ENVIRONMENTAL IMPACTS OF ACETYLENE PLANTS

Doc 109/21

Revision of Doc 109/14

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL

AVENUE DE L'ASTRONOMIE 30 • B – 1210 BRUSSELS
Tel: +32 2 217 70 98
E-mail: info@eiga.eu • Internet: www.eiga.eu

Doc 109/21

ENVIRONMENTAL IMPACTS OF ACETYLENE PLANTS

Prepared by WG-5 Environment

Disclaimer

EUROPEAN INDUSTRIAL GASES ASSOCIATION AISBL
Avenue de l'Astronomie 30 B 1210 Brussels Tel +32 2 217 70 98
E-mail: info@eiga.eu Internet: www.eiga.eu

Table of Contents

Amendments to 109/14

Section	Change
	Editorial to align style with EIGA Style Manual
	Update to current legislation
4.4.1	Added note on open generators
4.6	Removed chromic acid

NOTE Technical changes from the previous edition are underlined

1 Introduction

This publication details the environmental impacts of the management of acetylene plants and gives guidelines on how to reduce those impacts.

2 Scope and purpose

2.1 Scope

The publication concentrates on the environmental impacts of acetylene plants. This publication does not give specific advice on health and safety issues. On these issues, the relevant EIGA publications and / or national legislation should be consulted for advice and they shall be taken into account before undertaking any activity.

2.2 Purpose

This publication is intended to serve as a guide for acetylene plant operations to assist in putting in place a formal environmental management system that can be certified by an accredited third-party verifier. It aims to provide a guide for operations managers to identify and reduce 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 (IED) 2010/75/EU *on industrial emissions (integrated pollution prevention and control)* [1]. [1] This covers acetylene production in Annex I Section 4.1a, Production of organic chemicals, simple hydrocarbons and in the Common Waste Gas Treatment in the Chemical Sector (WGC).

3 Definitions

For the purpose of this publication, the following definitions apply.

3.1 Publication 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

Indicates 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

Elements of an organisation's activities, 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 organisation's environmental aspects as per ISO 14001 *Environmental Management Systems – Guidance with Requirements for Use* [2]. For example, the contamination of water with hazardous substances, or the reduction of air emissions.

4 Acetylene plants environmental impacts

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

This publication covers the environmental impact of acetylene plants which are summarised in Appendix 2.

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 publications and their links to ISO 14001 is provided in Appendix 1 [2]. Appendix 1 also shows which of these documents are relevant to acetylene plant operations.

4.2 Introduction

The basic philosophy is the minimisation of wastes, emissions and nuisances of any kind and their safe and clean disposal. By considering the potential wastes which a new process could generate when engineering a plant, future problems can be avoided. This analysis is a crucial element of environmental impact assessment and is strongly recommended before any decision on industrial plant investment.

Wastes should not be mixed but should be collected separately to aid further recycling, reuse or recovery.

Safety data sheets for all chemical substances shall be held on site and used to determine the best way to handle the chemical substances.

Acetylene is produced by two different methods:

- reaction of calcium carbide with water in special generators, and
- as a gaseous by-product from cracking crude oils.

The main method of production for the gas industry is by the first method. This is due to the lack of availability of the by-product material where the acetylene is required and the economics of production. The second method is generally used for production of acetylene as a chemical intermediate.

Consequently, this publication describes only the first process mentioned, i.e. the exothermic reaction between calcium carbide and water:

$$CaC_2 + H_2O \rightarrow C_2H_2 + Ca(OH)_2 + Heat$$

Hydrated lime, $Ca(OH)_2$, is also produced as a by-product. After separating from the carbide lime, excess water can be reused in the process and the lime can be recovered for use in various industrial or agricultural activities in accordance with applicable local legislation.

Due to the fact that technical grade CaC_2 contains various impurities in the raw products used in its manufacture, acetylene also contains impurities such as ammonia and phosphine.

The generated acetylene is purified, compressed, dried and filled into gas cylinders that are stored on site prior to distribution.

The main environmental impacts from acetylene plants are described below, following step by step the production process. A simplified drawing in Appendix 3 illustrates the acetylene production process. Technical details on acetylene production are described in EIGA Doc 123, *Code of Practice – Acetylene* [3].

4.3 Raw material storage

4.3.1 Calcium carbide

4.3.1.1 Calcium carbide containers

Calcium carbide is transported and stored in weatherproofed containers (drums, bags or returnable bins) to keep the carbide dry and prevent the conversion of calcium carbide to acetylene.

Where these containers are reused, they need to be regularly inspected to ensure they are in good condition in line with good practice or national regulations. They shall be stored in the correct location to prevent corrosion or damage.

Even when containers have been mechanically emptied, they contain carbide residuals (dust). Calcium carbide dust will generate acetylene when in contact with moisture.

Where containers are reused, the small amounts of residual carbide are a potential safety and environmental hazard.

If a calcium carbide container is disposed, it should be clearly marked and segregated and the following procedure should be adopted.

One acceptable method to remove the dust from the container is to wash it out with sufficient water and to leave the container open for some days to vent with air. This water shall be disposed of into the lime pit. Before the container is sent for disposal, it should be checked to ensure that no acetylene is left in it. The container may then be reused or recycled as scrap metal.

4.3.1.2 Calcium carbide drums

Drums that have been emptied should be stored without their tops for at least 24 hours in a designated area either outside or under cover or roof.

Returnable drums and barrels should preferably be sent back without the tops refitted. If, however, the top is replaced, great care is required to ensure that no acetylene is present or can be generated.

Non-returnable drums will have a scrap value and should be recycled as scrap metals.

4.3.2 Chemicals

4.3.2.1 Purifier materials

Sulphuric acid and sodium hydroxide shall be stored in dedicated containers on an impervious surface with secondary containment. Dry purifiers contain ferric / ferrous chloride and traces of mercury. The spent chemicals require disposing of by an approved contractor.

4.3.2.2 Solvents

Acetone or Dimethylformamide (DMF) shall be stored in above ground or underground double-jacketed storage tanks that are regularly inspected and maintained by qualified personnel.

4.3.2.3 Storage tanks

Storage tanks should be designed to be fit for purpose to the appropriate national or international standard and shall be regularly inspected and maintained by competent personnel.

When filling a tank, the operator shall attend the filling at all times. By installing overfill alarms, the risk of major spills can be further reduced. Minor spills can occur when filling or emptying the tank, precautions such as using spill plates over drains should be taken to avoid any environmental damage.

4.3.2.4 Underground storage tanks

Underground storage tanks should be avoided on new facilities, more details can be found in the EIGA Doc 106, *Environmental Issues Guide* [4].

4.3.2.5 Above ground storage tanks

Above ground storage tanks also risk contamination of soil and water if the tank starts to leak, although the control of tank leakage is less complicated than for underground tanks. Even a dripping valve could easily contaminate several cubic meters of soil. Spill plates should be used.

Large storage tanks are frequently used for fuel, while the smaller ones may contain oil, antifreeze and other substances. It is important to avoid spills and to label the tanks regardless of the size. Secondary containment shall be provided with a means of separating rainwater.

4.4 Acetylene generator

4.4.1 General

The procedure for charging the generator depends upon the type of system and shall be laid down in specific working manuals and instructions. Two types of generators exist:

- the ‘open’ generator, where acetylene escapes from the generator during carbide charging; or
- the ‘closed’ generator, where the charging system is sealed.

The open generator causes more emissions of acetylene and other gases (see 4.13).

NOTE Open generators are no longer installed for new systems but may still be in use in older plants.

Operating details are laid down in both the design documentation and the operation manuals, such as:

- working pressure
- temperature range
- carbide charging capacity, and
- maximum production rate.

For further information see EIGA Doc 123 [3].

All generator systems contain an interceptor that is generally fitted between generator and gasholder. It consists of a small tank containing water through which acetylene is bubbled. It is used as a hydraulic non-return valve, as well as a device to prevent a flame travelling back from the gasholder to the generator.

4.4.2 Calcium carbide residuals

Calcium carbide residuals normally contain non-reactive materials, for example stones, iron, ferrosilicon, coke, etc which are infused with lime. Carbide should be purchased in consistent quality to reduce impurities. Difficulties in disposal of calcium carbide residuals arise from the lime. Due to the alkaline properties of lime, it may not be possible to dispose of calcium carbide residuals on normal landfills without special treatment. This is due to the very high pH values and conductivity of the residual water mixture.

To dispose of calcium carbide residuals in landfill, permission from the competent authority may be necessary. Alternatively, the material can be used for road and parking place construction by mixing it into the concrete and thus encouraging recycling.

4.4.3 Lime

Lime storage and loading areas shall be watertight (basins, tanks, silos etc.) to avoid soil and groundwater contamination. Additionally, they shall be open to the atmosphere to avoid the hazard of generation of explosive air / acetylene mixtures.

Using a filter press or a centrifuge to remove excess water can reduce the volume of lime, which makes transport easier and more economical.

Examples of uses include:

- industries where spent acids and waters with low pH value need to be neutralised (lime is an excellent neutraliser);
- sewage water treatment;
- flue-gas purification;
- use as corrector of pH-value of soil (agriculture);
- building trade (mortar processing); or
- chemical processes.

Sulphuric acid from the acetylene purification may be neutralised in the lime pits under certain conditions (see 4.6.2). In this case the content of calcium-sulphate shall not exceed approximately 2% SO_4 in solid $Ca(OH)_2$.

If the concentration is greater than 2%, the lime cannot be used in sewage water treatment and the construction industry. If this activity is to be carried out specific authorisation is required in the site regulatory permit for this activity.

Lime slurry should be considered as a by-product and not as a waste because it is possible to market it for different uses (see EIGA Doc 143, *Guide to Lime Applications* and ASTM Special Technical Publication STP 931, *Lime for Environmental Use*) [5, 6]. Regular analysis should be carried out to promote lime as a product.

Lime can be classified as a by-product and not a waste provided if it meets the tests in EU Commission guidance COM 2007/59 *on the Interpretative Communication on waste and by-products*, for example when [7]:

- the intention is not to discard the lime from the process but to market it where the lime is produced to a specification and has a safety data sheet according to product legislation (registered or pre-registered under REACH); or

- Lime can be used directly without further processing, which should mean it is not classified as waste if it has a certain beneficial application.

In the unlikely event that there is no available use for the lime, it shall be disposed of as waste according to Commission Decision 2000/532/EC *establishing a list of wastes*, (waste number 06 02 01 for $Ca(OH)_2$) [8]. Permission from competent authorities is required.

Lime slurry contains small quantities of dissolved acetylene, which can be released if vacuum pumping systems are used to load road tankers. This requires careful consideration.

4.4.4 Generator waste

Water that is used in the acetylene generator (excluding the water that remains with the lime) should be re-circulated after separation from lime. Rainwater can also be used as generator water after having been properly filtered and checked.

The lime water shall not be drained uncontrolled into the sewage water system or ground water. Releasing limewater into the drainage or public sewage water system will cause problems due to its high pH-value.

Before draining the water, the local sewage water authorities shall be asked for permission and a method (depending on the sewage water composition) shall be agreed. This water can also contain ammonia, which is highly toxic to fish, so it also shall not be discharged directly to rivers.

4.4.5 Generator cleaning residuals

The generator may be cleaned mechanically or by using acids. Solid residuals of mechanical cleaning consist of slaked lime and can may be disposed of in the lime pits. If acids are used for cleaning, the spent mixture must be disposed of by an authorised waste disposal contractor or can be neutralised in the lime pits under the same circumstances as spent sulphuric acid (see sections 4.4.3 and 4.6.2).

4.5 Gas holder

Some generation systems use a gasholder. The purpose is to match the production of acetylene from the generator to the compressor demand. A gasholder usually consists of a rising bell that is immersed in water that forms a gas seal. The bell rises and falls to balance the production by controlling the calcium carbide feed to the generator.

4.5.1 Water

Gasholder water contains small amounts of acetylene and ammonia that should be taken into consideration when emptying the gasholder for maintenance or other reasons. Gasholder water should be emptied into the lime pit.

4.5.2 Oil

In some cases, oil is used as fluid in gasholders instead of or on top of water. If, due to contamination, oil cannot be reused in the gasholder it should be handled according to the recommendations in sections 4.7.1 and 4.7.2.

4.6 Purification

Acetylene contains impurities, i.e. phosphine, ammonia, hydrogen sulphide and organic sulphides. Purification involves the removal of these components by scrubbing and / or oxidation. Purification takes place in relatively narrow and tall washing towers to ensure an intensive contact between cleaning agent and gas or by passing the gas through beds of solid purification material. Sulphuric acid, sodium hydroxide and sodium carbonate are mostly in use as purification agents.

4.6.1 Sulphuric acid

Spent sulphuric acid shall never be drained into the sewage water system. Sulphuric acid should either be:

- returned back to the producer of sulphuric acid for purification and reuse;
- neutralised in the lime pits; or
- disposed of by a specialist.

When neutralising the acid with lime, the following shall be considered:

- this activity shall be included in the site regulatory permit (according the IED) [1];
- only small amounts of acid should be neutralised in large amounts of lime to avoid emissions of hydrogen-sulphide and phosphine and to prevent foaming in the generator when water from the lime pits is reused for acetylene generation; and
- the sulphuric acid must be fed into the lime such that both substances are mixed instantaneously, for example into the lime pipe between the generator and the lime pit, or underneath the surface of the lime in the pits. The neutralisation in the lime pipe, between the generators and the lime pit, is possible only when the generators are in use.

4.6.2 Sodium hydroxide and sodium carbonate

The sodium hydroxide (NaOH) and sodium carbonate (Na_2CO_3) can be diluted in the lime pits, provided this activity is included in the site regulatory permit. The concentration shall be kept low.

4.6.3 Solid purification media

Solid purification media that use ferric chloride ($FeCl_3$) and ferric oxide (Fe_2O_3) as active agents often contain catalysts such as mercuric chloride ($HgCl_2$) or cupric chloride ($CuCl_2$). These materials shall be disposed of in accordance with relevant waste regulations.

4.7 Compression

Acetylene is compressed in multistage compressors. The compression is also an important stage in the drying process because most of the water separates out. Despite acetylene being dry when leaving the sulphuric acid cleaning device, it becomes moist again after having passed the cleaning tower containing sodium hydroxide or sodium carbonate.

During compression a small quantity of acetylene emission is possible. It can be reduced by regular inspection and maintenance of the compressor equipment. Acetylene is dried by passing through vessels containing drying material such as calcium chloride, in some plants of an older design, or silica gel, alumina gel, molecular sieve or similar which can be regenerated. Maximum operating pressure is 25 bar.

4.7.1 Oil

Precautions must be taken to prevent oil from entering drainage systems:

- oil shall not be mixed with other substances if it can be avoided for example water, soil, and solvents;
- oil shall always be collected in a barrel or drum and be delivered for recycling;
- a bund (or secondary containment system / pit) on each compressor or transformer installation should be installed to collect potential leaks and purges; and

- oil drums should be stored above a catch pot.

4.7.2 Water / oil mixtures

When using water-soluble emulsifiers for cleaning purposes, the water emulsions shall be disposed of in a way acceptable to the authorities in the particular countries. Sometimes it may be possible to dispose of the emulsion by draining it into a suitable sewage water drainage system.

When no emulsifiers are used, oil and water shall be separated in special oil-water separators. Water can then be discharged into the drainage water system and the oil should be recycled, see 4.7.1.

4.8 Dryers

4.8.1 Silica gel / alumina gel

Used gel should be checked for oil contamination. Uncontaminated gel can be disposed of as non-hazardous waste. Consideration should be given to returning it to the supplier.

4.8.2 Calcium chloride

The normal way to dispose of the calcium chloride is to dilute it with the lime sludge in the lime pits, but when the lime is delivered to a water treatment plant the calcium chloride shall be diluted to a level of the chlorine ion concentration that does not adversely affect the functioning of the water treatment plant. The maximum level shall be agreed upon with the treatment plant operator.

4.8.3 Sodium hydroxide

See 4.6.3.

4.8.4 Packing materials

Packing materials (Raschig rings, Berl saddles, etc.) should be rinsed, where practicable, with suitable cleaning agent before being preferably reused or disposed of to a normal landfill. The cleaning agents should be disposed of according to their properties and in accordance with this document.

4.9 Cylinder filling

Acetylene is dissolved under pressure in cylinders, which contain porous mass and a solvent that is either acetone or DMF. During cylinder filling no significant emission of acetylene occurs. For safety reasons every cylinder is weighed after filling to ensure that it is correctly filled.

4.9.1 Cooling water

Recycling of cooling water is recommended.

As long as cooling water does not contain any impurities, it is permitted to drain it into the rainwater drainage or sewage water system in accordance with national or local regulations, for example requirements for pH value or temperature (companies in various countries require permission for this).

If cooling water is contaminated with oil or other chemicals (closed circuit cooling system) the procedure of draining the cooling water into the sewage water system shall be arranged in accordance with methods accepted by the local authorities.

Often chemicals, such as biocides, are added to prevent the development of legionella and other anti-fouling chemicals may also be added. Care shall be taken to prevent operator exposure to breathing overspray water containing these biocides, as they are hazardous to health.

Additionally, rainwater can be used for cooling water.

4.9.2 Ethanol / glycol

Cooling waters containing ethanol or glycol shall comply with local authority requirements before drainage into the sewage water system.

4.9.3 Acetylene emissions

Acetylene is an organic gas that contributes to the formation of photochemical oxidants and predicted warming of the atmosphere. It is therefore classified as a Volatile Organic Compound (VOC). Specific legal requirements on VOC emissions reporting may exist depending on the country.

Acetylene from overfilled cylinders, or from cylinders being prepared for testing, should always be discharged into a closed piping system and returned to the gasholder or compressor.

As a general principle of environmental protection and for safety reasons only very small amounts of acetylene should be allowed to escape into the atmosphere. When starting the generator, acetylene emissions to the atmosphere due to quality specifications shall be kept at the minimum.

4.9.4 Acetone from return gas

In some plants the acetone from the return gas is washed out with water in a scrubber. This water may be drained into the lime pits.

4.10 Cylinder maintenance

4.10.1 Scrap metals

It is necessary to separate different scrap metals. Steel, copper alloys and other nonferrous metals shall be separated. Scrap metals should be sent to a specialised dealer for recycling.

4.10.2 Scrap cylinders

Scrapped acetylene cylinders should be treated in accordance with the EIGA Doc 05, *Guidelines for the Management of Waste Acetylene Cylinders* [9].

4.10.3 Paint

Paint, solid or liquid, is normally considered hazardous waste and consequently it should be disposed of in accordance with national regulations.

4.10.4 Porous mass / material

Refer to the EIGA Doc 05 for dealing with porous mass [9].

4.10.5 Acetone and DMF

Refer to the EIGA Doc 05 for dealing with acetone and DMF [9]. In particular, due to the carcinogen risk of DMF, see EIGA TB10, *Requirements to inform Downstream Users about DMF being added in the Candidate List of SVHC subject to REACH Authorisation* [10]

4.11 General

Any material containing oil, oil binders and oily cloths shall be disposed of as hazardous waste in accordance with local regulations, for example burning in an incinerator plant or deposition on a licensed landfill site.

Valves, membranes, metallic packing materials, flame arrestors etc. should be handled as scrap metals.

4.12 Noise

The main sources of external noise at an acetylene site are:

- manual handling;
- use of vehicles; and
- compressors and pumps.

EIGA Doc 85, *Noise Management*, gives a comprehensive review of noise management and the actions which should be considered [11].

4.13 Air emissions

Methods for estimating the air emissions from an acetylene plant are given in EIGA Doc 84, *Calculation of Air Emissions from an Acetylene Plant* [12].

4.14 Emergency plan

See EIGA Doc 232, *Response to Operational Issues in Acetylene Plants*, [13].

5 References

Unless otherwise specified, the latest edition shall apply.

[1] Directive 2010/75/EU *on industrial emissions (integrated pollution prevention and control)*, www.europa.eu.

[2] ISO 14001, *Environmental Management Systems – Guidance with Requirements for Use*, www.iso.org.

[3] EIGA Doc 123, *Code of Practice – Acetylene*, www.eiga.eu.

[4] EIGA Doc 106, *Environmental Issues Guide*, www.eiga.eu.

[5] EIGA Doc 143, *Guide to Carbide Lime Applications*, www.eiga.eu.

[6] ASTM Special Technical Publication STP 931, *Lime for Environmental Use*, www.astm.org.

[7] EU Commission guidance COM 2007/59 *on the Interpretative Communication on waste and by-products*, www.europa.eu.

[8] Commission Decision 2000/532/EC *establishing a list of wastes*, www.europa.eu.

[9] the EIGA Doc 05, *Guidelines for the Management of Waste Acetylene Cylinders*, www.eiga.eu.

[10] EIGA TB10, *Requirements to inform Downstream Users about DMF being added in the Candidate List of SVHC subject to REACH Authorisation*, www.eiga.eu.

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

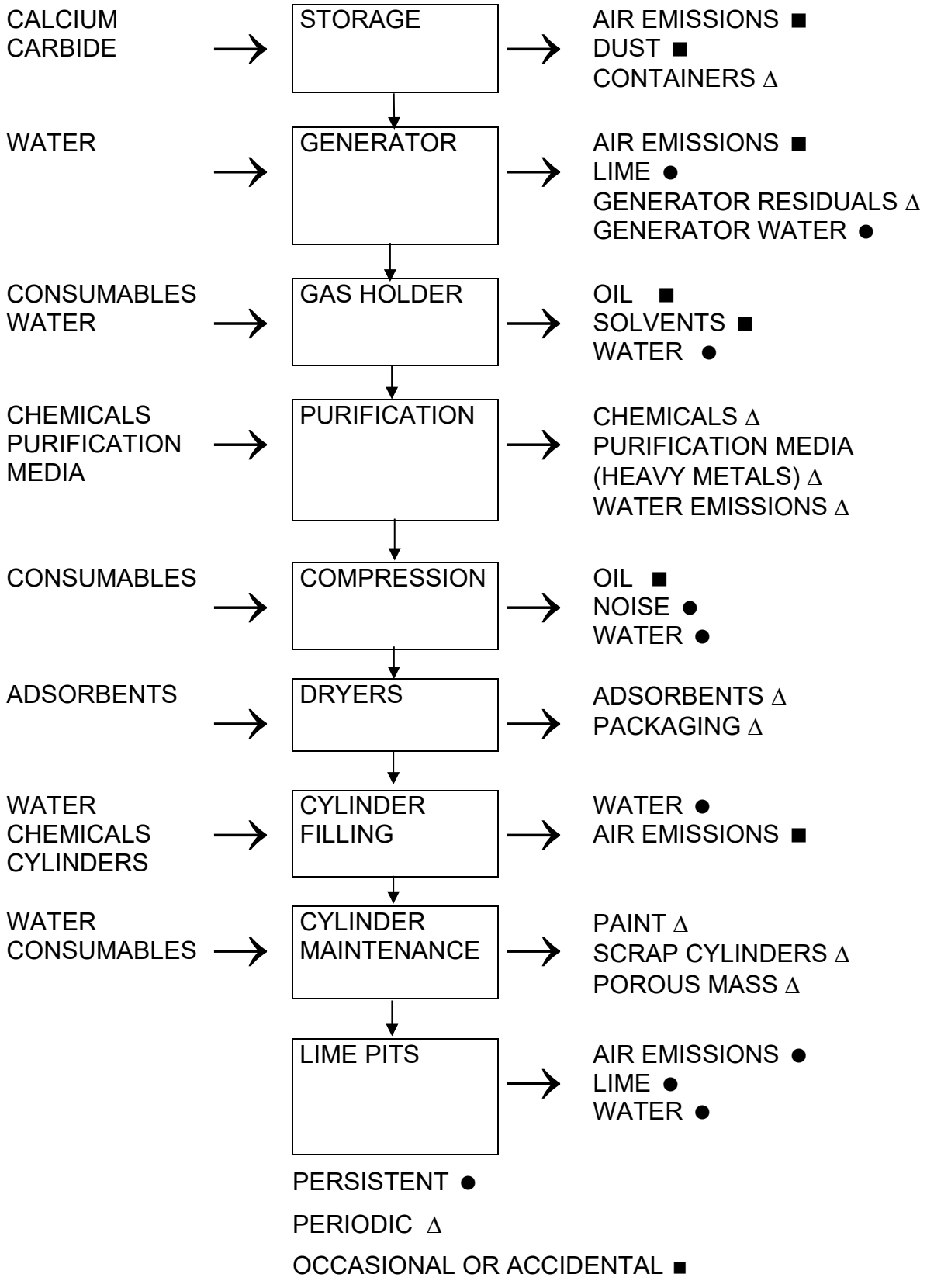
[12] EIGA Doc 84, *Calculation of Air Emissions from an Acetylene Plant*, www.eiga.eu.

[13] EIGA Doc 22X, *Emergency Response in Acetylene Plants*, www.eiga.eu.

Appendix 1 EIGA Document links to ISO 14001

EIGA Doc	Title of EIGA document	ISO 14001 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**
143	**Guide to lime applications**	**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
NOTE For Acetylene plants the relevant documents specific documents are highlighted in bold, and useful general documents in italics. There is an EIGA Training Package on Acetylene plant Environmental Issues			

Appendix 2 Acetylene plants environment impacts



Appendix 3 Simplified drawing for acetylene production process