# Noncatalytic removal of nitrogen in a recuperative container glass furnace[1)]

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## 1. Introduction

The Swiss Government has established limits for emissions and immissions. The legal $NO_2$ limit in Switzerland for the manufacturing of glass containers is set at 2.5 kg/t glass, or 2 500 mg/kg glass referred to 8 vol.% $O_2$. Responsibility for enforcing these limits rests with the individual cantons, so that whenever the immission values are exceeded the cantons must determine additional measures to obtain further emission reduction.

Vetropack Bülach Glassworks are located near Kloten International Airport, the City of Zurich and an agglomeration around Zurich consisting of much industry. Any increase in immission values is thus caused by the combination of these emitters. When higher immission values were registered in the region, Vetropack was asked to comply with a new regulation prescribing that its $NO_x$ values of 850 mg/m$^3$ flue gas[2)] referred to 8 vol.% $O_2$ – which are already below previously required limits – be reduced by half.

For many years Vetropack has undertaken primary measures to prevent the formation of $NO_x$. The $O_2$ contents of the furnace in the waste gas current have been controlled attaining values which are just above the stoichiometrical value (0.3 to 0.5 vol.% $O_2$). On the other hand, recuperative furnaces require the highest possible preheating of combustion air, a factor which increases $NO_x$ values. A general rule-of-thumb says that energy savings of 5 % can be achieved by increasing the temperature of combustion air by 100 °C. Such energy savings in turn positively influence $NO_x$ values.

## 2. Selective noncatalytic reduction process

The Selective Noncatalytic Reduction Process (SNCR) was developed and patented by the US company EXXON. Based on existing literature, the advantages and disadvantages of this process are defined as follows [1 and 2]:

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[1)] Presented in German at the 67th Annual Meeting of the German Society of Glass Technology (DGG) on May 19, 1993 in Königswinter (Germany).
[2)] At standard state.

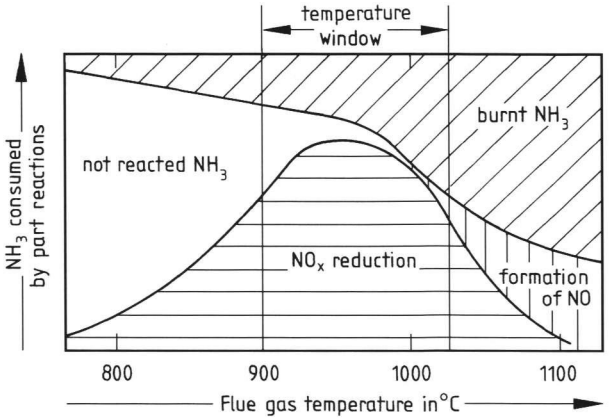


Figure 1. Qualitative representation of the transformation of ammonia as a function of the flue gas temperature.

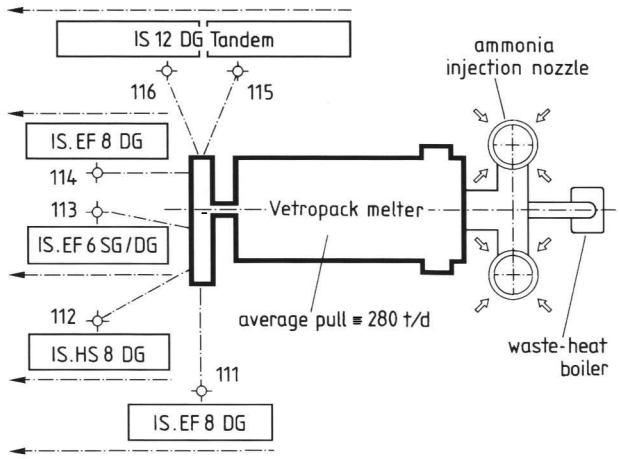


Figure 2. Technical specifications of the Vetropack melter, Bülach (Switzerland).

Advantages:
a) Installation is inexpensive;
b) investment costs are low;
c) operating costs are reasonable.

Disadvantages:
d) The proper mixing of reducing agents is difficult;
e) the overstoichiometrical addition of $NH_3$ increases the consumption of reducing agent.

The process of thermal nitrogen removal consists of adding a reducing agent to the waste gas at relatively high temperatures in order to decompose the nitrogen oxides. The reducing agent used at Vetropack is ammonia gas. In order to achieve a proper reaction between ammonia gas and $NO_x$, the waste gas must reach a temperature of approximately 900 to 1050 °C, which is considered the temperature window.

The SNCR process was first implemented in the industrial sector in 1974. Since 1980 a second process generation has been available which feeds the ammonia gas and the supporting air through wall nozzles into the boiler. Operation showed that this horizontal nozzle construction was better protected against high temperatures and that its operating capability was not limited by dirt formation. The necessary engineering work for this nitrogen removal installation was performed by ABB Boiler Plants Ltd. (ABB Kesselanlagen AG), formerly Sulzer Thermtec, Winterthur (Switzerland) [3].

The injected ammonia gas reacts mainly in accordance with the following chemical formula:

$$NO_x + NH_3 \rightarrow N_2 + H_2O\ .$$

Figure 1 shows a qualitative representation of the transformation of ammonia as a function of the flue gas temperature. In addition to the desired reactions for this reduction in nitrogen oxides there are also some undesirable side effects:

- The incomplete burn-up of ammonia gas contributes to the formation of nitrogen oxide and reduces the degree of $NO_x$ decomposition when the waste gas temperature is too high as a result of $NH_3$ reoxidation.
- Part of the injected ammonia gas is remote from any reaction area and thus slips unchanged through the reaction zone. This partial stream of unchanged ammonia gas is termed the ammonia slip in the waste gas. When temperatures are too low, only part of the $NH_3$ reacts, causing an increase in this slip. This also demonstrates how narrow the temperature window for the reaction really is (where ammonia loss through combustion and slippage is generally least), namely between about 900 and 1050 °C.
- Solid and liquid fuels both contain sulfur, thus, the combustion process results mainly in the production of sulfur dioxide or $SO_2$. In the case of an ammonia gas slip, i.e. when ammonia is present in cooled waste gas whose temperature is lower than 225 °C, $SO_3$ combines with $NH_3$ to form sulfates. Depending on the molecular composition of $NH_3$ to $SO_3$, this results in the creation of either a dry ammonia sulfate $(NH_4)_2SO_4$ or the sticky ammonia bisulfate $NH_4HSO_4$, the latter of which can lead to caking.

## 3. Technical specifications of the Vetropack melter in Bülach

In Bülach the SNCR process is used in a flint glass melter with the following technical specifications (figure 2):

| | |
|---|---|
| surface: | 136 $m^2$ |
| melting rate: | 280 t/d (average) with additional electrical boosting (340 kW in the melting area); |
| fuel: | HS with an acidity content of maximum 1.0 %; |
| number of burners: | 22 (11 per side); |
| recuperator: | tube bundle type, countercurrent; |
| energy consumption: | ≈4490 kJ/kg glass at 60 % cullet. |

## 4. DeNOx Installation and safety concept

This installation consists of the following aggregates (figure 3):

a) an ammonia warehouse with evaporator,
b) a flow measurement device,
c) an air fan which produces supporting air,
d) a mixing station (ammonia/supporting air), and
e) recuperators with injection nozzle levels.

The ammonia warehouse consists of four $NH_3$ containers, each with a capacity of 490 kg liquid and technically pure ammonia. Due to its physical characteristics this liquid ammonia is under pressure (10 bar at 25 °C and 4.3 bar at 0 °C). The full containers are delivered by truck and substituted for the empty containers. Weekly usage amounts to a little more than one container. The first reason for selecting this particular storage amount is that it provides the glassworks with enough ammonia to last for 3 to 4 weeks. The second reason concerns an existing ordinance on safety aspects. By maintaining this storage quantity the plant is not subject to this ordinance – even though Vetropack must obviously provide its own comprehensive safety measures. The liquid ammonia is transformed into gas in the ammonia evaporator. The required heat for this process is produced with electricity. Following evaporation, the gaseous ammonia is then slightly overheated to reach a temperature not exceeding 60 °C. The heater operates intermittently.

The device next to the evaporating installation is a flow measurement device. A control valve on the gas side regulates the dosage of needed ammonia. Since the amount of injected ammonia is insufficient to enable its thorough mixture with the waste gas through direct contact, it is first fed into a mixer where it is combined with moderately pressurized supporting air generated by a rotary fan. After this mixing process, the ammoniac content is less than 5 %.

The gas mixture of ammonia and air are now injected into the waste gas current using lances. Valves in the distribution station transfer the gas mixture to the appropriate injection nozzle group which provides the optimum rate of nitrogen removal for a specific amount of ammonia. The temperature difference of the waste gas between the injection nozzle groups is about 100 K. Each nozzle level consists of four operating injection nozzle lances. The lance points run the length of the recuperator tube into the stream of waste gas. This special

injection nozzle construction produces a spinning motion which causes the ammonia to blend with the waste gas. The actual chemical reaction of nitrogen removal takes place after the injection phase.

After the reaction, the $NO_x$ content of the waste gas is measured continually by a measuring system consisting of:

- a measuring probe,
- a heated wire from the probe to the measuring cabinet, and
- a gauge located in the measuring cabinet.

The measured values are shown on a process control system located in the control room.

## 5. Control systems

The installation for $NO_x$ extraction is equipped with a closed-loop control system which regulates the following elements:

a) the supporting air system,
b) the ammonia evaporation process,
c) the ammonia stream, and
d) the injection nozzle levels.

Since only a minimum of tonnage variations occur over a period of 24 h and the waste gas temperatures thus remain nearly constant, the ammonia quantity and the injection nozzle levels are still controlled manually.

Ammonia belongs to poison class 2. The amount of ammonia stored in the tank warehouse corresponds approximately to the amount used in an ice skating rink. It has the advantage of being detectable through smell in even very small concentrations above approximately 5 ppm. Nevertheless, several safety measures had to be taken in connection with this installation:

- No containers are put into storage until they have been checked at the entrance by specially trained personnel.
- The warehouse is equipped with a sprinkling device.
- A water curtain was installed in front of the warehouse doors in case of a fire in the immediate vicinity of the cooling device.
- A sump was built underneath the containers to hold any contaminated water stemming from firefighting actions.
- Ammonia detection devices were installed.
- Special safety fixtures prevent a tank change unless everything has been properly installed.
- Emergency equipment and protective clothing are stored in a special cabinet near the warehouse. Included are protective suits, breathing masks, eye sprays, as well as special tools to close the $NH_3$ tanks deposited there.

## 6. Operating results and costs

Operation of the installation began in November 1992 and experience gained over the first six months is

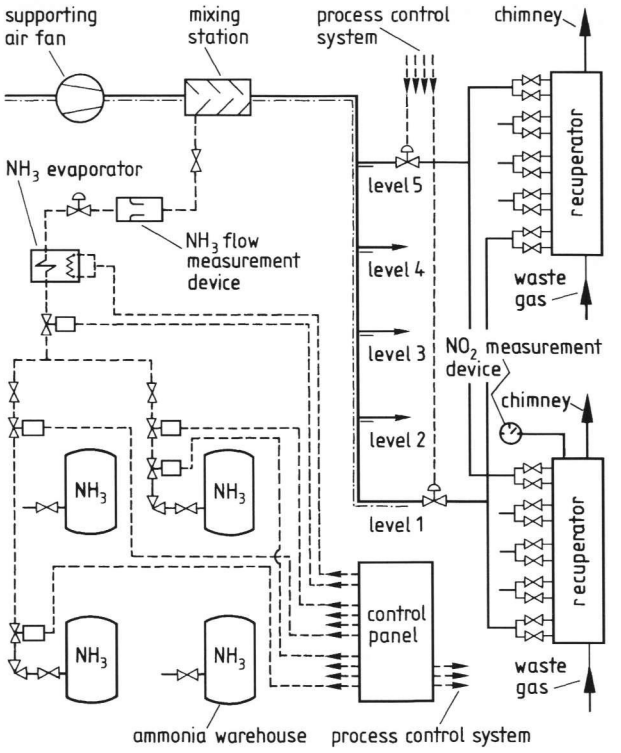


Figure 3. Flow chart of the DeNOx installation after the SNCR process.

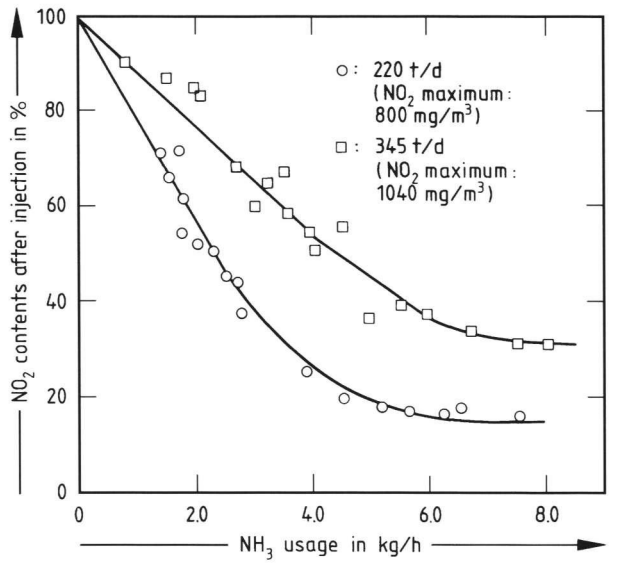


Figure 4. $NO_2$ reduction (referred to 8 vol.% $O_2$) in the waste gas as a function of the $NH_3$ usage for two melting rates.

marked by promising and convincing results. The prescribed 50 % $NO_x$ reduction was achieved right from the beginning without any problems (figure 4). Official measurements performed later on demonstrated the installation's excellent operating efficiency and registered only a minimum of ammonia slippage amounting to $\leq 2.0$ mg/m$^3$ flue gas[2)] (figure 5).

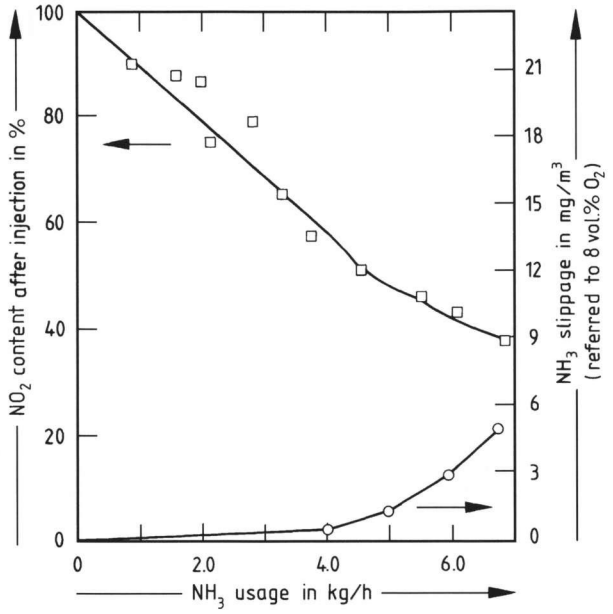


Figure 5. $NO_2$ reduction and $NH_3$ slippage (referred to 8 vol.% $O_2$) in the waste gas as a function of the $NH_3$ usage for a glass production of 340 t/d. $NO_2$ content without extraction ≡ ≡ 1035 mg/m³ flue gas referred to 8 vol.% $O_2$.

Investments amount to approximately SFr 800000. Yearly operating and maintenance costs are about SFr 80000. The ammonia price is SFr 1.52/kg.

## 7. Conclusions

The results achieved at Vetropack have disproved the disadvantages of the SNCR system as stated in section 2. under d) and e). Experience gained has demonstrated that:

- The installation is not expensive to build.
- Investments and operating costs are reasonable.
- Ammonia need only be added overstoichiometrically in small amounts (1 to 3 times).
- The excellent operating results achieved confirm that both the waste gas and ammonia mixture are of high quality, a factor which is obviously due to the newly developed injection nozzle concept from ABB Boiler Plants Ltd.
- The almost stoichiometric operation of the recuperative furnace and the minimum amount of excess air used for combustion and entering the waste gas channels eliminates the need for a higher dosage of reducing agent. A six-months operating period showed that the average amount of ammonia used does not amount to more than 30 %.

These satisfactory results thus disprove a widespread opinion that the thermal nitrogen removal process is automatically coupled with high ammonia usage.

## 8. Summary

A new installation for the extraction of nitrogen from flue gas has been in successful operation in a recuperative container glass furnace at Vetropack in Bülach (Switzerland) since November 1992. The installation was developed by Sulzer Thermtec, today known as ABB Boiler Plants Ltd. (ABB Kesselanlagen AG), a licensee of EXXON (USA). This Selective Noncatalytic Reduction (SNCR) process functions according to the principles of thermal nitrogen removal. No problems were encountered with the process and first measurement results are excellent.

### 9. References

[1] Fellows, W. D.: Application of the thermal DeNOx process to glass melting furnaces. EXXON Research and Engineering Company.

[2] Pütz, M.: Vollzug der Großfeuerungsanlagen-Verordnung zur Minderung der Stickstoffoxide – Aktueller Stand in Nordrhein-Westfalen. In: Steinmetz, E. (Hrsg.): Haus der Technik, Vortragsveröffentlichungen: $NO_x$-Emissionsminderung von Rauchgasen. Essen: Vulkan-Verl. 1988. p. 11–13.

[3] Sauter, J.: Anwendung der thermischen Entstickung SNCR an einer Glasschmelzanlage. ABB Kesselanlagen AG.

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