine is removed from the depleted brine solution, which is then resaturated with solid salt and purified for further use. Some facilities purge small amounts of brine solution and use new brine as make-up in order to prevent the build up of sulfate impurities in the brine.^{19,20}

The mercury process has the advantage over diaphragm and membrane cells in that it produces a pure chlorine gas with no oxygen, and a pure 50 percent caustic soda solution without having to further concentrate a more dilute solution. However, mercury cells operate at a higher voltage than diaphragm and membrane cells and, therefore, use more energy. The process also requires a very pure brine solution with little or no metal contaminants. Furthermore, elaborate precautions must be taken to avoid releases of mercury to the environment.

III.A.2. Diaphragm Cell

In the diaphragm cell process, multiple cells consisting of DSA anode plates and cathodes are mounted vertically and parallel to each other

(Exhibit 8). Each cell consists of one anode and cathode pair. The cathodes are typically flat hollow steel mesh or perforated steel structures covered with asbestos fibers, which serve as the diaphragm. The asbestos fiber structure of the diaphragm prevents the mixing of hydrogen and chlorine by allowing liquid to pass through to the cathode, but not fine bubbles of chlorine gas formed at the anodes. The diaphragm also hinders the back-diffusion to the anode of hydroxide (OH^-) ions formed at the cathode. The cells are operated at 90 to 95 °C and atmospheric pressure. Brine flows continuously into the anode chamber and, subsequently, through the diaphragm to the cathode. As in the mercury cell process, chlorine gas is formed at the anodes; however, in the diaphragm process, caustic soda solution and hydrogen gas are formed directly at the cathode. The chlorine gas is drawn off from above the anodes for further processing. The hydrogen gas is drawn off separately from the cathode chambers.^{21,22}

Two basic types of diaphragm cells are in use today. The first, monopolar cells, have an electrode arrangement in which the anodes and cathodes are arranged in parallel. As a result of this configuration, all cells have the same voltage of about three to four volts; up to 200 cells can be constructed in one circuit. The second basic type of diaphragm cell is the bipolar cell, in which the anode of one cell is directly connected to the cathode of the next cell unit. This type of arrangement minimizes voltage loss between cells; however, since the total voltage across the entire set of cells is the sum of the individual cell voltages, the number of cells per unit is limited. To compensate for the reduced anode and cathode surface area in the bipolar configuration, bipolar units tend to be much larger than monopolar units. Production of chlorine and caustic soda by the diaphragm process is split approximately equally between monopolar and bipolar systems.²³

(Source: Industrial Inorganic Chemistry, Büchner, et al., 1989)

Diaphragm cells are operated such that about 50 percent of the input NaCl is decomposed resulting in an effluent mixture of brine and caustic soda solution containing eight to 12 percent NaOH and 12 to 18 percent NaCl by weight. This solution is evaporated to 50 percent NaOH by weight at which point all of the salt, except a residual 1.0 to 1.5 percent by weight, precipitates out. The salt generated is very pure and is typically used to make more brine. Because the brine and caustic soda solution are mixed in a single effluent, a fresh brine solution (no recycled brine) is constantly entering the system. The diaphragm cell process does not, therefore, require a brine purge to prevent sulfate build up, or treatment to remove entrained chlorine gas, as in the mercury cell process.²⁴

Diaphragms are constructed of asbestos because of its chemical and physical stability and because it is a relatively inexpensive and abundant material. Beginning in the early 1970s, asbestos diaphragms began to be replaced by diaphragms containing 75 percent asbestos and 25 percent fibrous

polytetrafluoroethylene (PTFE). These diaphragms, trade named Modified Diaphragms, are more stable and operate more efficiently than the fully asbestos diaphragms. Modified Diaphragms are the most common diaphragms currently in use.²⁵

Diaphragm cells have the advantage of operating at a lower voltage than mercury cells and, therefore, use less electricity. In addition, the brine entering a diaphragm cell can be less pure than that required by mercury and membrane cells. The chlorine gas produced by the diaphragm process, however, is not pure and must be processed to remove oxygen, water, salt, and sodium hydroxide. Another disadvantage of the process is that the caustic soda produced contains chlorides and requires evaporation to bring it to a usable concentration.²⁶

III.A.3. Membrane Cell

In the membrane cell process, the anode and cathode are separated by a water-impermeable ion-conducting membrane (Exhibit 9). Brine solution flows through the anode compartment where chlorine gas is generated. The sodium ions migrate through the membrane to the cathode compartment which contains flowing caustic soda solution. Water is hydrolyzed at the cathode, releasing hydrogen gas and hydroxide (OH^-) ions. The sodium and hydroxide ions combine to produce caustic soda which is typically brought to a concentration of 32 to 35 percent by recirculating the solution before it is discharged from the cell. The membrane prevents the migration of chloride ions from the anode compartment to the cathode compartment; therefore, the caustic soda solution produced does not contain salt as in the diaphragm cell process. Depleted brine is discharged from the anode compartment and resaturated with salt.²⁷

The cathode material used in membrane cells is either stainless steel or nickel. The cathodes are often coated with a catalyst that is more stable than the substrate and that increases surface area and electrical conductivity. Coating materials include Ni-S, Ni-Al, and Ni-NiO mixtures, as well as mixtures of nickel and platinum group metals. Anodes are typically of the DSA type.²⁸

The most critical components of the membrane cells are the membranes themselves. The membranes must remain stable while being exposed to chlorine on one side and a strong caustic solution on the other. Furthermore, the membranes must have low electrical resistance, and allow the transport of sodium ions and not chloride ions and reinforcing fabric, and a perfluorocarboxylate polymer all bonded together.

(Source: Industrial Inorganic Chemistry, Büchner, et al., 1989.)

Membrane cells can be configured either as monopolar or bipolar. As in the case of the diaphragm cell process, the bipolar cells have less voltage loss between the cells than the monopolar cells; however, the number of cells connected together in the same circuit is limited.²⁹

Membrane cells have the advantages of producing a very pure caustic soda solution and of using less electricity than the mercury and diaphragm processes. In addition, the membrane process does not use highly toxic materials such as mercury and asbestos. Disadvantages of the membrane process are that the chlorine gas produced must be processed to remove oxygen and water vapor, and the caustic soda produced must be evaporated to increase the concentration. Furthermore, the brine entering a membrane cell must be of a very high purity, which often requires costly additional purification steps prior to electrolysis.³⁰

III.A.4. Auxiliary Processes

Brine Purification

Approximately 70 percent of the salt used in chlorine gas production is extracted from natural salt deposits; the remainder is evaporated from seawater. Salt from natural deposits is either mined in solid form or is leached from the subsurface. Leaching involves the injection of freshwater into subterranean salt deposits and pumping out brine solution. Brine production from seawater typically occurs by solar evaporation in a series of ponds to concentrate the seawater, precipitate out impurities, and precipitate out solid sodium chloride. Regardless of the method used to obtain the salt, it will contain impurities that must be removed before being used in the electrolysis process. Impurities primarily consist of calcium, magnesium, barium, iron, aluminum, sulfates, and trace metals. Impurities can significantly reduce the efficiency of the electrolytic cells, by precipitating out and subsequently blocking a diaphragm or damaging a membrane depending on the process used. Certain trace metals, such as vanadium, reduce the efficiency of mercury cells and cause the production of potentially dangerous amounts of hydrogen gas. Removal of impurities accounts for a significant portion of the overall costs of chlor-alkali production, especially in the membrane process.³¹

In addition to the dissolved natural impurities, chlorine must be removed from the recycled brine solutions used in mercury and membrane processes. Dissolved chlorine gas entering the anode chamber in the brine solution will react with hydroxide ions formed at the cathode to form chlorate which reduces product yields. In addition, chlorine gas in the brine solution will cause corrosion of pipes, pumps, and containers during further processing of the brine. In a typical chlorine plant, HCl is added to the brine solution leaving the cells to liberate the chlorine gas. A vacuum is applied to the solution to collect the chlorine gas for further treatment. To further reduce the chlorine levels, sodium sulfite or another reducing agent is added to remove the final traces of

chlorine. Dechlorinated brine is then resaturated with solid salt before further treating to remove impurities.³²

Depending on the amount of impurities in the salt and the electrolysis process utilized, different purification steps will be required. Brine solution is typically heated before treatment to improve reaction times and precipitation of impurities. Calcium carbonate impurities are precipitated out through treatment with sodium carbonate; magnesium, iron, and aluminum are precipitated out through treatment with sodium hydroxide; and sulfates are precipitated out through the addition of calcium chloride or barium carbonate. Most trace metals are also precipitated out through these processes. Flocculants are sometimes added to the clarifying equipment to improve settling. The sludges generated in this process are washed to recover entrained sodium chloride. Following the clarification steps, the brine solution is typically passed through sand filters followed by polishing filters. The brine passing through these steps will contain less than four parts per million (ppm) calcium and 0.5 ppm magnesium which is sufficient purification for the diaphragm and mercury cell processes. For brine to be used in the membrane process, however, requires a combined calcium and magnesium content of less than 20 parts per billion (ppb). Brine for the membrane process is, therefore, passed through ion exchange columns to further remove impurities.³³

Chlorine Processing

The chlorine gas produced by electrolytic processes is saturated with water vapor. Chlorine gas from the diaphragm process also contains liquid droplets of sodium hydroxide and salt solution. The first steps in processing the chlorine to a usable product consists of cooling the chlorine to less than ten degrees centigrade and then passing it through demisters or electrostatic precipitators to remove water and solids. Next the chlorine is passed through packed towers with concentrated sulfuric acid flowing countercurrently. The water vapor is absorbed by the sulfuric acid and the dry chlorine gas is then passed through demisters to remove sulfuric acid mist. If the chlorine is to

be liquefied, liquid chlorine is then added to the gas to further purify the chlorine and to prechill it prior to compression. Prechilling is primarily carried out to prevent the temperature from reaching the chlorine-steel ignition point during compression.³⁴

Chlorine gas is either used in gaseous form within the facility, transferred to customers via pipeline, or liquefied for storage or transport. Liquid chlorine is of a higher purity than gaseous chlorine and is either used within the facility or is transferred via rail tank car, tank truck, or tank barge. The demand for liquid chlorine has increased in recent years and, in 1987, accounted for about 81 percent of chlorine produced in the U.S.³⁵

Chlorine liquefaction processes typically liquefy only about 90-95 percent of the chlorine. This gas and the chlorine gas left inside tank truck tanks, rail car tanks, or barges after removal of liquid chlorine is impure and must be recovered in a chlorine recovery unit. The gas is compressed and cooled using cold water followed by Freon. The chilled gas is fed up through a packed column in which carbon tetrachloride flows downward absorbing the chlorine. The chlorine-rich carbon tetrachloride is fed to a chlorine stripper in which the chlorine and carbon tetrachloride separate as they are heated. The chlorine gas is cooled and scrubbed of carbon tetrachloride using liquid chlorine and the resulting pure chlorine is sent to the chlorine liquefaction system.³⁶

Caustic Soda Processing

Caustic soda solution generated from chlor-alkali processes is typically processed to remove impurities and to concentrate it to either a 50 percent or 73 percent water-based solution or to anhydrous caustic soda. The caustic soda from the mercury and membrane processes is relatively pure. Product from the mercury process requires only filtration to remove mercury droplets. The evaporators used to concentrate the caustic soda solution in the diaphragm process are typically multi-stage forced circulation evaporators. The evaporators have salt settling systems to remove precipitated salt. Sodium borohydride is often

added to reduce corrosion of the equipment. Evaporators for the membrane process are usually much simpler than those for the diaphragm process because the salt concentration in the membrane cell caustic solution is very low.³⁷

Hydrogen Processing

The hydrogen produced in all of the electrolytic processes contains small amounts of water vapor, sodium hydroxide, and salt which is removed through cooling. The hydrogen produced during the mercury cell process also contains small amounts of mercury which must be removed by cooling the hydrogen gas to condense the mercury and treating with activated carbon.³⁸

III.B. Raw Material Inputs and Pollution Outputs in the Production Line

Inputs and pollutant outputs of the chlor-alkali industry are relatively small both in number and volume in comparison to the chemical manufacturing industry as a whole. The inputs are primarily salt and water as feedstocks; acids and chemical precipitants used to remove impurities in the input brine or output chlorine and caustic soda; and freon used for liquefying and purifying the chlorine gas produced. The major pollutant outputs from all three electrolytic processes are chlorine gas emissions (both fugitive and point source); spent acids; freon (both fugitive and point source); impurities removed from the input salt or brine; and pollutants originating from electrolytic cell materials and other system parts.

Pollutant outputs have decreased in recent years as the industry moves away from the mercury and diaphragm cell processes to the more efficient (in terms of material and energy inputs and outputs) membrane cell process. In addition, improved cell part materials have been developed, such as DSA anodes and Modified Diaphragms, which are more stable and create less undesirable byproducts.

Inputs and pollutant outputs from the auxiliary processes such as brine purification, chlorine processing, caustic soda processing, and hydrogen processing are described in Section III.B.4.

III.B.1. Mercury Cell

Wastewater streams from mercury cell facilities arise from the chlorine drying process, brine purge, and miscellaneous sources. Small amounts of mercury are found in the brine purge and miscellaneous sources which include floor sumps and cell wash water. Before treatment, mercury concentrations (principally in the form of mercuric chloride, HgCl_4^{2-}) typically range from 0 to 20 ppm. Thereby segregating most mercury bearing wastewater streams from non-mercury bearing wastewater streams. Prior to treatment, sodium hydrosulfide is used to precipitate mercuric sulfide. The mercuric sulfide is removed through filtration before the water is discharged.³⁹

Air emissions consist of mercury vapor and chlorine gas released in relatively small amounts as fugitive emissions from the cells; and in the tail gases of the chlorine processing, caustic soda processing, and hydrogen processing. Process tail gases are wet scrubbed with caustic soda or soda ash solutions to remove chlorine and mercury vapor. Residual chlorine emissions in tail gases after treatment are less than one kg per 1,000 kg of chlorine produced and mercury emissions are negligible. The tail gas scrubber water is typically reused as brine make-up water.⁴⁰

Solid wastes containing mercury include: solids generated during brine purification; spent graphite from decomposer cells; spent caustic filtration cartridges from the filtration of caustic soda solution; spilled mercury from facility sumps; and mercury cell "butters," which are semisolid amalgams of mercury with barium or iron formed when an excess of barium is used during salt purification. Most mercury bearing solid wastes are shipped off-site to outside reclaimers who recover the mercury. The remaining wastes are disposed of in secure landfills using either chemical or physical methods to recover maximum feasible amount of mercury.⁴¹

III.B.2. Diaphragm Cell

Wastewater streams from the diaphragm cell process originate from the barometric condenser during

caustic soda evaporation, chlorine drying, and from purification of salt recovered from the evaporators. These wastewaters and their treatment are described below in Section III.B.4. The use of lead and graphite anodes and asbestos diaphragms generates lead, asbestos, and chlorinated hydrocarbons in the caustic soda and chlorine processing waste streams. Lead salts and chlorinated hydrocarbons are generated from corrosion of the anodes, and asbestos particles are formed by the degradation of the diaphragm with use. Over the past twenty years, all but a few diaphragm cell facilities have switched from the use of lead and graphite anodes with asbestos diaphragms to DSA anodes and Modified Diaphragms which resist corrosion and degradation. The lead, asbestos, and chlorinated hydrocarbon contaminants are, therefore, no longer discharged in significant amounts from most diaphragm cell chlor-alkali facilities. Those facilities that discharged caustic processing wastewater streams to on-site lagoons may, however, still have significant levels of these contaminants on-site.⁴²

Chlorine is released in relatively small amounts as fugitive emissions from the cells and in the process tail gases. Process tail gases are wet scrubbed with soda ash or caustic soda solutions to remove chlorine. Residual chlorine emissions in tail gases after treatment are negligible. The spent caustic solution is neutralized prior to discharge.⁴³

Solid wastes generated in the diaphragm process consist primarily of solids generated during brine purification and scrapped cell parts including, cell covers, piping and used diaphragms. Discarded cell parts are either landfilled on-site, as is typically the case for spent diaphragms, or shipped off-site for disposal. Used cathodes and DSA anodes are shipped off-site for recovery of their titanium content.⁴⁴

III.B.3. Membrane Cell

Wastewater from the diaphragm cell process originates from the barometric condenser during caustic soda evaporation, chlorine drying, and wash water from the ion exchange resin used to purify

the brine solution. The ion exchange wash water consists of dilute hydrochloric acid with small amounts of dissolved calcium, magnesium, and aluminum chloride. The wastewater is combined with the other process wastewaters and treated by neutralization.⁴⁵

Chlorine is released in relatively small amounts as fugitive emissions from the cells and in the process tail gases. Process tail gases are wet scrubbed with soda ash or caustic soda solutions to remove chlorine. Residual chlorine emissions in tail gases after treatment are negligible. The spent caustic solution is neutralized prior to discharge.⁴⁶

Solid waste generated in the diaphragm process consists primarily of solids generated during brine purification and used cell parts which include membranes, cathodes and DSA anodes. The used membranes are typically returned to the supplier and the used cathodes and DSA anodes are shipped off-site for recovery of their titanium content.⁴⁷

III.B.4. Auxiliary Processes

Brine Purification

Brine solutions are typically treated with a number of chemicals to remove impurities prior to input to the electrolytic cells. In the case of mercury and membrane cell systems, the brine is first acidified with HCl to remove dissolved chlorine. Next, sodium hydroxide and sodium carbonate are added to precipitate calcium and magnesium ions as calcium carbonate and magnesium hydroxide. Barium carbonate is then added to remove sulfates which precipitate out as barium sulfate. The precipitants are removed from the brine solution by settling and filtration. Pollutant outputs from this process include fugitive chlorine emissions and brine muds.⁴⁸

Brine muds are one of the largest waste streams of the chlor-alkali industry. On average, about 30 kilograms (kg) of brine mud are generated for every 1,000 kg of chlorine produced. The volume of mud will vary, however, depending on the purity of the salt used. Some facilities use pre-purified (i.e.,

chemical grade) evaporated salts which will produce only 0.7 to 6.0 kg of brine mud per 1,000 kg of chlorine produced. Brine mud typically contains magnesium hydroxide, calcium carbonate, and, in most cases, barium sulfate. Mercury cell brine muds usually contain mercury either in the elemental form or as the complex ion, mercuric chloride (HgCl_4^{2-}). Mercury-containing brine muds are typically disposed of in a RCRA Subtitle C landfill after treatment with sodium sulfide which converts the mercury to an insoluble sulfide.⁴⁹

Brine muds are usually segregated from other process wastes and stored in lagoons on-site. When the lagoons become filled, the brine mud is either dredged and landfilled off-site, or drained and covered over. Some plants that use brine solution leached from subterranean deposits inject brine muds into the salt cavities that are no longer being used.⁵⁰

Chlorine Processing

The chlorine gas recovered from electrolytic cells is cooled to remove water vapor. The condensed water is usually recycled as brine make-up although some facilities combine this waste stream with other waterborne waste streams prior to treatment. The remaining water vapor is removed by scrubbing the chlorine gas with concentrated sulfuric acid. The chlorine gas is then compressed and cooled to form liquid chlorine. Between six kg and 35 kg of 79 percent sulfuric acid wastewater is generated per 1,000 kg of chlorine produced. The majority of the spent sulfuric acid waste is shipped off-site for refortification to concentrated sulfuric acid or for use in other processes. The remainder is used to control effluent pH and/or is discharged to water or land disposed.⁵¹

The process of purifying and liquefying impure chlorine gas involves the absorption of the chlorine in a stream of carbon tetrachloride. The chlorine is subsequently removed in a stripping process in which the carbon tetrachloride is either recovered and reused, or is vented to the atmosphere.⁵²

Caustic Soda Processing

Caustic soda solution generated from chlor-alkali processes is typically processed to remove impurities and, in the case of the diaphragm and membrane processes, is concentrated to either a 50 percent or 73 percent water-based solution or to anhydrous caustic soda. About five tons of water must be evaporated per ton of 50 percent caustic soda solution produced. The water vapor from the evaporators is condensed in barometric condensers and, in the case of the diaphragm process, will primarily contain about 15 percent caustic soda solution and high concentrations of salt. If sodium sulfate is not removed during the brine purification process, salt recovered from the evaporators is often recrystallized to avoid sulfate buildup in the brine. If the salt is recrystallized, the wastewater from sodium hydroxide processing will also contain sodium sulfates. Significant levels of copper may also be present in the wastewater due to corrosion of pipes and other equipment. Wastewater from the membrane process contains caustic soda solution and virtually no salt or sodium sulfates.⁵³

Caustic soda processing wastewater is typically neutralized with hydrochloric acid, lagooned, and then discharged directly to a receiving water or land disposed. The caustic soda generated from the mercury process only requires filtration to remove mercury droplets which are typically recovered for reuse.

Hydrogen Processing

The hydrogen produced in all of the electrolytic processes contains small amounts of water vapor, sodium hydroxide, and salt which is removed through cooling. Condensed salt water and sodium hydroxide solution is either recycled as brine make-up or treated with other waterborne waste streams. The hydrogen produced during the mercury cell process, however, also contains small amounts of mercury which must be removed prior to liquefaction. Most of the entrained mercury is extracted by cooling the gas. The condensed mercury is then returned to the electrolytic cells. Some facilities further purify the hydrogen gas of mercury using activated carbon treatment. Spent activated carbon is typically shipped off-site as a hazardous waste.⁵⁴

III.C. Management of Chemicals In Wastestream

The Pollution Prevention Act of 1990 (PPA) 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.

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 treatment on-site have decreased between 1992 and 1995 (projected). 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 PPA 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 10 shows that the inorganic chemicals industry managed about 1.7 trillion 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, 15 percent was either transferred off-site 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 85 percent of the industry's TRI wastes were managed on-site through recycling, energy recovery, or treatment as shown in columns

E, F and G, 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 H, I and J, respectively. The remaining portion of the production related wastes (11 percent), shown in column D, is either released to the environment through direct discharges to air, land, water, and underground injection, or it is disposed off-site.

Exhibit 10: Source Reduction and Recycling Activity for Inorganic Chemicals Industry (SIC 281) as Reported within TRI									
A	B	C	D	On-Site			Off-Site		
Year	Quantity of Production-Related Waste (10 ⁶ lbs.) ^a	% Released and Transferred ^b	% Released and Disposed ^c Off-site	E	F	G	H	I	J
				% Recycled	% Energy Recovery	% Treated	% Recycled	% Energy Recovery	% Treated
1992	1,642	16%	12%	42%	0%	42%	<1%	<1%	3%
1993	1,712	15%	11%	45%	0%	40%	<1%	<1%	3%
1994	1,759	---	11%	47%	<1%	39%	<1%	<1%	3%
1995	1,732	---	10%	48%	0%	40%	<1%	<1%	3%

^a Within this industry sector, non-production related waste is < 1% of production related wastes for 1993.

^b Total TRI transfers and releases as reported in Section 5 and 6 of Form R as a percentage of production related wastes.

^c Percentage of production related waste released to the environment and transferred off-site for disposal.