ENVIRONMENTAL IMPACTS OF CARBON DIOXIDE AND DRY ICE PRODUCTION

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1 Introduction

This document details the environmental impacts of Carbon dioxide and dry ice plants and gives guidelines on how to reduce the impacts.

2 Scope and purpose

2.1 Scope

The document concentrates on the environmental impacts of Carbon dioxide and dry ice plant. This document 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 documents, and or national legislation should be consulted for advice.

2.2 Purpose

This document is intended to serve as a guide for Carbon dioxide and dry ice plants to assist in putting in place a formal environmental managment 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 (EC Directive (2008/1/EC) Integrated Pollution Prevention and Control). This covers Carbon dioxide and dry ice plants production in section 4.2 a) Manufacture of basic inorganic chemicals.

3 Definitions

3.1 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 Environmental Impact

Any change to the environment, whether adverse or beneficial, wholly or partially resulting from an organization’s environmental aspects. [Source: ISO 14001:2004]. For example: the contamination of water with hazardous substances or the reduction of air emissions.

4 Carbon Dioxide and Dry Ice Production Environmental Impacts

4.1 General Environmental Aspects and Impacts and links to other EIGA documents

This document covers the environmental impact of Carbon Dioxide and Dry Ice Production units. At the end of the document, all these environmental impacts are summarised in Appendix 2 and 3. 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 environmental management systems standard is provided in Appendix1. Appendix 1 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 document describes only the process to obtain pure and liquefied Carbon Dioxide from raw gas. There are many different alternatives, depending on the raw gas, for the 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 gasses 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.

Carbon Dioxide is also released in other biological processes, such as bacterial degradation in waste dumps and sewage treatment plants.

4.2.1.3 Natural sources

Geological activity over hundreds of millennia has created of 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, Asia. The CO_2 is recovered as saturated gas or 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, are deciding 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

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 (CO_2) 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.

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 according to the production process step by step.

4.4 Design, Planning and Control

The basic philosophy is the minimization of wastes of any kind and their safe and clean disposal. By considering the potential wastes 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 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

Sources with a rich Carbon Dioxide purity over 95% the installation will include only the Basic Plant (see below).

When the source gas purity contains less than 50% of Carbon Dioxide, and has also some impurities, a first concentration of the raw gas is necessary before the basic unit and it is also necessary to include the different equipment to remove the mentioned impurities.

The process is as follows:

CONCENTRATION
- Cooling and water scrubbing.
- Absorption and Desorption system.
- Cooling and water separation.

BASIC PLANT
- Compression.
- Drying.
- Purification.
- Liquefaction and Distillation.
- Storage.

4.5 Concentration

The concentration process typically consist in an absorption system most of the times using any type of amines (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 that became 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 there is a reboiler to further heat the amine at about 120ºC to desorb 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 condensable 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 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 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 mean of an external NH_3 or chlorinated hydrocarbons unit and the incondensables 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 liquefy economically the purified gaseous Carbon Dioxide, typically between 16 bar and 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. A contractor should treat the Oil waste.

Improving maintenance of the compressors and also a better design can reduce these waste sources. Precautions must be taken to prevent oil from entering the drainage system. Oil never is 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 equipments of the installation (generally the receiver). For immediate action, appropriate absorbents should be storage 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 also contains solid particles and dust that affect at OBD, OQD.

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 (e.g. the provision of an interceptor). In accordance with National Regulations a permit or consent may be necessary. 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 IGC Doc 85 Noise Management for the Industrial Gases Industry Typical sources of noise are:

- Compressors of Carbon Dioxide and Ammonia
- Trucks and loading pumps

4.6.3 Drying

This operation is done, condensing the major part of remaining water in a battery of two drums successively in operation or regeneration.

A moisture analyser constantly monitoring the water contained in the exit gas controls the inversion of the drums automatically. The gas vaporized by the heat entries into the storage tanks normally does the regeneration; it is heated in the first part of the cycle. In this process also some impurities are removed depending of the absorbent, 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 IGC Document 70 Carbon Dioxide Source Certification, Quality Standards and Verification.

- The typical process to remove sulfur 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 basically in the type of removal.
  - With activated carbon, a twin carbon bed is used in which one of these is working adsorbing this impurity while the other one is under regeneration with steam.
  - Other processes use 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 an authorised contractor 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 incondensables part of the CO_2. 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 reducing in this way the product losses. Liquid NH_3 is injected into the shell to condensate the gases. For cooling the dry Gaseous CO_2 leaving the dryers coil in the reboiler shell approximates the gas to its condensing temperature. 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 –40ºC to –20ºC 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 by a certified waste contractor and in such a way to prevent release of asbestos fibres. The disposal operations have to be tracked in details.

4.6.6.2 Air Emissions

The 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 the EIGA IGC Doc 88 Good Environmental Management Practices for the Industrial Gas Industry.

4.6.7 Ammonia or Chlorinated hydrocarbons (HFC or HCFC) Refrigeration Unit

A close 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

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

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

4.6.7.2 Oil

Oil concentrates in the evaporation process and need to be purged periodically. A contractor will treat the oil.

4.7 Dry Ice Production

Liquid Carbon Dioxide is supplied from road tankers, rail tankers, or directly from the CO_2-production plant into the storage tanks. The usual working pressure is 15 bar g.

The liquid Carbon Dioxide is injected into appropriate presses with snowing towers or chambers and expanded to approx. 1 bar g. Approximately 50 % CO_2-snow and 50 % cold CO_2-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 CO2-gas), the noise and the solid waste from packing.

More information about dry ice production and supply chain can be found in EIGA IGC Doc 150 Code of Practice Dry Ice.

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 drawn off for compression and liquefaction.

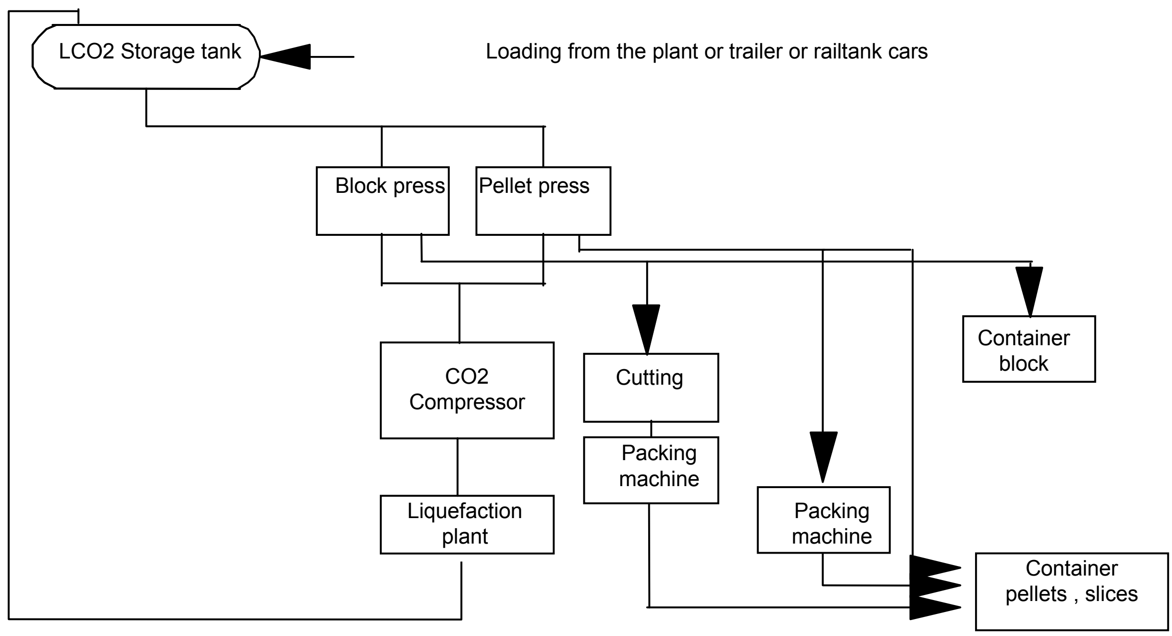
Smaller dry ice plants are usually not equipped of recovery of the Carbon Dioxide gas. Nevertheless, gas industry should have a policy to reduce CO2 emissions from the dry ice production units as part of their commitment to climate change.

The necessary refrigeration is obtained by a closed loop refrigeration system using a refrigerant gas. See point 4.4.7 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 CO_2-liquefier, and then recycled into the dry ice process. Leaks of Oil and Water-Oil mixtures are the main risk. See point 4.4.2.

Fig. 1 - Block diagram Dry Ice Production



APPENDIX 1 EIGA DOCUMENT LINKS TO ISO 14001

Doc No	Title of EIGA IGC document	ISO 14001 (2004) SECTIONS	Clause
107	*Guidelines on Environmental Management Systems*	*General Requirements*	*4.1*
		Environmental Policy	*4.2*
		Planning	*4.3*
		Objectives, targets and programme(s)	*4.3.3*
		Implementation and operation	*4.4*
		Resources, roles, responsibility	*4.4.1*
		Competence, Training and awareness	*4.4.2*
		Communication	*4.4.3*
		Documentation	*4.4.4*
		Control of documents	*4.4.5*
		Emergency Preparedness and response	*4.4.7*
		Checking	*4.5*
		Monitoring and measurement	*4.5.1*
		Evaluation and compliance	*4.5.2*
		Non-conformity, corrective preventive action	*4.5.3*
		Control of records	*4.5.4*
		Management review	*4.6*
106	*Environmental Issues Guide*	*Environmental aspects*	*4.3.1*
108	*Environmental Legislation guide*	*Legal and other requirements*	*4.3.2*
30	Disposal of Gases	Operational control	4.4.6
85	*Noise Management for the industrial gas industry*	*Operational control*	*4.4.6*
88	***Good Environmental Management Practices for the industrial gas industry***	***Operational control***	***4.4.6***
109	Environmental Impacts of Acetylene plants	Operational control	4.4.6
84	Calculation of Air Emissions from Acetylene Plants	Operational control	4.4.6
05	Guidelines for the management of waste acetylene cylinders	Operational control	4.4.6
94	Environmental Impacts of Air Separation Units	Operational control	4.4.6
110	Environmental Impacts of Cylinder Filling Plants	Operational control	4.4.6
117	Environmental Impacts of Customer Installations	Operational control	4.4.6
111	**Environmental Impacts of Carbon Dioxide and Dry Ice Production**	**Operational control**	**4.4.6**
122	Environ. Impacts of Hydrogen Plants	Operational control	4.4.6
112	Environ. Impacts of Nitrous Oxide Plants	Operational control	4.4.6
113	Environmental Impacts of Transportation of Gases	Operational control	4.4.6
137	*Decommissioning*	*Operational control*	*4.4.6*
135	*Environmental auditing guide*	*Internal Audit*	*4.5.3*

What Documents are relevant to me? For Carbon dioxide and dry ice plants the relevant documents specific documents are highlighted in bold, and useful general document in italics. There is an EIGA Training Package on Environmental Impact of Carbon Dioxide Plants. TP18. All EIGA documents are obtainable from the website.

APPENDIX 2 Environmental Impacts of CARBON DIOXIDE PRODUCTION

INPUTS				OUTPUTS
RAW GAS CONSUMABLES ENERGY	→	BLOWERS	→	NOISE ● OIL ■
		↓		
CONSUMABLES ENERGY	→	COMPRESSORS	→	NOISE ● OIL ■
		↓		
CONSUMABLES CHEMICALS WATER	→	SCRUBBERS	→	CHEMICALS ■ NOISE ● COOLING WATER ●
		↓		
CONSUMABLES ENERGY	→	DRYERS	→	CHEMICALS ■
		↓		
CONSUMABLES		ADSORBERS		NOISE ∆ ABSORBENT ■
CONSUMABLES		PURIFICATION	→	PRODUCT ■ CHEMICALS ●
		↓		
CONSUMABLES CHEMICALS REFRIGERANT	→	REFRIGERATION	→	CHEMICALS ■ NOISE ∆ ABSORBENT ■ AIR EMISSIONS ∆
		↓		
CONSUMABLE		STORAGE AND DISTRIBUTION	→	AIR EMISSIONS ● NOISE ● REFRIGERANT ■ OIL ■ INSULATION ■

_PERSISTENT ●
PERIODIC ∆
OCCASIONAL OR ACCIDENTAL ■

APPENDIX 3 Environmental Impacts of DRY ICE PRODUCTION

INPUTS		OUTPUTS
CARBON DIOXIDE →	STORAGE	→ AIR EMISSIONS ●
	↓ PRESS INSTALLATION	NOISE ● OIL ■ AIR EMISSIONS ●
CONSUMABLES →	↓ COMPRESSION	→ NOISE ● OIL ■
CHEMICALS →	↓ COOLING	→ CHEMICALS ■ NOISE ●
CONSUMABLES →	↓ REFRIGERATION	→ NOISE ● OIL ■ AIR EMISSIONS ■
CONSUMABLES →	↓ MANUFACTURING	→ PLASTIC BAGS Δ PACKAGING Δ

PERSISTENT ●
PERIODIC Δ
OCCASIONAL OR ACCIDENTAL ■