

7.16 Nitric acid production

7.16.1 Coverage

Nitric acid (HNO₃) is one of the most produced chemical. Emissions to the atmosphere from nitric acid production which cause the greatest concern are nitrous oxide (N₂O) and nitrogen oxides (NO_x) emissions. The Gothenburg protocol deals with transboundary air pollution and particularly with acidification and Eutrophication. It sets emission ceilings for sulphur, nitrogen oxide, VOC, ammonia and dust but it does not cover N₂O which is a green house gas with high global warming potential. Hence, this chapter is mainly focused on NO_x emission reductions.

7.16.2 Emission sources

HNO₃ is produced from ammonia (NH₃), which is evaporated, filtered and oxidised to form nitric oxide (NO). Ammonia filtration is necessary in order to remove all dust. It avoids interaction between dust particles and catalysts on which ammonia oxidation takes place.

The NO formed during the oxidation is then also oxidised to form nitrogen dioxide (NO₂). NO₂ is then absorbed in H₂O to form nitric acid and nitric oxide. The absorption process is an important source of NO_x emissions; hence NO_x need to be controlled and reduced. Different techniques are available to reduce these emissions.

7.16.3 BAT, Associated Emission Levels (AEL)

Primary measures

Major NO_x emissions come from the step of formation of HNO₃. One of the different applicable techniques to reduce NO_x emissions involves the optimisation of the absorption stage. The more the absorption is efficient, the more HNO₃ is formed and the less NO_x is emitted. [1].

The efficiency increase of this absorption is based on the optimization of 3 parameters; the **temperature**, the **pressure** and the **contact between NO_x, O₂ and H₂O**.

- Due to the reaction exothermia, heat removal is needed to optimise the temperature process. The absorption stage takes place in the first third of the column, thus heat removal can be applied before the column.
- High pressure increases the efficiency of the absorption and then nitric acid formation. It also reduces the formation of NO_x.
- Optimising the contact in the absorption tower mainly means changing the tower design. The volume, the number of trays and the residence time are the main parameters to play with so as to optimise the absorption. The longer the residence time is, the more NO_x is recovered and the more nitric acid is formed. The increase of the number of trays and of the volume enhances the nitric acid formation too.

Tail gas concentration level of 82 – 103 mg/Nm³ is technically feasible with completely optimised absorption (heat removal, high pressure, optimised contact).

The HNO₃ yield can also be increased by addition of H₂O₂ to the last absorption stage. It avoids the implementation of a SCR.[1]

Secondary measures

NO_x emissions can be reduced by a tail gas treatment, such as a combined N₂O and NO_x abatement technique or a SCR can also be used.

The combined N₂O and NO_x abatement technique consists of 2 catalyst layers. In the first layer, N₂O is reduced in N₂ and O₂. In the second layer, NO_x is reduced by addition of NH₃ (comparable to a SCR) and N₂O further decomposition is also taking place. This process can lead to a NO_x abatement of 99 %.The process is applicable for nitric acid plants with a tail gas temperature of more than 400 degree Celsius. [1]

For installations with a tail gas temperature of more than 340 degree Celsius N₂O and NO_x emissions can be reduced in a combined N₂O and NO_x abatement system with the addition of hydrocarbons. [4] As in the combined N₂O and NO_x abatement process, there are 2 catalyst layers. In the first one, NO_x is removed in reacting with NH₃ and N₂O is removed by a catalytic reduction with hydrocarbon (natural

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gas or propane) in the second step. Similar emission levels as in the N₂O and NO_x combined abatement technique can be expected. [1]

The following table gives an overview of BAT associated NO_x emission levels for nitric acid production.

Table 1: Associated NO_x emission levels with BAT to reduce emissions in nitric acid production.

Emission source	Techniques	Associated emission level with BAT (mg/Nm ³) ¹
Nitric acid production	Optimisation of the absorption stage, Combined NO _x and N ₂ O abatement technique, SCR, Addition of H ₂ O ₂ to the last absorption stage	New plants 10 - 154
		Existing plants 10 - 185 ²

¹ emissions were converted from ppmv to mg / Nm³ using: 1ppmv = 2.05 mg NO₂ / Nm³.

² up to 307 mg/Nm³, where safety aspects due to deposits of AN restrict the effect of SCR or with addition of H₂O₂ instead of applying SCR.

7.16.4 Emerging techniques

There is no emerging technique available in the non ferrous metal processing industry to reduce SO₂, dust or NO_x emissions. [1].

7.16.5 Cost data for emission reduction techniques

The investment of a combined N₂O and NO_x treatment unit is about 1.7 Meuros. A comparison of various N₂O reduction strategies does not show a significant difference in cost effectiveness and the cost per tonne HNO₃. Operating costs are between 0.71-0.87 euros per tonne CO₂-eq reduced and 0.98 – 1.20 euros per tonne HNO₃ produced.

There is no available information about the cost of the hydrocarbon addition technique.

The total cost for a SCR technique is around 1.3 USD per tonne HNO₃ produced. This estimation was made in 1998 assuming certain price of catalyst and fuel, which are now significantly different.[1]

The specific cost of the implementation of the addition of H₂O₂ to the last absorption stage is 2.5 USD per tonne HNO₃.

7.16.6 References used in chapter 7.16

- [1] Reference document on Best Available Techniques for the manufactures of large volume chemicals – ammonia, acids and fertilizers, August 2007.
- [2] Comments from Birgit Brahner, German Federal Environment Agency, 12/2008
- [3] "Compilation of the answers-to-questions-and proposal of EGTEI secretariat.doc",EGTEI, 02/2009.
- [4] Comments from Thomas Krutzler, UBA Austria, March 2009.
- [5] EGTEI-State of progress.doc", for WGSR, March 2009.