ENVIRONMENTAL IMPACTS OF NITROUS OXIDE PLANTS

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Amendments to 112/13

Section	Change
	Editorial to align style with IHC associations
	Minor updates for terminology and references
4.5	Added monitoring of acid strength

NOTE Technical changes from the previous edition are underlined

1 Introduction

This publication details the environmental impacts of the management of nitrous oxide plants and provides guidelines on how to reduce those impacts.

2 Scope and purpose

2.1 Scope

The publication concentrates on the environmental impacts of nitrous oxide plants. This publication does not give specific advice on health and safety issues, which shall be taken into account before undertaking any activity. On these issues relevant EIGA documents (in particular EIGA Doc 175, *Safe Practices for the Production of Nitrous Oxide from Ammonium Nitrate*, and EIGA Doc 176, *Safe Practices for Storage and Handling of Nitrous Oxide*), and / or national legislation should be consulted for advice [1, 2].[1]

2.2 Purpose

This publication is intended to serve as a guide for nitrous oxide plant operations to assist in putting in place a formal environmental management system that can be certified by an accredited 3rd party verifier. It aims to provide a guide for operating 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)* [3]. The IED covers nitrous oxide production in Annex I, section 4.2 a), Manufacture of basic inorganic chemicals.

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 activities, products or services. For example, the contamination of water with hazardous substances or the reduction of air emissions.

3.2.3 Pressure

In this publication bar shall indicate gauge pressure unless otherwise noted i.e., (bar, abs) for absolute pressure and (bar, dif) for differential pressure.

4 Nitrous oxide plants – Environmental impacts

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

This publication covers the environmental impact of nitrous oxide plants. There are several linked EIGA publications that provide more details on general environmental issues, legislation for the industrial and medical gas industry and operational good environmental practices. A list of these publications and their links to ISO 14001, *Environmental Management Systems – Requirements with Guidance for Use*, is provided in Appendix 1 [4]. Appendix 1 also shows which of these publications are relevant to nitrous oxide plant operations.

In Europe, Best Available Techniques (BAT) shall be used to prevent and minimise nitrous oxide emissions. The emission of nitrous oxide from commercial production is less than 1% of total nitrous oxide emissions.

4.2 Introduction

Nitrous oxide is primarily manufactured commercially by the thermal decomposition of ammonium nitrate. Ammonium nitrate, used for nitrous oxide manufacture, is typically supplied as a liquid. To reduce the risk of explosion during transit, it is supplied at a lower concentration, for example with a maximum concentration of 93%, according to ADR, *European Agreement concerning the International Carriage of Dangerous Goods by Road* [5]. Ammonium nitrate may also be supplied in solid form in individual bags.

The manufacturing process heats the ammonium nitrate to approximately 250 °C producing nitrous oxide by an exothermic reaction. At the reactor temperature, the main reaction products are nitrous oxide and water, with the generation of impurities such as nitric oxide, nitrogen dioxide, nitrogen, oxygen, carbon monoxide, carbon dioxide, ammonia and ammonium nitrate carryover.

Typically, these impurities are stripped out of the basic bulk material by a series of scrubbing towers consisting of:

- water to remove any ammonia / ammonium nitrate carryover;
- caustic permanganate solution to remove traces of nitric oxide;
- sulphuric acid solution to remove traces of any caustic carryover; and
- alumina driers to remove moisture.

The nitrous oxide, manufactured as a gas, is then compressed above its saturated vapour pressure and stored as a liquid. One of the impurities produced by a side reaction is nitrogen, which shall be controlled for the product to meet the latest European pharmacopoeia specification. As the nitrogen is partially soluble in the liquid nitrous oxide and the solubility reduces with temperature, nitrogen is removed by storing the bulk gas at sub-zero temperatures (requiring the use of a refrigeration unit) and venting the top gas to atmosphere or by distillation or similar purge recovery systems, until the gas is at the correct purity.

The main environmental impacts from nitrous oxide plants are described according to the production process steps.

4.3 Raw material storage

4.3.1 Liquid ammonium nitrate storage

Liquid ammonium nitrate (LAN) storage has secondary containment to ensure that any product leakage is prevented from entering surface drainage. Secondary containment should be capable of holding at least 110% of the LAN capacity of the largest tank. The tanks shall be sited as close as possible to reactors to minimise potential leaks and heat loss. Any associated piping shall be insulated and steam traced to keep the LAN in solution and minimise heat loss. Storage should preferably be under cover to prevent any water penetration. Tanker discharge systems should be protected to prevent inadvertent discharge into the drainage system.

4.3.2 Solid ammonium nitrate storage

Solid ammonium nitrate, supplied in sealed bags, should be kept dry and intact to prevent any loss of product. Storage arrangements should prevent or minimise the risks of reaction with incompatible materials and the risk of fire. Ideally it should also be stored in a covered storage area, adjacent to the plant room.

4.3.3 Purification system chemical storage

All purification system chemicals should be stored in a defined covered storage area, away from any open drains. All purification chemicals shall be stored in chemically compatible containers suitable for use and with adequate protection from spillage.

4.4 Nitrous oxide reactor

To maximise the yield from the plant, whilst operating at the optimum temperature for safety reasons, the reactor temperature and level of solution shall be continuously controlled and monitored.

It is important to ensure that the specified quantity of catalyst is added to the reactor. Provided the temperature is controlled and the reactors maintained clean the reaction requires no other intervention.

In the event of a runaway reaction, the ultimate safety device is to discharge the reactor contents via a bursting disc and / or hydraulic overpressure device fitted to the reactor vent. To minimise the probability of this system operating, water quenching systems (both internal with an option for external) should be available as methods of reactor temperature control to minimise the loss of product to atmosphere.

4.5 Purification

Conventionally, passing it through a series of scrubbing towers purifies the crude nitrous oxide.

Initially a water scrubber is used to remove any ammonium nitrate carryover and any free ammonia produced in the reaction. Water quality should be monitored to ensure that any water discharged to drain is of an acceptable quality.

The gas is then scrubbed using a caustic solution of potassium permanganate, recycled through the system.

This scrubber is intended to remove any traces of nitric oxide, which could be fatal to a patient when the nitrous oxide is administered as an anaesthetic. Hence, the quality of the permanganate solution shall be monitored and disposed of as a controlled waste when changed.

The gas is then sometimes scrubbed in a dilute sulphuric acid tower, to remove any carryover of caustic solution. The strength of the acid shall be monitored and maintained according to the design. Acid shall be disposed of as a controlled waste stream.

Finally, the purified gas is scrubbed again in a water tower to remove any traces of acid carryover, with controls as per the initial water scrubber.

At the end of the purification system, the nitrous oxide should be monitored for purity and the level of specified impurities. Levels of nitric oxide should indicate the effectiveness of the purification system.

Care shall be taken when disposing of water with low ammonium nitrate content to ensure that the water discharge complies with the applicable regulations.

4.5.1 Sulphuric acid, sodium hydroxide and potassium permanganate

Spent purifier materials shall not be drained into the sewage system. Sulphuric acid should either be:

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

4.6 Compression and drying

The choice of compressor for nitrous oxide shall take into account the materials need to be oxygen compatible as it is an oxidising gas.

NOTE Water lubricated compressors are favoured as materials used in dry lubricated machines could generate poisonous gases if they were to ignite.

The quality of water used for lubrication should be checked to ensure that it meets any applicable water quality standards (for example microbiological for medical applications).

Disposal of lubrication oil for the bottom end of the machine shall be controlled. Care is required to ensure that any oil leakage is monitored and cleared immediately to prevent any loss to the drainage system.

Following compression, the nitrous oxide is dried using a desiccant such as alumina pellets. The gas quality should be monitored continuously and the desiccant regenerated using a heated dry gas. The desiccant should be disposed of as described in 4.7.1.

Having dried the gas, it should then be liquefied and transferred to the batch storage vessel. Gas is stored at ambient temperature at approximately 50 bar, or at –25 °C and approximately 15 bar. Only approved refrigerants should be used. The refrigeration unit should be regularly serviced to maintain its efficiency and to ensure that there is no loss of refrigerant to atmosphere.

Having filled the batch vessel it is necessary to monitor the gas phase purity to ensure that, when first used, the gas meets the required specification. This may be done either by venting the top gas from the vessel to atmosphere until the nitrogen content falls to an acceptable level or by passing the top gas through a re-condenser, to allow the nitrogen gas to be separated preferentially. If venting to atmosphere, care is required to operate the storage tank at a temperature as low as possible, to minimise the loss of nitrous oxide to atmosphere (nitrous oxide is a potent greenhouse gas).

4.6.1 Oil

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

- Oil shall never be mixed with other substances for example water, soil, and solvents.
- Oil shall be collected in a barrel or drum and be delivered for recycling.
- A bund (or pit) on each compressor or transformer installation should be installed to collect any potential leaks and purges.
- Oil barrels should be stored above a catch pot or basin.

4.6.2 Water-oil mixtures

When using water soluble emulsifiers for cleaning purposes, the water emulsions shall be disposed of in a way acceptable to local authorities. It may be possible to dispose of the emulsion by releasing it into a suitable sewage drainage system if permitted by local regulations.

When no emulsifiers are used, oil and water shall be separated in special oil-water separators. Water can then be discharged into the drainage system and the oil should be recycled (see 4.6.1).

4.7 Dryers

4.7.1 Silica and alumina gel

Used desiccant 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.

4.7.2 Packing materials

Packing materials (Raschig rings, Berl saddles, etc.) should be rinsed, where practicable, with a suitable cleaning agent before being reused or disposed of to landfill. The cleaning agent should be disposed of according to its properties and in accordance with local regulations.

4.8 Cylinder filling

Cylinder filling operations should take into account the oxidising properties of nitrous oxide and the risk of product exothermic decomposition at high temperature, for example heating to vaporise product, or friction.

Cylinder filling can involve transferring product from the batch storage vessel to the main storage or filling direct from the batch vessel. When transferring product, care is required to ensure that losses are kept to a minimum.

It is necessary to vent any residual nitrous oxide left in the medical nitrous oxide cylinders before they are refilled (or to carry out a full analysis of the gas to ensure that the residual gas has not been contaminated). For further information see EIGA Doc 30, *Disposal of Gases* [6]. As the product returned from the customer after use is generally of high quality (with extremely low nitrogen content), consideration should be given to recycling this product for non-medical customers. If a recycling system is used, gas from the filling system should be collected and not vented to atmosphere.

Where a recycling system is not used, a scavenging system is necessary to ensure that levels of nitrous oxide vented into areas where operators are working are maintained below recommended levels.

4.9 Cylinder maintenance

4.9.1 Scrap metals

Scrap shall be separated into different metals. Steel and other ferrous metals shall be separated from non-ferrous metals. Scrap metals should be sent to a specialised dealer for recycling. For further information see EIGA Doc 166, *Guideline on the Management of Waste Gas Cylinders* [7].

4.9.2 Paint

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

4.10 Storage of chemicals

4.10.1 Underground storage tanks

Underground storage tanks should be avoided on new facilities. More details can be found in EIGA Doc 106, *Environmental Issues Guide* [7].

4.10.2 Above ground storage tanks

Details can be found in EIGA Doc 106 [7].

4.10.3 All tanks

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

4.11 Noise

The main sources of external noise at a nitrous oxide site are:

- manual handling;
- use of vehicles; and
- compressors, pumps and refrigeration equipment.

EIGA Doc 85, *Noise Management* gives a comprehensive review of noise management and the actions that should be taken [9].

4.12 Emergency plan

Gas company employees and contractors shall be aware of the site emergency plans, trained and competent in the requirements. The emergency plan should contain:

- actions in the event of an emergency;
- actions in the event of environmental events such as major leakage of chemicals or oil;
- the location of absorption material to clean up spills on the ground;
- actions in the event of fire;
- actions to contain contaminated fire water runoff; and
- action in the event of dispersal of hazardous materials, for example asbestos.

The emergency plan should be regularly tested with drills, simulations etc.

For further information see EIGA Info HF06, *Organisation – Site Emergency Response* [10].

5 References

Unless otherwise specified, the latest edition shall apply.

[1] EIGA Doc 175, *Safe Practices for the Production of Nitrous Oxide from Ammonium Nitrate*, www.eiga.eu.

[2] EIGA Doc 176, *Safe Practices for Storage and Handling of Nitrous Oxide*, www.eiga.eu.

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

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

[5] ADR, *European Agreement concerning the International Carriage of Dangerous Goods by Road*, www.unece.org.

[6] EIGA Doc 30, *Disposal of gases*, www.eiga.eu.

[7] EIGA Doc 166, *Guideline on the Management of Waste Gas Cylinders*, www.eiga.eu.

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

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

[10] EIGA Info HF06, *Organisation – Site Emergency Response*, www.eiga.eu.

[11] EIGA Training Package TP 21, *Nitrous Oxide Plant Environmental Issues*, www.eiga.eu.

Appendix 1 EIGA Document links to ISO 14001

Doc No	Title of EIGA Publication	ISO 14001 Sections	Clause
107	Guidelines on Environmental Management Systems	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	Environmental aspects	6.1.2
108	Environmental Legislation Applicable to Industrial Gases Operations within the EU	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
		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	Operation	8
30	Disposal of Gases		
85	Noise Management		
109	Environmental Impacts of Acetylene Plants		
84	Calculation of Air Emissions from Acetylene Plants		

Doc No	Title of EIGA Publication	ISO 14001 Sections	Clause
05	Guidelines for the Management of Waste Acetylene Cylinders		
166	Guideline on the 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		
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
		General	9.1.1
		Evaluation of compliance	9.1.2
135	Environmental Auditing Guide	Internal audit	9.2
		Management review	9.3
		Improvement	10
		Non-conformity and corrective action	10.1
		Continual improvement	10.2

NOTES

1 See also EIGA Training Package TP 21 *Nitrous Oxide Plant Environmental Issues* [11]

Appendix 2 Nitrous oxide plant environmental impacts

INPUTS		OUTPUTS
AMMONIUM NITRATE →	STORAGE	→ CONTAINERS ∆
	REACTOR	→ AIR EMISSIONS ■
CHEMICALS PURIFICATION MEDIA →	PURIFICATION	→ CHEMICALS ∆ PURIFICATION MEDIA ∆ WATER EMISSIONS ∆
CONSUMABLES →	COMPRESSION	→ OIL ■ NOISE ●
ADSORBENTS →	DRYERS	→ ADSORBENTS ∆ PACKAGING ∆
WATER CHEMICALS →	CYLINDER FILLING	→ WATER ● AIR EMISSIONS ●
WATER CONSUMABLES →	CYLINDER MAINTENANCE	→ PAINT ∆ SCRAP CYLINDERS ∆

PERSISTENT ●

PERIODIC ∆

OCCASIONAL OR ACCIDENTAL ■