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SAFETY INFORMATION PROFILE

Production, Storage and Handling of Cryogenic Materials

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A safety information profile is presented for the production, storage, and handling of cryogenic materials (Standard Industrial Classification 2831). The generally automated processes used for these materials are described. Potential safety and health hazards are reviewed, especially fire and explosion hazards and those from exposure to toxic vapors and frostbite. Existing hazard controls are listed. Accident and illness data are tabulated. Industry trends are mentioned and existing standards are discussed. Names and addresses of industry associations, unions, and other interested parties are provided. It is concluded that injury rates for workers primarily engaged in the production and bulk storage of cryogens is low when compared to rates of other industrial classifications. Readily available data are inadequate to judge the injury experience related to transportation and handling of cryogens. It is recommended that existing association guidelines and more comprehensive regulations for the industry be adopted by the federal government.

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PREFACE

The information in this profile was prepared in accordance with the provisions of NIOSH Contract #210-78-0130-0000 and is only one of twenty-seven Industry Profiles prepared under the contract. The reader should understand that this study is not intended to be an in-depth analysis, but rather, a limited overview of the industry. Each individual profile was prepared by a Profile Manager utilizing approximately 45 hours of professional time. Each profile is a reflection of the available literature, and other information obtained from industry, government, and labor contacts. Information Profiles are primarily intended for use in determining future study needs, priorities and directions. From this preliminary study may come various in-depth studies such as criteria documents, technology assessments, epidemiological studies, etc.

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EXECUTIVE SUMMARY

The cryogenics industry is of moderate size and is rapidly expanding. While the production, storage and handling of cryogenics is generally carried out in automated, closed systems, workers in the cryogenics industry are exposed to certain rather unique hazards as well as to hazards which are common to the chemical industry. Hazards most peculiar to the cryogenics industry are exposure to extreme cold, potentially explosive liquid to gas volume expansions, and flammability and detonability characteristics of certain condensed phase cryogens. Proper control of these hazards requires implementation of a number of safeguards. Although available statistics indicate that workers employed in the cryogenics industry have a good safety record, anecdotal reports indicate that the use and handling of liquefied nitrogen by workers in other industries may be associated with unsafe practices and serious accidents. Review of governmental regulations pertaining to the production, storage and handling of cryogens leads to the conclusion that they are incomplete and could be usefully supplemented by existing association codes.

PRODUCTION, STORAGE AND HANDLING OF CRYOGENIC MATERIALS

A. Standard Industrial Classifications Included

This profile covers the cryogenic industrial activities associated with SIC 2813, Industrial Gases. This category is comprised mostly of industries engaged in bulk production and storage of cryogens, i.e., gases which are handled at relatively low pressures and extremely low temperatures, usually below minus 150 degrees Fahrenheit.(1-5)

This SIC category is comprised of "Establishments primarily engaged in manufacturing gases for sale in compressed, liquid and solid forms".(1) The value of shipments of cryogenic industrial gases was $2,300 million in 1978, produced and stored in 507 establishments employing 9,000 people.(6) Approximately 84% of cryogenic materials produced in the United States are produced by one of the four major U.S. cryogenic companies.(6)

The major cryogenic industrial gases are nitrogen and oxygen.(4) Over 100,000 establishments use the former.(3) Essentially all hospitals and steel manufacturing facilities, as well as many other facilities (e.g., NASA space program and various chemical plants) store and handle liquid oxygen.(3) Carbon dioxide is also widely used in liquid and solid form. Cryogenic fluids used in lesser amounts include helium, hydrogen, argon, neon, ethylene, carbon monoxide and liquid air.(2)

The figures above do not include liquefied natural gas (LNG), which generated over $1.5 billion in production and capital expenditures in 1978 and is growing rapidly.(6)

B. Process Descriptions

The production, storage and handling of cryogens is generally carried out in automated, closed systems.(3, 8)

(1) Production

Cryogenic materials are produced by cooling air or compressed gases to their boiling (or liquefying) points by one of three basic methods: liquid expansion, Joule-Thomson expansion, or expansion in an engine.(2)

(2) Storage

H. H. Benton states: "After production, cryogenic liquids generally are stored in specially designed tanks using super insulation or in dewar vessels, i.e., flasks with double walls of silvered glass or highly polished metal having an evacuated space between them, very similar except for size to the common thermos bottle. Liquid air, oxygen, nitrogen and even hydrogen can be kept for several hours in such vessels without further thermal protection".(2) Transportation of cryogenic fluids is presently conducted by truck, tank car, pipeline and ship. Transfer of these fluids from one container to another is conducted via double walled evacuated transfer lines.(2) Pressures in smaller cryogenic containers are typically less than 100 pounds per square inch and mass storage tanks normally operate at only 2 to 5 psi.(13)

(3) Handling

Cryogenic materials are used in a variety of ways. Generally, they do not involve direct worker exposure to the material unless the cryogenic application requires it, as in cryosurgery.(3,8) Generally, after use the material is disposed of by venting to the atmosphere, combustion through a vented natural gas- or propane- air burner, by passage through an absorbable filter, or by burning (flaring).(7)

C. Potential Hazards

Workers in the cryogenics industry are exposed to potential work hazards that are common to the entire chemical industry, i.e., exposure to toxic vapors and dangers of working with explosive materials.(7) Certain hazards, i.e., exposure to extreme cold, and the highly explosive potential of certain cryogenic fluids, are particularly severe hazards in the cryogenics industry.(7) In cryogenics, problems of safety and health are of two classes: those problems arising as a result of the fluid properties and those arising from the changes in properties of materials of construction as temperature is lowered. The hazards arising from the fluids are perhaps the most obvious. These include such phenomena as pressure buildup from confined fluids, air condensation in the colder cryogens, buildup of explosive mixtures, asphyxiation and low temperature burns. Hazards arising from material property changes include low-temperature embrittlement and excessive thermal contraction.(8)

(1) Safety Hazards

The principal safety hazards with cryogenic fluids are those of fire and explosion. These hazards arise from the spillage or venting of flammable or strongly oxidizing cryogenic materials or by formation of a combustible cryogenic fluid mixture or by a boiling liquid expanding vapor explosion (BLEVE). Several ways this can happen are:(7,8)

(a) Outward leakage of vapor or liquid. This can occur when the storage container or transfer line develops a leak due to material failure or inadequate sealing of transfer couplings, through venting valve malfunction, or due to exceeding of container pressure with consequent over-pressure venting. A tragic example of this was the October, 1944 collapse of an LNG storage tank in Cleveland, Ohio. It led to a fire and explosion in which 130 lives were lost and 80 dwellings destroyed.(9)

(b) Improper disposal of fluids or their vapors, i.e., unsafe dumping of a flammable or oxidizing cryogenic fluid.(7)

(c) Contamination of a cryogenic fluid by inward leakage during production orthrough liquefaction of a flammable mixture.(7)

(d) Accidental mixing of a flammable cryogen with an oxidizing cryogen.(7)

(e) Contamination of liquid oxygen with carbonaceous materials or other reactants.(7) A detonation can even be initiated in condensed phase mixtures (e.g., liquid hydrogen-solid oxygen) by mechanical impact.(7) This even includes materials that are not normally considered flammable. Numerous mishaps have occurred, for example, with shock-sensitive liquid oxygen-asphalt mixture formed when the liquid was accidentally spilled on asphalt-coated roads and storage areas. Liquid oxygen forms explosive mixtures with many common substances, including petroleum-based lubricants and other organic materials.(7, 28)

(f) Condensation of liquid oxygen from air contact with container surface or cryogen cooled below 82 degrees Kelvin (i.e., liquefied nitrogen, neon, hydrogen, helium).(3, 25)

(g) Failure (i.e., reduction of internal pressure to atmospheric level) of liquefied gas containers leading to the release of large quantities of gas at a very high level of potential energy. For example, liquid-to-gas expansion ratios are 862 for oxygen, 847 for nitrogen, 726 for air, and 85 for hydrogen (B.P. to $70^{o}F$).(30) Liquefied gas container failure is called a BLEVE, for Boiling Liquid-Expanding Vapor Explosion.(10) Although container failure is most often due to weakening of the container metal from flame contact, failure will happen if the container is punctured or fails for any other reason.(10) Furthermore, a container of liquefied gas, including a cryogenic gas, exhibits a greater rise in pressure with heating than does a compressed gas because of the added factors of liquid expansion and increase in vapor pressure of the liquid with increasing temperature. A most serious pressure rise can occur if the liquid expansion results in the container becoming liquid full (the gas phase condensing). If this happens, a small amount of additional heating results in a large increase in pressure.(10)

(2) Health Hazards

The asphyxiation or poisonous properties of vapors of cryogens are shared with the general category of compressed gases. In addition, cryogenic fluid vapors can cause asphyxiation by displacement of and consequent decrease in the amount of oxygen in the blood. Even small quantities of a cryogenic liquid can contaminate and displace the air in a relatively short period of time. For example, Zabetakis et. al. "found that a spill of 65 liters of liquid hydrogen on the floor of a 3,800 cubic foot air filled enclosure resulted in a hydrogen concentration of about 60 per cent at head height after 5 seconds. This would leave an oxygen concentration of only about 8.5 per cent, too low for sustained exposure."(11)

Frostbite is an obvious hazard with cryogenic materials. In general, frostbite occurs only after prolonged exposure of tissue to temperatures below 0 degrees Centigrade.(7) Reider says that "the contact of a cryogen with warm tissue creates a gas film which is not a good conductor of heat".(9) Once the surface of the tissue is frozen, however, the remaining tissue freezes rapidly. Cardiac disturbances and death may occur when the internal body (rectal) temperature drops below 80 degrees Fahrenheit.(7)

D. Existing Hazard Controls

Various design and procedural safeguards are used to control the hazards associated with cryogenic materials. Along with routine safeguards employed in most industries, these include:

(1) Fire and Explosion Safeguards

These can be summarized as follows:(10, 12-14, 24-25, 26, 28)

(a) Cryogenic fluid containers and transfer lines must be constructed of materials that retain ductility and do not become weak at cryogenic temperatures, can withstand stresses of thermal contraction and severe temperature gradients and (in the case of hydrogen) do not undergo hydrogen embrittlement. Carbon steels, for example, have precipitous transition to low breaking strength impact values;

(b) Glass dewars should not be used for containing or handling oxidizers or combustibles;

(c) Cryogenic facilities should contain adequate ventilation systems, approved electrical equipment, service facilities, leak detectors, flame sensors, fire-fighting equipment, and deluge systems;

(d) Cryogenic production and storage facilities should be carefully located with consideration given to closeness to populated areas, major highways, and ignition sources;

(e) Operations involving large volumes of flammable gases or vapors should be separated by a safe distance from other operations and should be suitably diked to avoid flow of hazardous liquids and vapors toward other structures in the event of spillage;

(f) Adequate ventilation is necessary where flammable gases and vapors are used and transported, in the spaces around equipment in which the combustibles may be present and in conduits, trenches and tunnels carrying pipelines. Whenever possible, operations should be carried out in the open air with closed structures being used to house instruments and equipment that must be protected from the weather;

(g) Ignition sources or combustibles should not be present near areas where liquefied oxygen or flammable liquids are being produced, stored or handled. In addition, all ignition sources must be removed from the areas through which the vapors might pass;

(h) Flammable liquids should not ordinarily be transferred within inhabited buildings unless adequate precautions are taken to prevent the escape and accumulation of vapors;

(i) Particularly hazardous operations should be conducted in remote barricaded areas and personnel in the area must be protected by concrete bunkers, blast mats or pressure vessels;

(j) In general, storage container support surfaces should be coated with an insulating material to protect them from direct contact with cold liquid should a spill occur and from heat should a fire result;

(k) Some insulation systems may have organic constituents, which in contact with oxygen enriched gases constitute a fire and explosion hazard. Caution should be taken to exclude atmospheric gases from these insulations where such oxygen enrichment could occur (i.e., around containers of liquid nitrogen, neon, helium and hydrogen);

(l) In general, organic materials should not be cooled to temperatures below about 82 degrees Kelvin in the presence of air or oxygen;

(m) All parts of an oxygen-handling system, including pumps, metering devices and gaskets, must be monitored for the presence of combustible materials, including many plastics, lubricants, solvents, paving materials, organic insulation foams and other organic materials;

(n) In general, any materials that might react with the process gas (i.e., air in the case of hydrogen, methane or ethylene) should be purged from process containers before process start-up;

(o) Never place more liquefied gas in the liquid phase into a container than can be accommodated - leaving a gas space - if the liquid temperature is raised to a level commensurate with the ambient temperatures expected, i.e., don't exceed the "filling", or "loading density";

(p) Generally, all cryogenic fluid containers should be equipped with spring-loaded safety relief valves and bursting discs or both to limit container pressure to a level the container can safely withstand. Other spaces that should be equipped with relief valves include the bath space, vacuum space and isolatable spaces such as sections of transfer lines between valves in series;

(q) Large containers should be structurally designed for "explosion venting";

(r) Cryogen disposal burners (flare stacks) should be equipped with appropriate devices to prevent flashback and to shut off the flow of gas if the flame is extinguished for any reason;

(s) When gases to be liquefied are drawn from a gas holder or a compressed gas cylinder, one must be careful not to starve the liquefaction unit either by introducing contaminants that can freeze or by exhausting the gas supply. In addition, only gases of known purity should be used;

(t) Flammable liquids should be stored in uninhabited areas;

(u) When flushing out equipment containing a nonflammable gaseous and/or liquid mixture, it must be done without running through the flammable range. This can be done with the use of flushing mixtures containing inert gases/fluids like nitrogen;

(v) The temperature of liquid combustibles should be held low enough that the liquid's flash point is never reached;

(w) Operating personnel should be familiar with the hazards and control measures associated with the cryogenic materials they work with as well as with emergency procedures;

(x) Cryogenic facilities should be given regular, systematic inspections and preventive maintenance;

(y) Cryogenic material containers should be labeled with the contents and an indication of the type and severity of associated hazards;

(z) Fast-acting valves, operated often by safely contained explosive activators, are often used to release very rapidly an agent (e.g., Halons) to reduce the oxygen content of a potentially explosive atmosphere or to limit the magnitude of an explosion;

(aa) Should a fire occur, fire control techniques appropriate to the control of cryogenic fluid fires must be employed;

(bb) When handling oxidizers special precautions must be taken to prevent contamination of clothing, gloves and footwear with combustibles such as oils and greases. Furthermore, all wearing apparel must be impervious to the oxidizer liquids and vapors;

(cc) There should be standardization of connector fittings to prevent cross filling and mixing of cryogenic liquids;

(dd) Only transfer lines designed for cryogenic liquids shall be used. Transfer of cryogenic liquids shall be performed slowly enough to minimize rapid cooling and contraction of warm containers and equipment.

(2) Asphyxia and Poisoning

The handling of cryogenic materials with toxic vapors requires generally the same safeguards as does the handling of these materials in their gaseous form. Such materials should be handled only in closed systems.(8) In addition, inert liquids must not be stored in inhabited areas as they can create a hazard by displacing the air. Their vapors must not be permitted to enter any inhabited enclosure or to contact personnel.(7)

(3) Frostbite

Zabetakis states that "basically, cryogenic fluids and their vapors must not be permitted to contact any part of the body. If this is a possibility, appropriate protective equipment should be worn. All clothing and accessories must be designed to prevent the freezing of body tissue".(7)

(No known federal government standard includes all of these safeguards. OSHA requirements generally cover these only as they apply to liquefied hydrogen and oxygen - see standards section.)

E. Accident and Illness Statistics

(1) General Statistics

The most readily available and pertinent statistics have been compiled by the U.S. Bureau of Census(15), the Bureau of Labor Statistics(16), and the National Safety Council(17). The following figures do not include LNG, which is classified under SIC 1311.(1)

Table 1 compiled by the U.S. Bureau of Census and published in 1976 indicates the size and extent of the cryogenics industry. It is apparent that the industry is of moderate size in terms of both the number of establishments providing such services and the number of employees involved, i.e., 512 establishments employing 8,000 employees.(6)

Tables 2 & 3 indicate that the incidence rate of injuries and illnesses per 100 fulltime employees and the number of lost workdays per 200,000 hours per year are uniformly lower than found in the larger subsamples of Chemicals and Allied Products (SIC 28), Nondurable Goods Manufacturing and the Private Sector. Table 4 prepared by the National Safety Council utilizing unspecified sources tend to agree with BLS statistics for the category Chemicals and Allied Products (SIC 28) but are not specific for Industrial Gases.

Table 5 prepared by the Bureau of Labor Statistics indicates that for 1975 the greatest mean incidence rate of accidents occurred in the establishments with 50 to 99 employees, which had a mean rate of 17.1 per 100 fulltime workers.

UNITED STATES - ESTABLISHMENTS, EMPLOYEES, AND PAYROLL BY INDUSTRY BY EMPLOYMENT - SIZE CLASS: 1976

TABLE 1

(Excludes government employees, railroad employees, self-employed persons, etc. - see "General Explanation" for definitions and statement on reliability of data. Size class 1 to 4 includes establishments having payroll but no employees during mid-March pay period. "D" denotes figures withheld to avoid disclosure of operations of individual establishments, the other alphabetics indicate employment-size class - see footnote.)

SIC code	Industry, establishments, employees, and payroll	Total	Employment-size class								
			1 to 4	5 to 9	10 to 19	20 to 49	50 to 99	100 to 249	250 to 499	500 to 999	1000 or more
2813	Industrial Gases										
	Number of Establishments	512	194	120	91	75	22	9	1	-	-
	Number of Employees	7,948	NA	816	1,254	2,449	1,665	1,117	NA	-	-
	Payroll, 1st. qrtr. ($1,000)	28,265	NA	2,664	4,407	9,110	5,670	3,873	NA	-	-
	Payroll, Annual ($1,000)	118,375	NA	11,306	19,592	37,638	22,963	16,171	NA	-	-

A: 0-19; B: 20-99; C: 100-249; E: 250-499; F: 500-999; G: 1,000-2,499; H: 2,500-4,999; I: 5,000-9,999; J: 10,000-24,999; K: 25,000-49,999; L: 50,000-99,999; M: 100,000 or more.

U.S. Bureau of the Census, County Business Patterns, 1976, Table 1B.

OCCUPATIONAL INJURY INCIDENCE RATES, PRIVATE SECTOR, BY INDUSTRY
UNITED STATES, 1975 AND 1976

TABLE 2

Industry 1/	SIC code 2/	Incidence rates per 100 full-time workers 3/							
		Total cases 4/		Lost workday cases		Nonfatal cases without lost workdays		Lost workdays	
		1975	1976	1975	1976	1975	1976	1975	1976
Industrial Gases	2813	-	7.1	-	2.6	-	4.4	-	42.8
For Comparison:									
Chemical & Allied Products	28	7.5	7.5	2.6	2.9	4.9	4.6	46.1	48.0
Nondurable Goods Manufacturing	-	10.9	11.3	3.9	4.2	7.0	7.1	65.7	70.4
Private Sector	-	8.8	8.9	3.2	3.4	5.6	5.5	54.6	57.8

1/ Totals for divisions and 2- and 3-digit SIC codes include data for industries not shown separately.

2/ Standard Industrial Classification Manual SIC, 1972 Edition.

3/ The incidence rates represent the number of injuries or lost workdays per 100 full-time workers and were calculated as: (N/EH) X 200,000, where
N = number of injuries or lost workdays
EH = total hours worked by all employees during calendar year
200,000 = base for 100 full-time equivalent workers (working 40 hours per week, 50 weeks per year).

4/ Includes fatalities. Because of rounding, the difference between the total and the sum of the rates for lost workday cases and nonfatal cases without lost workdays do not reflect the fatality rate.

5/ Excludes farms with fewer than 11 employees.

6/ Data conforming to the OSHA definitions for coal and lignite mining (SIC 11 and 12) and metal and nonmetal mining (SIC 10 and 14), and for railroad transportation (SIC 40) were provided by the Mining Enforcement and Safety Administration, U.S. Department of the Interior, and by the Federal Railroad Administration, U.S. Department of Transportation.

NOTE: Dashes indicate no data reported, or data that do not meet publication guidelines.

n.e.c. = not elsewhere classified.

SOURCE: Bureau of Labor Statistics, U.S. Department of Labor.

Chartbook on Occupational Injuries and Illnesses in 1976, U.S. Department of Labor, Bureau of Labor Statistics, 1978, Report 535, Table 5.

OCCUPATIONAL INJURY AND ILLNESS INCIDENCE RATES, PRIVATE SECTOR, BY INDUSTRY, UNITED STATES, 1975 AND 1976

Industry 1/	SIC code 2/	1976 annual average employment (in thousands) 3/	Incidence rates per 100 full-time workers 4/							
			Total cases 5/		Lost workday cases		Nonfatal cases without lost workdays		Lost workdays	
			1975	1976	1975	1976	1975	1976	1975	1976
Industrial Gases	2813	18.6	-	7.4	-	2.7	-	4.7	-	44.8
For Comparison:										
Chemicals & Allied Products	28	1,043.7	8.4	8.2	2.9	3.1	5.5	5.1	48.9	50.6
Nondurable Goods Manufacturing	-	7,867.5	11.4	11.8	4.1	4.4	7.3	7.4	66.7	72.8

1/ Totals for divisions and 2- and 3-digit SIC codes include data for industries not shown separately.

2/ Standard Industrial Classification Manual SIC, 1972 Edition.

3/ Annual average employment for nonagricultural industries is based primarily on employment covered by State unemployment insurance program. For those industries in which the unemployment insurance program does not have complete coverage and there is no change in the content of the industry classification between the 1967 and 1972 SIC manuals, estimates from the U.S. Department of Labor's Employment and Earnings Survey, which are based on the 1967 manual, are used. Annual average employment for the agriculture, forestry and fishing division in a composite of data from the unemployment insurance program, and estimates of hired-farm workers engaged in agricultural production (SIC 01 and 02) provided by the Statistical Reporting Service, U.S. Department of Agriculture. The agricultural production estimates are adjusted to excluse employment on farms with fewer than 11 employees.

4/ The incidence rates represent the number of injuries and illnesses or lost workdays per 100 full-time workers and were calculated as: (N/EH) x 200,000 where

N = number of injuries and illnesses or lost workdays
EH = total hours worked by all employees during calendar year
200,000 = base for 100 full-time equivalent workers (working 40 hours per week, 50 weeks per year).

5/ Includes fatalities. Because of rounding, the difference between the total and the sum of the rates for lost workday cases and nonfatal cases without lost workdays does not reflect the fatality rate.

6/ Excludes farms with fewer than 11 employees.

7/ Data conforming to the OSHA definitions for coal and lignite mining (SIC 11 and 12) and metal and nonmetal mining (SIC 10 and 14), and for railroad transportation (SIC 40) were provided by the Mining Enforcement and Safety Administration, U.S. Department of the Interior, and by the Federal Railroad Administration, U. S. Department of Transportation.

NOTE: Dashes indicate no data reported, or data that do not meet publication guidelines.

n.e.c. = not elsewhere classified.

SOURCE: Bureau of Labor Statistics, U.S. Department of Labor.

Chartbook on Occupational Injuries and Illnesses in 1976. U.S. Department of Labor, Bureau of Labor Statistics, 1978, Report 535, Table 1.

Table 4

Recordable Occupational Injury and Illness Incidence Rates*, 1975-1977, by Industry, Reporters to the National Safety Council

A more complete list of SIC Code industry rates is included in the separate publication Work Injury and Illness Rates, 1978 edition

Industry†	SIC Code‡	Incidence Rates per 100 Full-Time Employees*					
		Total Recordable Cases	Total Lost Workday Cases	Cases Involving Days Away From Work & Deaths	Nonfatal Cases Without Lost Workdays	Total Lost Workdays	Days Away From Work
All Industries		8.47	3.14	2.28	5.31	57	43
Agriculture, Forestry, & Fishing		17.66	5.06	4.88	12.58	86	80
Agricultural production—crops	01	23.85	6.90	6.66	16.93	81	73
Agricultural production—livestock	02	5.72	2.34	2.34	3.37	40	40
Forestry	08	9.85	2.36	2.19	7.48	100	96
Mining		10.80	2.53	2.27	8.24	80	75
Metal mining	10	14.93	3.23	2.47	11.68	102	93
Bituminous coal & lignite mining	12	12.31	4.91	4.99	7.28	183	183
Oil & gas extraction	13	6.21	1.53	1.46	4.66	44	42
Nonmetallic minerals, except fuels	14	18.00	4.15	4.13	13.81	140	133
Construction		14.20	3.69	3.47	10.48	72	65
General building contractors	15	12.85	2.39	2.28	10.45	62	56
Heavy construction contractors	16	13.14	3.78	3.53	9.33	72	65
Highway & street construction	161	12.50	4.38	4.33	8.09	73	69
Heavy construction, except highway	162	14.46	3.40	2.89	11.03	77	65
Special trade contractors	17	30.03	5.01	4.87	24.93	90	85
Manufacturing		9.23	3.15	2.10	6.07	57	43
Nondurable Goods		*8.42*	*2.65*	*2.00*	*5.76*	*55*	*45*
Food & kindred products	20	14.50	4.85	4.50	9.64	91	83
Meat products	201	21.82	8.68	7.06	13.15	118	99
Dairy products	202	12.28	4.49	4.44	7.79	83	81
Preserved fruits & vegetables	203	13.02	3.84	3.31	9.18	73	61
Grain mill products	204	13.47	4.41	4.18	9.05	103	95
Bakery products	205	12.68	4.78	4.71	7.89	86	83
Sugar & confectionery products	206	15.02	5.61	5.23	9.40	114	106
Cane sugar refining	2062	11.46	4.31	4.16	7.13	81	74
Beet sugar	2063	19.19	11.45	11.14	7.74	264	257
Fats & oils	207	19.13	4.56	4.41	14.52	84	81
Beverages	208	18.25	4.97	4.69	13.28	102	91
Malt beverages	2082	19.00	4.95	4.87	14.04	99	90
Distilled liquor, except brandy	2085	14.49	3.92	3.64	10.57	97	87
Misc. foods & kindred products	209	10.29	3.75	3.71	6.54	73	69
Tobacco manufactures	21	9.13	5.52	1.95	3.61	72	36
Textile mill products	22	7.12	1.00	0.82	6.12	34	29
Weaving mills, cotton	221	6.54	0.98	0.76	5.57	33	28
Weaving mills, synthetics	222	7.15	0.69	0.56	6.46	45	41
Weaving & finishing mills, wool	223	10.50	0.73	0.60	9.77	23	21
Narrow fabric mills	224	7.43	0.71	0.57	6.72	16	13
Knitting mills	225	7.94	1.09	1.07	6.85	27	26
Textile finishing, except wool	226	8.00	1.14	0.95	6.86	37	32
Floor covering mills	227	9.41	1.30	1.10	8.11	43	37
Yarn & thread mills	228	5.96	0.82	0.68	5.14	24	21
Miscellaneous textile goods	229	8.21	1.60	1.39	6.60	51	39
Apparel & other textile products	23	7.74	1.61	1.42	6.14	25	22
Paper & allied products	26	10.68	3.03	2.51	7.64	79	70
Pulp mills	261	12.66	2.59	2.56	10.04	82	77
Paper mills, except building paper	262	8.62	2.68	2.00	5.93	75	65
Paperboard mills	263	12.31	2.57	2.35	9.72	81	74
Misc. converted paper products	264	9.96	2.69	2.27	7.27	64	56
Paperboard containers & boxes	265	13.91	4.23	3.62	9.68	97	86
Folding paperboard boxes	2651	11.02	3.29	2.80	7.73	78	69
Corrugated & solid fiber boxes	2653	16.37	4.87	4.31	11.50	108	97
Building paper & board mills	266	11.00	2.91	2.74	8.08	81	77
Printing & publishing	27	7.39	3.03	2.66	4.36	54	49
Chemicals & allied products	28	5.57	1.83	1.11	3.73	37	25
Industrial inorganic chemicals	281	7.90	2.41	1.31	5.48	59	40
Plastics materials & synthetics	282	3.65	1.10	0.58	2.54	25	16
Plastics materials & resins	2821	5.23	1.84	1.08	3.38	39	25
Synthetic rubber	2822	5.07	1.69	0.77	3.38	32	23
Cellulosic man-made fibers	2823	3.70	0.90	0.39	2.78	22	12
Organic fibers, noncellulosic	2824	2.16	0.46	0.20	1.70	12	8
Drugs	283	5.45	2.29	1.47	3.16	39	25
Soap, cleaners, & toilet goods	284	8.04	2.99	2.05	5.04	49	35
Paints & allied products	285	8.23	3.63	1.96	4.60	63	37
Industrial organic chemicals	286	5.44	1.88	1.05	3.56	39	25
Cyclic crudes & intermediates	2865	9.50	3.49	2.48	6.02	54	42
Agricultural chemicals	287	9.25	2.25	1.55	6.98	43	31
Miscellaneous chemical products	289	7.74	2.64	2.10	5.10	54	44
Explosives	2892	5.05	1.33	0.70	3.71	35	23
Petroleum & coal products	29	6.36	2.16	1.35	4.19	45	33
Petroleum refining	291	5.97	2.15	1.23	3.81	45	30
Paving & roofing materials	295	19.18	4.41	4.19	14.72	103	98

See footnotes on page 33.

TABLE 5

Occupational injury and illness incidence rates, private sector, by industry and employment size, United States, 1975

Industry and employment size 1/	SIC code 2/	Incidence rates per 100 full-time workers 3/		Middle range 4/	
		Mean 4/	Median 4/	First quartile	Third quartile
Industrial Chemicals	281				
All Sizes		7.6	7.0	0.0	17.3
1 to 19		11.9	0.0	0.0	17.4
20 to 49		11.2	7.1	0.0	19.1
50 to 99		17.1	12.7	4.8	28.0
100 to 249		11.5	9.2	3.8	15.7
250 to 499		8.4	6.6	2.9	12.7
500 to 999		6.2	4.8	2.4	8.9
1,000 to 2,499		5.6	3.7	1.9	7.8
2,500 to over		3.9	<.05	<.05	<.05

1/ Totals for divisions and 2- and 3-digit SIC codes include data for industries not shown separately.

2/ Standard Industrial Classification Manual, 1967 Edition.

3/ The incidence rates represent the number of injuries and illnesses per 100 full-time workers.

4/ The mean incidence rate is calculated as (N/EH) X 200,000, where

N = number of injuries and illnesses
EH = total hours worked by all employees during calendar year
200,000 = base for 100 full-time equivalent workers (working 40 hours per week, 50 weeks per year).

The median incidence rate is the middle measure in the distribution; half of the establishments have an incidence rate lower than or equal to the median and half have a rate higher than or equal to the median rate.

The middle range (interquartile) is defined by 2 measures; one-fourth of the establishments have a rate higher than or equal to the first quartile rate and one-fourth of the establishments have a rate lower than or equal to the third quartile.

5/ Data conforming to the OSHA definitions for coal and lignite mining (SIC 11 and 12) and metal and nonmetal mining (SIC 10 and 14), and for railroad transportation (SIC 40) were provided by the Mining Enforcement and Safety Administration, U.S. Department of the Interior, and by the Federal Railroad Administration, U.S. Department of Transportation.

NOTE: Asterisk (*) indicates incidence rate of less than 0.05 per 100 full-time workers.

n.e.c. = not elsewhere classified.

SOURCE: Bureau of Labor Statistics, U.S. Department of Labor.

Occupational Injuries and Illnesses in the United States by Industry, 1975. U.S. Department of Labor, Bureau of Labor Statistics, 1978, Bulletin 1981, Table 2.

Incidence rates in the largest establishments were much less, reaching a rate of only 3.9 per 100 fulltime workers in establishments employing 2,500 and over.

(2) Comments

The Bureau of Labor Statistics indicates that, excluding LNG, approximately 8,000 persons are employed in the industrial gas industry.(16) Most of them work for one of four large establishments and most are primarily engaged in the production and storage of cryogenic materials. The accident statistics above indicate that this industry has an enviable safety record. However, most persons who transport and use cryogenic substances are not included in the industrial gas industry category. In particular, Dr. T. Flinn, director of the Cryogenics Engineering Conference, estimates that there are over 100,000 establishments which handle or transport liquid nitrogen but which are not classified as primary cryogenic facilities.(3) These include long and short haul refrigeration trucks, dairy farms and ranches ("50% of all dairy cattle in the U.S. are from artificial insemination with semen preserved in liquid nitrogen"), food processors, electronics factories (LN is used in the production of semiconductors), blood banks and other users.(3) Since it is inert and readily available, most users and transporters are unaware of its oxygen enrichment (i.e., air condensation) hazard. According to Dr. Flinn this has resulted in several recent explosions, including one in a Brooklyn bubble gum factory which killed three or four people. In this case, liquid nitrogen was being used to freeze gum to make it easier to cut.

F. Exposure Levels

Exposure levels to the safety and health hazards were not readily available in the literature. Generally, cryogenic materials are produced, stored and (with the exception of liquid nitrogen) handled in closed systems.(3, 8)

G. Related Studies

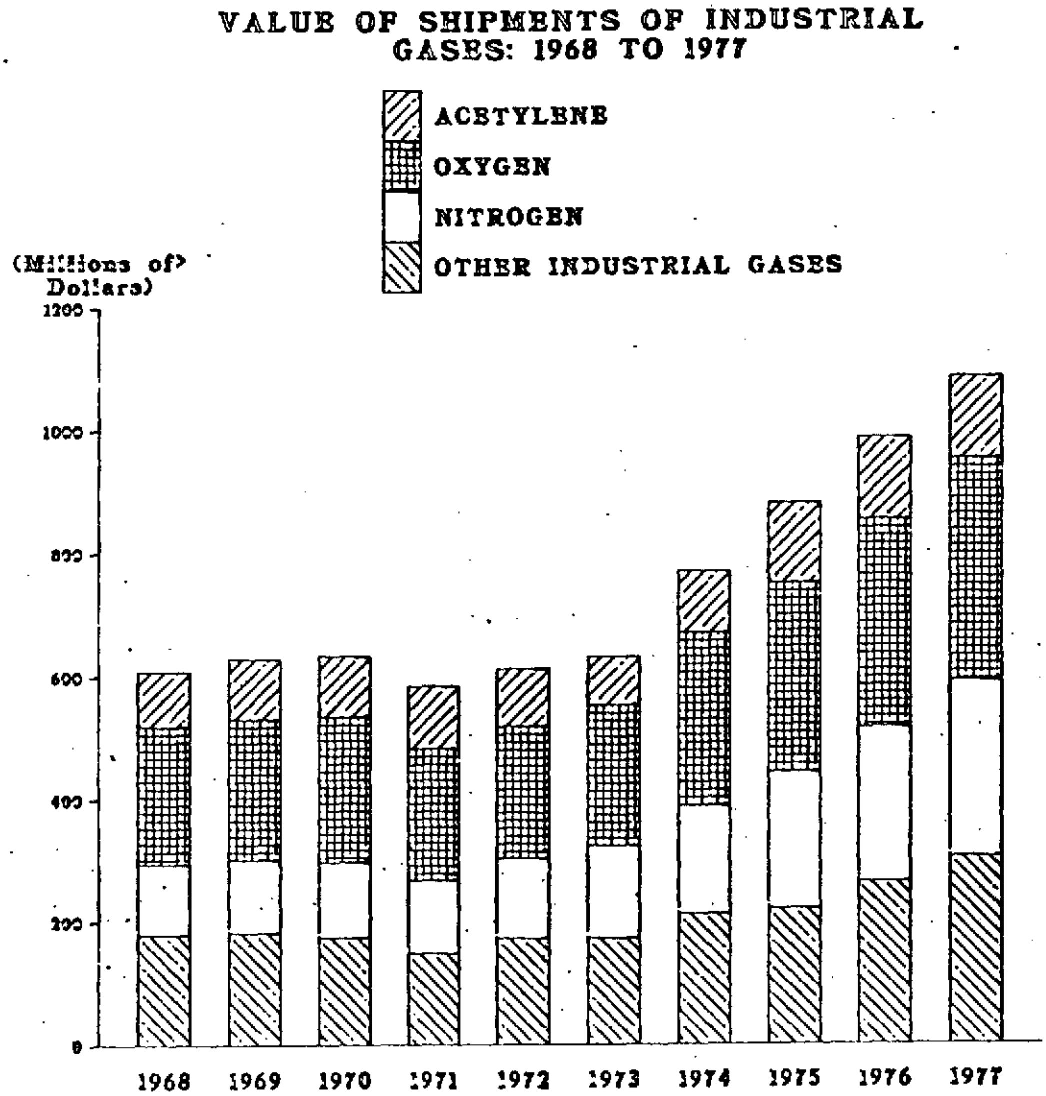
No ongoing or planned studies of cryogenic occupational safety or health hazards were identified.

H. Industry Trends

According to the Compressed Gas Association, "Gases are handled more and more as cold liquids and cryogenic fluids with steadily improved equipment and materials for low-temperature work, largely because many gases are most compact and exert little or no pressure when cooled down to liquids. Methane or natural gas liquefied at about -260 degrees Fahrenheit, already referred to as 'LNG' (liquefied natural gas), may be expected to become as commonplace as LP-Gas. Compatible shipping, handling and receiving facilities for low-temperature liquid transportation of gases appear with growing frequency. A host of new materials and methods for containing and piping cryogenic fluids have been originated in recent years, and will certainly be augmented in years ahead by many new materials now completely unknown".(18)

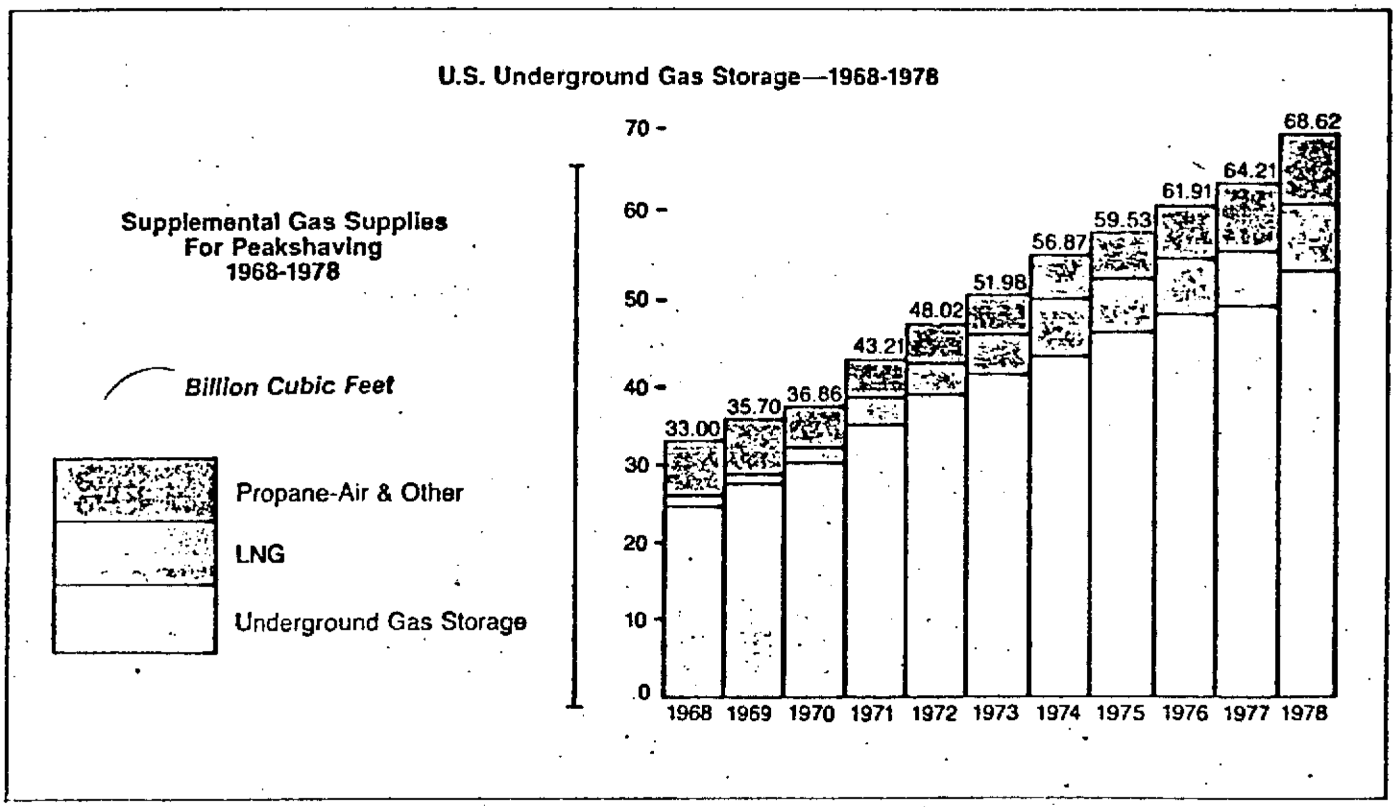
This statement, made in 1966 has been borne out by the subsequent annual production statistics illustrated in Table 6. Furthermore, it is expected that the production and use of cryogenic materials will continue to expand. The production and use of liquid nitrogen is expected to accelerate as more and more industries discover its usefulness.(3) The production and use of the other cryogenic materials is expected to grow at about an annual rate of 10 to 15%(3) except for liquefied natural gas, which is expected to grow the fastest of all cryogens (see Table 7).

Table 6



Address inquiries concerning these figures to U.S. Department of Commerce, Bureau of the Census, Industry Division, Washington, D.C. 20233, or call Géoff Embrey (301) 763-7837.

Table 7


U.S. Underground Gas Storage—1968-1978
Supplemental Gas Supplies
For Peakshaving
1968-1978
Billion Cubic Feet
Propane-Air & Other
LNG
Underground Gas Storage
70
60
50
40
30
20
10
0
33.00
35.70
36.86
43.21
48.02
51.98
56.87
59.53
61.91
64.21
68.62
1968
1969
1970
1971
1972
1973
1974
1975
1976
1977
1978

I. Existing Standards

(1) General

According to G. G. Haselden, "Existing codes cover container construction, electrical equipment, some phases of facility design, and the transport of cryogens. As a rule, cryogenic storage vessels are designed, built and tested according to provision of the American Society of Mechanical Engineers' Boiler and Pressure Vessel Code, Section III (1965) or Section VIII (1968). This code covers material selection, protection against excess pressure by relief devices, design and fabrication criteria, and gives test procedures to be carried out before and after fabrication. Materials must be suitable for the use temperature and pressure and must retain ductility at the use temperature. The National Electrical Code (National Fire Protection Association, 1968) covers the design of electrical equipment to be used where combustible gases can accumulate in flammable concentrations. Hydrogen and methane are covered by this code."(20) The Compressed Gas Association and/or the National Fire Protection Association have developed standards for liquefied hydrogen, oxygen and natural gas storage facilities, including standards for fire protection, operating instructions, storage distance requirements, diking, and tank construction.

Inter-state shipments of cryogens in the U.S. are controlled by federal regulations and are administered by the various branches of the Department of Transportation (20,22) although control of shipments of LNG is shared with the Department of Energy. Similar regulations for intra-state shipment are possible but in general do not exist specifically for cryogens.(20) Pipeline transmission of flammable compressed gases (presumably including flammable cryogenic liquids) are regulated by CFR, Title 49.(22) Some cryogenic liquids are handled in small quantities in open and low-pressure thermos type containers. These containers are not pressurized sufficiently to bring them under the jurisdiction of the DOT Regulations covering compressed gases but they are regulated by the AIA (domestic) and the IATA (foreign) Tariffs when transported by air.(21) There are no restrictions imposed upon the sale of cryogens, although the producers have assumed some responsibility in delivering certain cryogens (i.e., liquid hydrogen) only to qualified users. No restrictions have been imposed on the distribution of liquefied nitrogen. Transportation of cryogenic fluids has been considered to come under the purview of the Bureau of Explosives Tariff, No. 13.(20)

(2) OSHA

OSHA regulations do not specifically mention cryogens except for liquefied hydrogen and oxygen. Pertinent regulations are sections 1910.101, 1910.103, and 1910.104.(23)

(a) 1910.101 Compressed Gases (General Requirements)

These cover cylinder construction; in-plant handling, storage and utilization of compressed gases; and safety relief devices for compressed gas containers. This section is simply an adoption of certain standards of the Department of

Transportation and the Compressed Gas Association. The standards adopted appear adequate with regard to cylinder construction and safety relief devices but inadequate with regard to in-plant handling, storage and utilization of cryogens. The most serious inadequacies include lack of provisions regarding storage of inert cryogens in uninhabited areas, requirements for gas detectors, requirements for non-uniformity of connecting hook-ups, filling density and purity requirements and lack of safeguards regarding oxygen enrichment through air condensation.

(b) 1910.103 and 1910.104 (Liquefied Hydrogen and Liquefied Oxygen)

As supplements to 1910.101, these regulations appear to adequately cover the hazard controls for liquefied hydrogen and oxygen. However, they appear to specifically exclude large segments of exposed workers. Specifically excluded from the standards governing liquefied hydrogen systems are liquid hydrogen portable containers of less than 150 liter capacity and liquid hydrogen manufacturing storage and distribution facilities. The standard is specifically limited to "liquefied hydrogen systems on consumer premises". In similar fashion, the liquefied oxygen standard is directed to "bulk oxygen systems (of greater than 13,000 cubic feet capacity) on industrial and institutional consumer premises" and "does not apply to oxygen manufacturing plants or other establishments operated by the oxygen suppliers or his agent of storage (or distribution)". These sections incorporate National Fire Protection Association guidelines that are quite thorough.

Various other government, industrial and university organizations have drafted guidelines for the safe production, storage and handling of cryogens. An example of the variety of such guidelines are the safety guidelines and applicable regulatory codes referenced in reference 22.

J. Names of Industry Associations, Unions and Other Interested Parties

Any future study should include contact with the groups listed below.(27)

Cryogenics Engineering Conference
Room 4001 Radio Building
National Bureau of Standards
Boulder, Colorado 80302
(303) 499-1000

Cryogenic Society of America
1637 Chelsea Road
Palos Verdes Estates, California 90274
(213) 378-0528

Compressed Gas Association
500 Fifth Avenue
New York New York 10036
(212) 354-1130

Oil, Chemical and Atomic Workers International Union
Box 2812
Denver, Colorado 80201
(303) 893-0811

American Gas Association

1515 Wilson Blvd.

Arlington, Virginia 22209

(703) 524-2000

National Fire Protection Association

470 Atlantic Avenue

Boston, Massachusetts 02210

(617) 482-8755

Aerospace Safety Research and Data Institute

NASA Lewis Research Center

Cleveland, Ohio 44135

(216) 433-4000

Occupational Safety and Health Admininstration

200 Constitution Avenue, N.W.

Washington, D.C. 20210

(202) 523-8165

U.S. Department of Transportation

400 Seventh Street, N.W.

Washington, D.C. 20590

(202) 426-4000

U.S. Department of Energy
Washington, D.C. 20545
(202) 376-4000

K. Names and Addresses of Companies

Ten large industrial gas firms are listed below.(28)

The four largest producers of cryogens are:

Union Carbide Corporation
270 Park Avenue
New York, New York 10017

Chemtron Corporation
111 E. Wacker Drive
Chicago, Illinois 60601

Air Products and Chemicals
P. O. Box 538
Allentown, PA 18105

Airco, Inc.
85 Chestnut Ridge Road
Montvale, NJ 07645

The other six are:

CVI Corp.
P. O. Box 2138
Columbus, Ohio 43216

Chicago Bridge and Iron Co.
800 Jorie Blvd.
Oak Brook, Illinois 60521

M.W. Kellogg Co.
1300 Three Greenway
Plaza E
Houston, Texas 77046

Superior Air Products Co.
2001 Jernee Mill Road
Sayreville, NJ 08872

Cryogenic Technology Inc.
266 Second Ave.
Waltham, MA 02154

American Air Liquid
405 Lexinaton Ave.
New York, NY 10017

Ten users of relatively small amounts of cryogens

Aluminum Co. of America
1501 Alcoa Building
Pittsburgh, PA 15219

Armco Steel Corp.
P. O. Box 723
Houston, Texas 77001

Cosmodyne Division
Cordon Int. Corp.
2920 Columbia Street
Torrance, CA 90509

Cryolab Div. of Crogenic Tech. Inc.
2280 Sunset Drive
Los Osos, CA 93401

Kaiser Aluminum
300 LaReside Drive
Oakland, CA 94623

Liquid Carbonic Corp.
135 S. LaSalle Street
Chicago, Illinois 60603

Lotepro Corp.
305 E. 45 Street
New York, New York 10017

Lox Equipment Co.

734 Grace Street

Livermore, CA 94550

Reynolds Metals Co.

Reynolds Metals Building

West Broad Street

Richmond, VA 23218

Pittsburgh-Des Moines Steel Co.

Neville Island

Pittsburgh, PA 15229

L. Summary Analysis of Data

Analysis of readily available data leads to the following conclusions:

(1) Injury rates for workers primarily engaged in production and bulk storage of cryogens is low when compared to rates of other industrial classifications. This statement needs to be confirmed by review of more industry-specific injury rate data.

(2) Readily available data is inadequate to judge the injury experience related to transportation and handling of cryogens. Anecdotal reports indicate that there may be unnecessary injuries resulting from cryogen use, particularly of liquefied nitrogen.

(3) There are apparent inadequacies in government regulations regarding control of occupational hazards associated with the production, storage and handling of cryogens. Federal adoption of certain existing association codes and extension of existing OSHA regulations concerning cryogens to cover all workers significantly exposed to cryogen-related hazards would greatly alleviate these inadequacies.

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