ENVIRONMENTAL IMPACTS OF CARBON DIOXIDE AND DRY ICE PRODUCTION

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<u>Amendments to 111/16</u>

Section	Change
4.6.2.3	Addition of noise sources
4.6.6.1	Addition of removal requirements
4.7.3	Addition of paragraph ‘Noise’

Note: Significant technical changes from the previous edition are underlined

1 Introduction

This publication details the environmental impacts of carbon dioxide (CO_2) and dry ice plants and gives guidelines on how to reduce the impacts.

2 Scope and purpose

2.1 Scope

The publication concentrates on the environmental impacts of carbon dioxide and dry ice plant. This publication does not give specific advice on health and safety issues, which must be taken into account before undertaking any activity. On these issues the relevant EIGA publications, and or national legislation should be consulted for advice.

2.2 Purpose

This publication is intended to serve as a guide for carbon dioxide and dry ice plants to assist in putting in place a formal environmental management system that can be certified by an accredited 3rd party verifier. It also aims to provide a guide for operating managers for identifying and reducing the environmental impacts of these operations.

It also provides the basis for establishing the best available techniques for the purposes of the industrial emissions directive, see EC Directive 2010/75/EU, industrial emissions (*integrated pollution prevention and control)* [1][1]. This covers carbon dioxide and dry ice plants production, see Section 4.

3 Definitions

For the purposes of this publication, the following definitions apply:

3.1 Publications terminology

3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

3.1.2 Should

Indicates that a procedure is recommended.

3.1.3 May and need not

Indicate that the procedure is optional.

3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

3.1.5 Can

Indicates a possibility or ability.

[1] References are shown by bracketed numbers and are listed in order of appearance in the reference section

3.2 Technical definitions

3.2.1 Environmental aspect

These are elements of an organization's activities or products or services that can interact with the environment. For example, use of energy or transportation of products.

3.2.2 Environmental impact

Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organization's environmental aspects, see ISO 14001, *Environmental Management System* [2]. For example, the contamination of water with hazardous substances or the reduction of air emissions.

4 Carbon dioxide and dry ice production environmental impacts

Any industrial installation which carries out the activities listed in Annex I to the Industrial Emissions Directive must meet certain basic obligations [2]:

- preventive measures are taken against pollution;
- the Best Available Techniques (BAT) are applied;
- no significant pollution is caused;
- waste is reduced, recycled or disposed of in the manner which creates least pollution;
- energy efficiency is maximised;
- accidents are prevented and their impact limited; and
- sites are remediated when the activities come to an end.

4.1 General environmental aspects and impacts and links to other EIGA documents

This publication covers the environmental impact of carbon dioxide and dry ice production units. At the end of the publication, all these environmental impacts are summarised in Appendix A and B. There are several linked EIGA publications that provide more details on general environmental issues, legislation for the gas industry and operational good environmental practices. A list of these linked documents and their links to the ISO 14001 is provided in Appendix A [2]. Appendix C also shows which of these documents are relevant to carbon dioxide and dry ice plant operations.

4.2 Introduction

4.2.1 Production methods

This publication only describes the process to obtain pure and liquefied carbon dioxide from raw gas. There are many different alternatives, depending on the raw gas, for carbon dioxide production. The production process and associated plant is dependent on the concentration of carbon dioxide in the raw gas.

4.2.1.1 Chemical processes

A significant percentage (over 80%) of the carbon dioxide recovered in Europe by the gas industry is obtained from the waste gases of chemical processes. If not recovered, those gases are usually vented to atmosphere. Because of their high carbon dioxide concentration (over 98%) the process gases from the production of ammonia, steam methane reformers and ethylene oxide are preferred for the recovery of carbon dioxide. The waste gases from the chemical reaction of carbonates provide an alternative but relatively minor source of carbon dioxide.

4.2.1.2 Biological processes

The metabolism of yeast is an economical source of carbon dioxide, in particular, from the production of alcohol both for human consumption and industrial purposes. The relatively high capital investment necessary for the recovery of carbon dioxide from fermentation processes limits its use to a small number of large breweries and alcohol producers. Production of carbon dioxide from biomass is also possible.

4.2.1.3 Natural sources

Geological activity over hundreds of millennia has created underground deposits of carbon dioxide. Some of these carbon dioxide deposits are also of biological origin, caused by the degradation of prehistoric life forms.

Carbon dioxide from natural deposits is limited to areas with past volcanic activities, such as the USA, Europe such as the northern regions and UK, Africa and Asia. The carbon dioxide is recovered as saturated gas together with thermal or mineral water.

4.2.2 Recovery from natural gas

Some natural gas sources contain natural gas (methane) with a high content of carbon dioxide that can be recovered. The amounts of carbon dioxide, and of critical impurities, determine whether a natural gas source may be used for this purpose or not. These sources are common in Asia.

4.2.3 Combustion of oil and gas

Where no other source is technically or economically available, oil and gas can be burned with the only purpose to produce carbon dioxide. Special recovery units are provided for this purpose.

4.3 Properties

The particular properties of carbon dioxide, such as its inertness and its high degree of solubility in water, make carbon dioxide the ideal partner in many fields of our everyday life. Carbon dioxide is 1.5 times heavier than air, it is a colourless, non-flammable gas, of neutral odour and flavour. When added to water carbon dioxide forms carbonic acid (H_2CO_3). The name carbonic acid is often inaccurately used as a synonym for carbon dioxide. Carbon dioxide will not burn or support combustion. Air with a carbon dioxide content of more than 10% will extinguish an open flame, and, if breathed, can be life-threatening.

In liquid and solid cryogenic form, carbon dioxide is used as a refrigerant down to a temperature of –78 °C.

The main environmental impacts from carbon dioxide and dry ice plants are described step by step according to the production process.

4.4 Design, planning and control

The basic philosophy is the minimization of waste of any kind and its safe and clean disposal. By considering the potential waste which a new process could generate, or when engineering a plant, future problems can be avoided. This *waste analysis* is a crucial element of environmental impact assessment that is strongly recommended before any decision of industrial investment. Wastes should not be mixed but collected separately to aid further recycling, reuse or recovery.

Material safety data sheets (MSDS) for all chemical substances should be held on site and used to determine the best way to handle the chemical substances.

4.4.1 Process description

When a source has a rich carbon dioxide purity, over 95%, the installation will include only the basic plant as listed in the following:

BASIC PLANT

- compression,
- drying,
- purification,
- liquefaction and distillation, and

- storage.

When the source gas purity contains less than 50% of carbon dioxide, and also has some impurities, a first concentration of the raw gas is necessary before the basic unit and it is also necessary to include the following equipment to remove the impurities:

CONCENTRATION

- cooling and water scrubbing,
- absorption and desorption system, and
- cooling and water separation.

4.5 Concentration

A typical concentration process consists of an absorption system that uses any type of amine, concentration in water 10–40%.

The raw gas at close to ambient temperature is passed into an absorber, which is a column, where the gases are in counter current with the lean amine. The carbon dioxide is absorbed in the amine to become rich amine and the rest of the gases, typically nitrogen or syngas leave the top of the column to the atmosphere.

The rich amine is heated in a heat exchanger before reaching the desorption column. In this column a reboiler further heats the amine to about 120 ºC to outgas the carbon dioxide. The lean amine is recycled to the absorption column being cooled by the rich amine coming from the absorber.

Hot carbon dioxide leaves the desorption column and is cooled with water and sent to the basic plant to be liquefied and purified. The carbon dioxide gas is now in a concentration of 98–99.5%

4.5.1 Air emissions

Small indirect air emissions from the purification column could include emissions of carbon dioxide and ammonia from the condensate in the water that is returned to the cooling tower. This is minimised by running the plant at the design operating conditions.

4.5.2 Water use

Normally water is reused in the cooling tower and soluble impurities of the raw gas could produce an emission (alcohol) or be saturated in the pool ($CaCO_3$), but normally they are very low quantities.

4.5.3 Liquid waste

The amines depleted by the process should be removed and disposed by an authorized waste contractor. The rates would vary depending on the impurities from the carbon dioxide, but 2 kg amines/ton carbon dioxide could be reached.

4.5.4 Solid waste

The amine concentration systems are equipped with active carbon or other types of filters, which are periodically changed and disposed of.

4.6 Basic plant (carbon dioxide purification and liquefaction)

The basic process consists of compressing the raw gas to allow it to overcome the pressure drops in the different purification steps. Once dried and free of the heavy hydrocarbons it is liquefied by means of an external NH_3 or chlorinated hydrocarbons unit and the non-condensables are stripped in a special packed column. Finally it is sub cooled and stored in low temperature insulated tanks.

4.6.1 Cooling and condensation

To protect the compressors, it is necessary to remove the maximum of water moisture. A knock out drum, equipped with a special automatic valve commanded by a level transmitter actuating on a solenoid valve, drains the condensate produced.

4.6.1.1 Water emissions

At this stage condensed water could be normally sent to the drainage system. In some cases pH and soluble impurities could be checked to make sure the discharge is authorized.

4.6.2 Compression

To reach the required pressure to economically liquefy the purified gaseous carbon dioxide, typically 16 to 25 bar, two stages of compression are necessary.

4.6.2.1 Oil and water mixtures

Typically the environmental impact in this process is the oil and water-oil mixtures especially in the screw type compressors. The Oil waste could be produced by leaks, vapour emissions and cleaning. These wastes will need to be disposed of as hazardous waste by a certified waste disposal company in line with local or national regulations, after confirmation of an independent laboratory.

Improving maintenance of the compressors and a better design can reduce these waste sources. Precautions must be taken to prevent oil from entering the drainage system. Oil is never mixed with other substances like water, solvents etc.

Oil and water must be controlled and separated in appropriate installations. A bund or pit should be installed on each compressor to collect the potential leaks and purges. The size of the bund or pit should be equal to 100% of the largest capacity of the installation equipment; generally the receiver. For immediate action, appropriate absorbents should be stored in the facility.

4.6.2.2 Emissions to water

Recycled cooling water usually contains chemical treatment products used as biocides and to control corrosion. Cooling water also contains solid particles and dust that impact the chemical oxygen demand (COD) and biological oxygen demand (BOD) of the effluent.

The use of treatment chemicals must be minimized to achieve adequate system protection and in compliance with local and national regulation limit values.

Detergent from container washing should be directed to the sewer but precautions should be taken to prevent oil from entering drains; for example, the provision of an interceptor. A permit or consent may be necessary in accordance with national regulations. It is important that water that contains detergent is not directed to any oil/water separating system. This is because it will prevent the correct functioning of such a system.

4.6.2.3 Noise

Noise can be considered as an environmental nuisance. Noise level control should be made periodically to make sure that all regulation is respected. See EIGA Doc 85, *Noise Management* [3]. Typical sources of noise are:

- compressors of carbon dioxide and ammonia,
- trucks, fork lift trucks (FLTs) and pumps,
- activation of a safety relief device.

4.6.3 Drying

This operation is done by condensing the majority of the remaining water in a battery of two drums successively in operation or regeneration.

A moisture analyser constantly monitors the water contained in the exit gas and automatically controls the inversion of the drums. The drier material is regenerated by heat generated by the gas vaporized by the heat entry in the storage tanks. In this process some impurities are also removed depending on the absorbent material, normally some kind of alumina gel.

4.6.3.1 Alumina gel

The used alumina gel should be checked for oil and impurities contamination. Uncontaminated gel can be disposed as non-hazardous waste.

4.6.4 Purification

The gas has to be cleaned from the impurities it contains, if necessary, using a water scrubber, carbon beds, desulphurisation process, heavy hydrocarbon removal (catox), etc.

At this stage a particular analysis must be made for the different products involved depending on the kind of impurities from the carbon dioxide. These are related to the sources for the raw gas, see EIGA Doc 70, *Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification* [4]:

- The typical process to remove sulphur oxides consists in passing the carbon dioxide stream through a washing tower with a solution of soda ash in water.
- To remove hydrogen sulphide there are different systems based on the type of removal:
  - with activated carbon, a twin carbon bed is used. One of these is working adsorbing this impurity while the other one is under regeneration with steam, or
  - other processes using the reaction of the hydrogen sulphide with different products such as ZnO or iron oxide. Typically in this process when the reagent is consumed it has to be replaced for a new one.

4.6.4.1 Activated carbon

Contaminated material should be removed from site for disposal by an authorised contractor.

4.6.4.2 Zinc oxide

This is converted over time to zinc sulphides and is taken off site by a certified waste disposal company for recycling or disposal.

4.6.5 Liquefaction and distillation

Once the carbon dioxide has been dried it is liquefied into a condenser. carbon dioxide contains volatile impurities that have to be distilled.

A final step of purification starts in a special rectification column. The column has a reboiler where impure liquid carbon dioxide falls on two coils that heat it vaporizing most of the incondensable parts of the carbon dioxide. The upward gases mixture enriches the *impure* liquid carbon dioxide falling from the top of the stripping column.

The upper part is a vent condenser shell and tubes where part of the carbon dioxide vaporised in the reboiler is recondensed to reduce product losses. Liquid NH_3 is injected into the shell to condense the gases using dry gaseous carbon dioxide leaving the dryers on the tube side of the condenser. On the other side of the reboiler another coil sub cools the liquid NH_3.

4.6.5.1 Air emissions

Emissions of a mixture of carbon dioxide are sent to the atmosphere, these are minimised by optimising the process efficiency.

4.6.6 Liquid carbon dioxide storage

Once the product is distilled and purified from volatile impurities, it is sent to the liquid carbon dioxide storage tanks after being sub-cooled to minimize the storage losses.

The pressures are between 10 to 25 bar; the temperature is between –40 ºC to –20 ºC requiring the storage tanks to be insulated. This minimises the heat losses.

4.6.6.1 Insulation material

Insulation material containing asbestos must be identified. When removing this material precautions and control have to be taken. Material shall be disposed of as hazardous waste by a certified waste disposal company and in such a way to prevent release of asbestos fibres. The disposal operations have to be tracked in details and removal must be carried out by authorised, trained subcontractor in compliance with local regulations.

4.6.6.2 Air emissions

Adequate maintenance of the tanks will lower the emissions of carbon dioxide to the atmosphere. Anti-tow away system and special devices to protect against major release of carbon dioxide to atmosphere are also considered.

Typically non-cryogenic tanks need a refrigeration unit to maintain the temperature into the stipulated ratio. The system could leak and the refrigerant gases escape to the atmosphere. Adequate maintenance and control is needed. Advice on good environmental management practice of chlorinated hydrocarbons systems is found in the EIGA Doc 88, *Good Environmental Management Practices for the Industrial Gas Industry* [5].

4.6.7 Ammonia or chlorinated hydrocarbons (HFC or HCFC) refrigeration unit

A closed refrigeration cycle brings the cooling requirements for the different steps of purification up to the sub cooling of carbon dioxide.

4.6.7.1 Air emissions

Accidental or fugitive releases or leaks of refrigerant could occur. They should be minimised with adequate maintenance and using purging systems designed to minimise refrigerant releases. The installation should allow for the maximum refrigerant recovery possible during maintenance through receivers, using isolation valves.

The risk of ammonia leakage is moderated by a water deluge system. Should the system be used; the contaminated water must be treated before entering the drainage system.

4.6.7.2 Oil

Oil concentrates in the evaporation process and needs to be purged periodically. Oil needs to be treated by a certified waste disposal company.

4.7 Dry ice production

Liquid carbon dioxide is supplied from road tankers, rail tankers, or directly from the carbon dioxide production plant into the storage tanks. The usual working pressure is 15 bar gauge (barg).

The liquid carbon dioxide is injected into appropriate presses with snowing towers or chambers and expanded to approximately 1 barg. Approximately 50% carbon dioxide—snow and 50% cold carbon dioxide—gas (–79 °C) is generated.

The carbon dioxide—snow is pressed hydraulically into blocks, pellets, or slices. Sawing up blocks produces slices of special sizes. Despatch, packed or unpacked, is done in special insulated containers. The environmental impact in this process is the air emissions (linked to the production of 50% cold carbon dioxide—gas), the noise and the solid waste from packing.

More information about dry ice production and the supply chain, see EIGA Doc 150, *Guidelines for Safe and Hygienic Handling of Dry Ice* [6].

4.7.1 Air emissions

Liquid carbon dioxide allowed to expand to atmospheric pressure converts to gas and solid (snow). When this occurs in a cool, closed chamber, the snow represents 40% of the liquid and can be compacted to dry ice. Wherever possible, the gas called reverted or flash gas is drawn off for compression and liquefaction.

Smaller dry ice plants are not usually equipped for the recovery of carbon dioxide gas. Nevertheless, the gas industry should have a policy to reduce carbon dioxide emissions from the dry ice production units as part of their commitment to climate change.

The necessary refrigeration is obtained by a closed loop refrigeration system using a refrigerant gas. See 4.6.7 to get a description of the environmental impacts.

4.7.2 Water emissions

For larger production plants where recovery is required, the cold gas is compressed by means of compressors, condensed in the carbon dioxide—liquefier, and then recycled into the dry ice process. Leaks of oil and water-oil mixtures are the main risk, see 4.6.2.1.

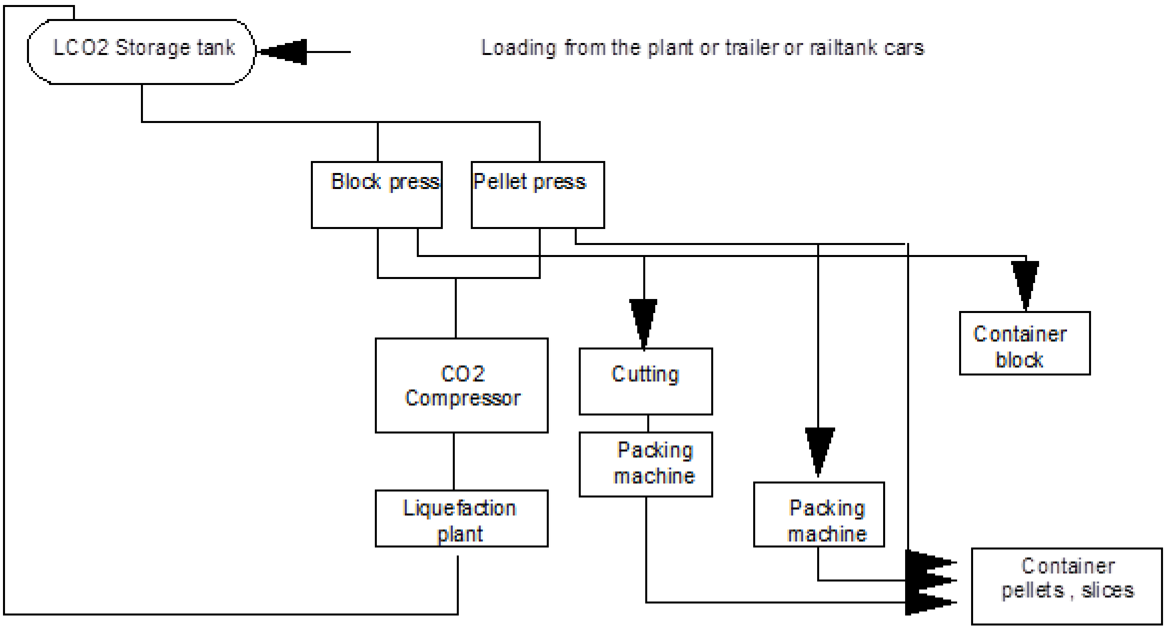


Figure 1—Block diagram dry ice production

4.7.3 Noise

Noise can be considered as an environmental nuisance. Noise level control should be made periodically to make sure that all regulation is respected. See EIGA Doc 85, *Noise Management* [3]. Typical sources of noise are:

- dry ice machine,
- trucks, fork lift trucks (FLTs) and pumps,
- activation of a safety relief device.

5 References

Unless otherwise specified, the latest edition shall apply.

[1] EC Directive 2010/75/EU, *industrial emissions (integrated pollution prevention and control)* http://eur-lex.europa.eu

[2] ISO 14001 *Environmental Management System* www.iso.org

[3] EIGA Doc 85*, Noise Management* www.eiga.eu

[4] EIGA Doc 70, *Carbon Dioxide Food and Beverages Grade, Source Qualification, Quality Standards and Verification* www.eiga.eu

[5] EIGA Doc 88, *Good Environmental Management Practices for the Industrial Gas Industry* www.eiga.eu

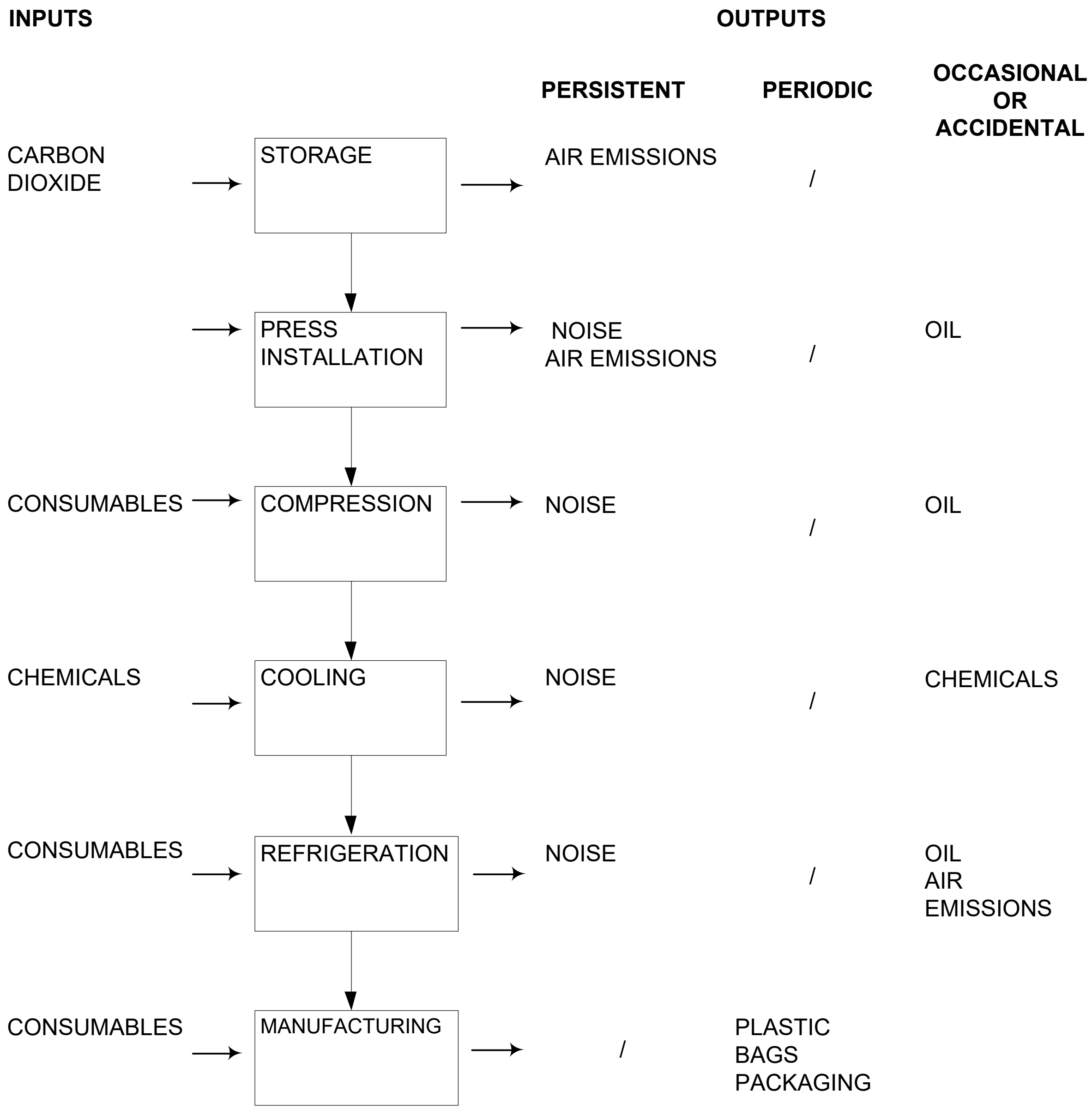
[6] EIGA Doc 150*, Guidelines for Safe and Hygienic Handling of Dry Ice* www.eiga.eu

[7] EIGA TP18, *Carbon Dioxide Plants Environmental Issues* www.eiga.eu

Appendix A—Environmental impacts of carbon dioxide production (Informative)

INPUTS	PROCESS	OUTPUTS: PERSISTENT	OUTPUTS: PERIODIC	OUTPUTS: OCCASIONAL OR ACCIDENTAL
RAW GAS CONSUMABLES ENERGY	BLOWERS	NOISE	/	OIL
CONSUMABLES ENERGY	COMPRESSORS	NOISE	/	OIL
CONSUMABLES CHEMICALS WATER	SCRUBBERS	NOISE COOLING WATER	/	CHEMICALS
CONSUMABLES ENERGY	DRYERS	/	/	CHEMICALS
CONSUMABLES	ABSORBERS	/	NOISE	ABSORBENT
CONSUMABLES	PURIFICATION	CHEMICALS	/	PRODUCT
CONSUMABLES CHEMICALS REFRIGERANT	REFRIGERATION	/	NOISE AIR EMISSIONS	CHEMICALS ABSORBENT
CONSUMABLE	STORAGE AND DISTRIBUTION	AIR EMISSIONS NOISE	/	REFRIGERANT OIL INSULATION

Appendix B—Environmental impacts of dry ice production (Informative)



Appendix C—EIGA Document links to ISO 14001 (Informative)

Table C—EIGA Document links to ISO 14001

Doc No	Title of EIGA Document	ISO 14001 SECTIONS	Clause
107	Guidelines on Environmental Management Systems [1)]	Context of the organization	4
		Understanding the organization and its context	4.1
		Understanding the needs and expectations of interested parties	4.2
		Determining the scope of the environmental management	4.3
		Environmental management system	4.4
		Leadership	5
		Leadership and commitment	5.1
		Policy	5.2
		Organization roles, responsibilities and authorities	5.3
		Planning	6
		Actions to address risks and opportunities	6.1
		General	6.1.1
106	Environmental Issues Guide [1)]	Environmental aspects	6.1.2
108	Environmental Legislation Applicable to Industrial Gases Operations within the EU [1)]	Legal requirements and voluntary obligations	6.1.3
		Environmental objectives and planning to achieve them	6.2
		Environmental objectives	6.2.1
		Environmental improvement programmes	6.2.2
		Support	7
		Resources	7.1
		Competence	7.2
		Awareness	7.3
		Communication	7.4
		General	7.4.1
		Internal communication	7..4.2
		External communication and reporting	7.4.3
		Documented information	7.5

Doc No	Title of EIGA Document	ISO 14001 SECTIONS	Clause
		General	7.5.1
		Creating and updating	7.5.2
		Control of documented information	7.5.3
88	Good Environmental Management Practices for the Industrial Gas Industry [1 and 2)]	Operation	8
30	Disposal of Gases		
85	Noise Management [1)]		
109	Environmental Impacts of Acetylene Plants		
84	Calculation of Air Emissions from Acetylene Plants		
05	Guidelines for the Management of Waste Acetylene Cylinders		
166	Guidelines on Management of Waste Gas Cylinders		
94	Environmental Impacts of Air Separation Units		
110	Environmental Impacts of Cylinder Filling Plants	Operational planning and control	8.1
117	Environmental Impacts of Customer Installations		
101	The Carbon Dioxide Industry and the Environment		
106	Environmental Issues Guide		
111	Environmental Impacts of Carbon Dioxide and Dry Ice Production [2)]		
122	Environ. Impacts of Hydrogen Plants		
112	Environ. Impacts of Nitrous Oxide Plants		
113	Environmental Impacts of Transportation of Gases		
137	Environmental Aspects of Decommissioning		
		Value chain planning and control	8.2
		Emergency preparedness and response	8.3
		Performance evaluation	9
		Monitoring, measurement, analysis and evaluation	9.1

Doc No	Title of EIGA Document	ISO 14001 SECTIONS	Clause
		General	9.1.1
		Evaluation of compliance	9.1.2
135	Environmental Auditing Guide [1)]	Internal audit	9.2
		Management review	9.3
		Improvement	10
		Nonconformity and corrective action	10.1
		Continual improvement	10.2
NOTES 1 Specific document relevant to CO_2 and dry ice. 2 General document useful to CO_2 and dry ice.			

NOTE There is an EIGA training package TP18, *Carbon Dioxide Plants Environmental Issues* [7].