CALCULATION OF EMISSIONS FROM A NITROUS OXIDE PLANT

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Prepared by WG-5 Environment

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Amendments to 191/14

Section	Change
	Editorial to align style with EIGA style manual

NOTE Technical changes from the previous edition are underlined

1 Introduction

This publication provides details on nitrous oxide emissions from a nitrous oxide plant. The user may adapt this information with their information specific to their own plant and obtain an estimate of the emissions to air.

The basic philosophy behind the publication is the minimisation of emissions, nuisance and wastes of any kind and their disposal as it is stated in ISO 14001, *Environmental Management Systems -- Requirements with Guidance for Use* [1][1]:

"Organizations of all kinds are increasingly concerned to achieve and demonstrate sound environmental performance by controlling the impacts of their activities, products or services on the environment, taking into account their environmental policy and objectives."

Additionally, nitrous oxide is considered a greenhouse gas (GHG) with a Global Warming Potential (GWP) of 100 years, expressed in carbon dioxide equivalent as 298 as per The Intergovernmental Panel on Climate Change (IPPC) Fourth Assessment Report [2]. It is one of the six gases included in the scope of the Kyoto Protocol [3].

2 Scope and purpose

2.1 Scope

This publication considers the potential environmental impact of air emissions from nitrous oxide plants. It deals only with nitrous oxide emissions to air because of its high Global Warming Potential).

The influence of the European pharmacopoeia rules for medicinal nitrous oxide is also taken into account where relevant.

Further details of best practices and other environmental impacts can be found in the publications:

- EIGA Doc 112, *Environmental Impact of Nitrous Oxide Plants* [4];
- EIGA Doc 175, *Safe Practices for the Production of Nitrous Oxide from Ammonium Nitrate* [5]; and
- EIGA Doc 176, *Safe Practices for Storage and Handling of Nitrous Oxide* [6].

2.2 Purpose

This publication provides guidance on the estimation of nitrous oxide losses as emissions from nitrous oxide plants, based on the most common process features.

It also provides a better understanding of the origin of the nitrous oxide emissions or losses allows improvements in productivity and savings in production costs and helps the estimate of the quantities of nitrous oxide to be as accurate as possible.

3 Definitions

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

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

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.

3.2 Technical definitions

3.2.1 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 emissions from a nitrous oxide plant

4.1 Chemical reactions

Nitrous oxide is produced by thermal decomposition of ammonium nitrate at a temperature of approximately 250 °C:

(1) $NH_4NO_3 \rightarrow N_2O + 2\ H_2O$

Side reactions can occur and can lead to production of ammonia (NH_3) and decomposition reactions producing nitrogen (N_2) and oxygen (O_2):

(2) $NH_4NO_3 \rightarrow NH_3 + NO_3H$

(3) $12\ NO_3H + 16\ NH_3 \rightarrow 30\ H_2O + 14\ N_2 + 3\ O_2$

These side reactions shall be taken into account when calculating the theoretical yield of the reaction and the associated theoretical nitrous oxide losses. This accounts for a maximum loss of 5% of ammonium nitrate, expressed as dry matter. Typical consumption of ammonium nitrate is between 1.8 to 2 kg of ammonium nitrate per kg nitrous oxide.

4.2 Sources of emission

Typical nitrous oxide emission sources from a nitrous oxide plant are:

- purification process (to remove nitrogen);
- transfer of the end product into storage;

- filling of trucks or trailers;
- inspection of the trailers; and
- safety tests and maintenance.

The amount of gas which is emitted depends additionally on various parameters of the production process. The following sections give an explanation of how to estimate gaseous emissions releases during normal operation.

4.2.1 Purification process to remove nitrogen

Nitrous oxide losses from the purification process step depend on the actual process that is used. Each process will have different nitrous oxide vents that should be taken into account when estimating the nitrous oxide losses and emissions.

The following three main unit processes are considered:

- pressure swing absorption;
- column distillation; and
- cryogenic heat exchange.

4.2.1.1 Pressure swing absorption

A simplified drawing of the purification process by pressure swing absorption is shown in Figure 1.

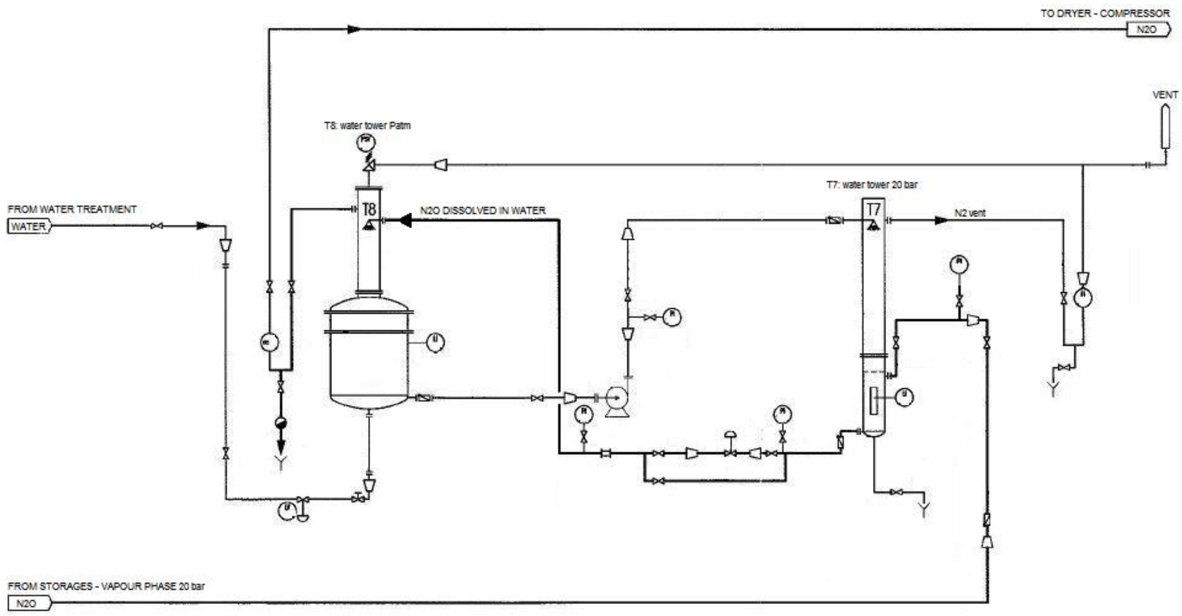

Figure 1: Purification through pressure swing absorption

This process relies on the solubility difference of nitrous oxide and nitrogen in water at different pressures. At the end of the production process, nitrous oxide is dissolved in water at high pressure (20 bar). Next, the nitrous oxide dissolved in the water is sprayed into a second column maintained at atmospheric pressure.

The vent from this second water tower is enriched in nitrogen and is vented to the atmosphere. It still contains around 80% nitrous oxide. Additional nitrous oxide treatment devices may be used to abate the nitrous oxide content of this vent stream.

4.2.1.2 Column distillation

A simplified drawing of the purification process using a distillation column is shown in Figure 2.

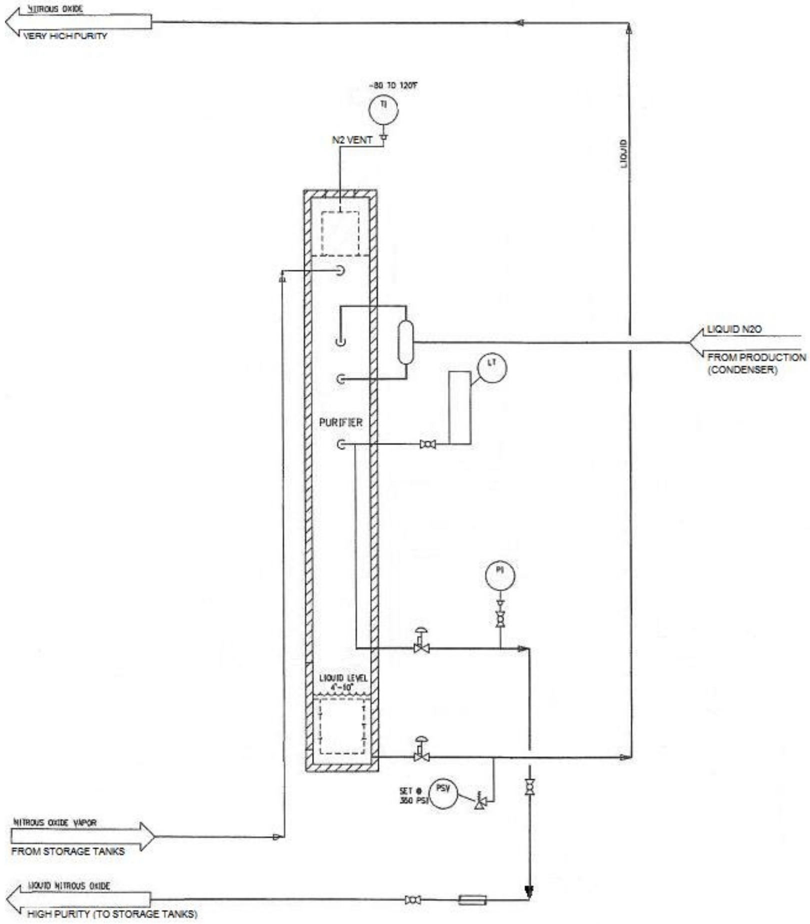

Figure 2: Purification process using a distillation column

The principle of this purification process is cryogenic distillation of the nitrous oxide / nitrogen mixture from the production step. Different levels of purity for the final nitrous oxide product can be obtained depending on the height of the extraction point in the distillation column.

The vent at the top of the column contains approximately 30% nitrous oxide.

4.2.1.3 Cryogenic heat exchange

A simplified drawing of the purification process using a cryogenic heat exchanger is shown in Figure 3.

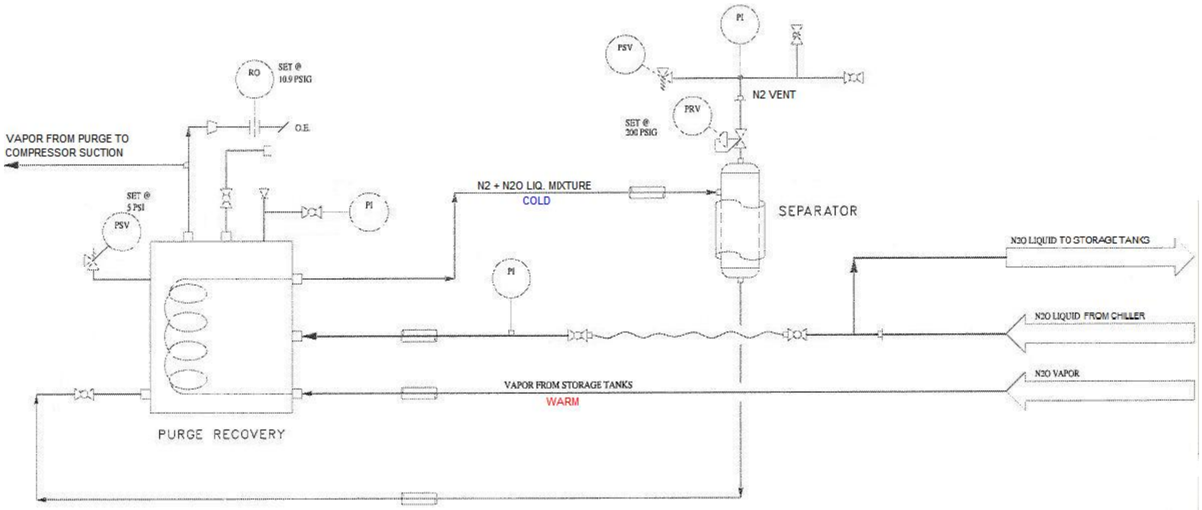

Figure 3: Purification process using a cryogenic heat exchanger

The nitrogen to be purified flows in a coil which is submerged into a liquid nitrogen cryogenic bath. Due to the temperature, a two-phase liquid mixture is created, the gaseous nitrogen is purged and the purified nitrous oxide is introduced in the liquid bath. Purified nitrous oxide vapour is led to the compressor suction. The vent at the top of the separator contains less than 20% nitrous oxide.

4.2.2 Transfer of the end product into storage

During the transfer of the end product into cryogenic storage, the gaseous phase of medical grade storage is recycled into the production loop (just before the compressor). Depending on how European pharmacopoeia rules are nationally implemented, the gaseous phase of industrial grade storage may not be recovered in the process (even at the purification step), to prevent back contamination. This may lead to nitrous oxide emission to the atmosphere. This may be limited by installing flow restriction devices on the storage to limit the flow rate of the venting.

If an intermediate liquid storage is used, between the end of the production process and the final product storage (in order to define a batch number before release of the product by a qualified person), more losses may be expected at this point due to liquid transfer (1 liquid litre expands into 662 gaseous litres).

4.2.3 Tanker / trailer filling

When filling tankers / trailers, approximately 20 minutes before the end of the filling, an overflow gauge is opened to prevent overfilling. Attention shall be paid to the setting and the use of the possible overflow devices.

The filling of the trailers or cylinders with industrial grade nitrous oxide sometimes involves venting nitrous oxide to the atmosphere in order to prevent the mixing of medicinal and industrial grade products. Before filling, attention shall be paid to whether there is still some liquid in the storage to prevent the material of the trailer cooling down too quickly.

4.2.4 Inspection of tankers / trailers

Trailers follow a periodic inspection of all their safety devices and to check the integrity of their loading / unloading equipment. Before this inspection, the nitrous oxide content is purged into nitrogen service and after the inspection the container is purged back into nitrous oxide service before the first filling to ensure compliance with quality specifications. Both of these processes can result in nitrous oxide emissions.

4.2.5 Safety test and maintenance

Plant maintenance, safety equipment and quality tests are required to be performed during operation. These can lead to nitrous oxide emissions and losses through venting. These emission losses can arise from periodic rinsing of the reactors, sampling for quality analysis and rinsing of the sampling cylinder, the change out of a leaking valve on cryogenic liquid storage, losses from hoses when connecting / disconnecting.

4.3 Minimisation of nitrous oxide emissions

The best available techniques for minimisation of nitrous oxide emissions include reduction at source. If this is not feasible then residual gases shall be vented and disposed of according to legislation or by referring to EIGA Doc 30, *Disposal of Gases* [7].

4.3.1 Reduction at the source

As far as nitrous oxide is concerned, reduction at the source by recycling of the emissions is the best way to decrease or to abate the emissions. This option requires the least investment in abatement equipment.

Therefore, once nitrous oxide emissions have been collected, any possibility of recycling them into the nitrous oxide production process has to be investigated. This recycling may be restricted and regulated by the pharmacopoeia authorities and each country has a different situation.

When recycling is possible, it is recommended to route the collected nitrous oxide emissions to the suction of the compressor if the pressure level is compatible. Of course, it is much better to directly recover the collected nitrous oxide emissions in the end product conditioning step, but this might not be possible due to purity requirements.

5 References

Unless otherwise specified, the latest edition shall apply.

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

[2] The Intergovernmental Panel on Climate Change (IPPC) Fourth Assessment Report, www.ippc.ch.

[3] The Kyoto Protocol, www.unfccc.int.

[4] EIGA Doc112, *Environmental Impact of Nitrous Oxide Plants*, www.eiga.eu.

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

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

[7] EIGA Doc 30, *Disposal of Gases*, www.eiga.eu.