Information note

AM0028 "Catalytic N2O destruction in the tail gas of Nitric Acid or Caprolactam Production Plants" and "AM0034 Catalytic reduction of N2O inside the ammonia burner of nitric acid plants"

(Version 01.0)

I. Background and mandate

1. During the sixty-sixth meeting of the CDM Executive Board (hereinafter referred to as the Board), the secretariat made a presentation regarding potential issues with the approved methodologies AM0028 “N_2O destruction in the tail gas of Nitric Acid or Caprolactam Production Plants” and AM0034 “Catalytic reduction of N_2O inside the ammonia burner of nitric acid plants”. At its sixty-sixth meeting, the Board requested the Meth Panel to assess the approved methodologies AM0028 and AM0034 for N_2O abatement from nitric acid production, taking into account the potential issue brought to the attention of the Board by the secretariat, and to provide an assessment of this issue for consideration by the Board.[1] This note is prepared in response to this request.

II. N_2O formation from nitric acid production

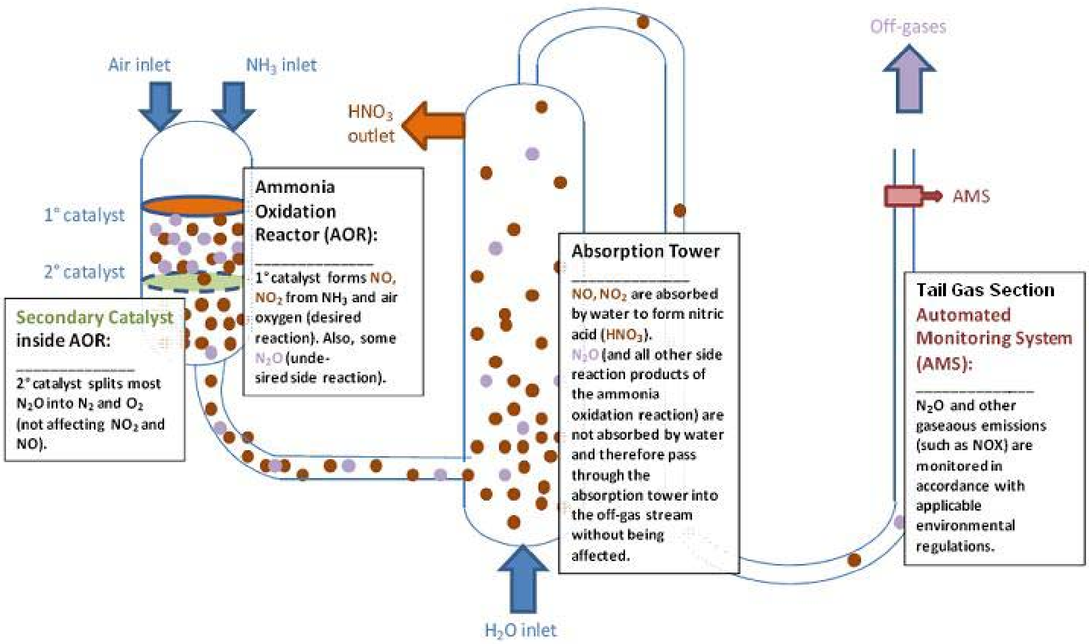
2. Nitric acid (HNO_3) is produced through the oxidation of ammonia (NH_3) to nitrogen oxide (NO) on a precious metal catalyst gauze in the ammonia burner of a nitric acid plant. Nitrous oxide (N_2O) is an unwanted by-product gas produced in the manufacture of nitric acid. The N_2O formed during nitric acid production is typically released into the atmosphere, as it does not have any economic value or toxicity at emission levels typical of nitric acid manufacture.

3. Nitric acid plants operate on discrete production runs called “campaigns”. The start of a campaign is characterized by the installation of a new set of primary catalyst gauzes in the oxidation reactor. A set of precious metal alloy gauzes (generally made of platinum, palladium and rhodium) is designed to operate either for a specific number of days or for a specific output of nitric acid. Over time, the gauze pack degrades due to metal loss becoming gradually less selective for the formation of NO. The productivity, therefore, drops and the formation of by-products (N_2O and N_2) increases. At the end of the design operating life of each gauze pack, the nitric acid plant is shut down and the gauze is replaced by a new set of gauzes. The period of time comprised from the installation of a new gauze pack until the subsequent plant shut down is defined as a campaign.

---

[1] EB 66 report, paragraph 92.

Figure 1: Schematic illustration of N_2O formation and secondary and tertiary abatement of N_2O in nitric acid plants



III. Issues identified by the secretariat

4. The secretariat had identified that new technologies have emerged in the sector which result in different benefits like increasing the durability of the gauzes minimizing metal loss reduction and possibly, improvement of the catchment gauzes and lowering the N_2O formation in the process of producing nitric acid. The approved methodologies AM0028 and AM0034 provide disincentives to apply these new technologies. For example, under the methodology AM0034 a new baseline measurement campaign would need to be conducted if a different catalyst is used during the crediting period than prior to the registration of the CDM project activity (see IV below for further details). This could potentially result in a situation where, as a result of the incentives from the CDM, the new technologies are not applied under the project activity, while they would have been applied in the baseline without the incentives from the CDM. Such a situation may result in an over-estimation of the calculated N_2O emission reductions.

IV. CDM projects using approved methodologies AM0028 and AM0034

5. By June 2012, there were 19 registered project activities using methodology AM0028 and 53 registered project activities using methodology AM0034 generating around 7.7 million CERs and 12.9 million CERs per year respectively. There were also 24 project activities under validation using methodology AM0028 that could generate 11.6 million CERs per year and 30 under AM0034 that could generate 6.4 million CERs per year.

V. Technological options available to increase the NO yield

6. There is a broad range of technological options available to improve the performance of nitric acid plants and reduce the formation of N_2O. The technological improvements that nitric acid plants could implement are divided in two main areas:[2]

(a) Improvements to the ammonia oxidation catalyst;

(b) Optimization of the operating conditions.

A. Improvements to the ammonia oxidation catalyst

7. Modifications in composition, orientation and the geometry of the gauze could lead to a higher ammonia conversion to NO and at the same time to a possible reduction in the production of N_2O. Simultaneously, an extension of the campaign length is possible. The use of improved ammonia oxidation catalysts could generate the following benefits:[3]

(a) Possible reduction in N_2O emissions in the range of 30% - 90%.[4] This includes optimized conventional catalysts which involve changes in the geometry or layer distribution of the catalyst (up to 30%), as well as alternative oxidation catalysts, which use other elements to manufacture the catalyst (up to 80-90%). Although a number of CDM plants operates with such new catalysers it was not possible to verify this improvement from the available data;

(b) Increased conversion efficiency with subsequent rise in revenues;

(c) Stronger material and greater mechanical stability;

(d) Greater surface area for catalysis;

(e) Lower metal losses and extended campaign lengths.

8. There are several technology providers for ammonia gauzes all over the world.5 In principle most advanced primary gauzes can be installed in any plant and catalyst manufacturers are able to design the gauze pack for each burner and tailored-made alloys can be obtained on request.

9. According to information provided by the primary gauze manufacturer Heraeus, advanced primary catalyst systems can be optimized either for reducing precious metal losses (and thereby increasing the campaign length) or for lowering N_2O formation. Reaching both targets with the same advanced primary catalyst gauze configuration is currently not feasible.

10. New gauzes are used to different extents in different regions of the world. According to information provided by the manufacturers of the gauzes more than 90% of the plants in Europe use

---

[2] Oxide catalysts for ammonia oxidation in nitric acid production: properties and perspectives. V.A. Sadykov, et al, Applied Catalysis : General 204 (2000) 59–87.

[3] Platinum catalyst gauze for nitric acid production. Shi Yichun, et al. China national chemical supply & sales corporation Taiyuan precious metals co., ltd, Taiyuan, China.
Knitted platinum alloy gauzes. Catalyst development and industrial application. B. T. Horner. Johnson Matthey, materials technology division.

[4] Reduction of Nitrous Oxide (N2O) in the Nitric Acid Industry. 2001. InfoMil

[5] Some examples: <http://www.chinachemtpm.com/english/e_product.htm>
<http://pmgroupusa.com/index.php?p=products/catalytic_gauze_line>
<http://www.krastsvetmet.com/en/dm-en/katalsistemi/katsistemy.wbp>.

advanced primary gauzes. This development may partially be driven by environmental legislation and incentives, such as the participation in JI projects and the inclusion of N_2O emissions from nitric acid in the EU Emissions Trading Scheme (EU ETS) from 2013 onwards. In the United States, about one third of the plants use advanced primary gauzes. Advanced primary gauzes are also used in some CDM projects and have been installed in non-CDM plants in developing countries.

B. Optimization of the operating conditions

11. There are different opportunities to improve the operating conditions in a nitric acid plant that could increase the NO yield. The impact of these measures in terms on N_2O emission reductions depends on the specific situation of the plant and information on possible improvements is limited. The list of measures that improve the operating conditions are:[6]

(a) Optimising the filtration of raw materials;

(b) Optimising the mixing of raw materials;

(c) Optimising the gas distribution over the catalyst;

(d) Optimising the oxidation temperature and the overall combustion reaction;

(e) Monitoring catalyst performance and adjusting the campaign length.

12. Expert opinion suggests that to properly know if the plant is operating properly the following parameters need to be monitored:

(a) Composition of the gauze pack (that is, number of gauzes, composition, wire diameter, geometry per gauze);

(b) Ammonia concentration at the reactor inlet;

(c) Ammonia combustion conditions (pressure, gauze temperature, and load i.e. ton N per day);

(d) Diameter of the basket on which the metal catalyst gauze rest;

(e) Depth of the basket (typically filled with Raschig rings) and space occupied by the secondary catalysts in case of in-process N_2O abatement.

VI. Current requirements with regard to operating conditions and the use of ammonia gauzes in the approved methodologies AM0034 and AM0028

13. This section describes the existing requirements in the approved methodologies AM0028 and AM0034 regarding the operating conditions of the nitric acid plant and the limitations regarding a potential change in the primary gauze during the crediting period of the project activity.

A. AM0028

Operating Conditions

14. In order to avoid that the operation of the nitric acid or caprolactam production plant is manipulated in order to increase the N_2O generation, the methodology establishes a set of procedures to determine the permitted operating conditions of the nitric acid or caprolactam production plant. In order

[6] Integrated Pollution Prevention and Control. European Commission, 2007.

to avoid an "overestimation of emission reductions", the operating conditions cannot be changed over the crediting period.

<u>Ammonia gauze</u>

15. The plant operator is allowed to use any primary gauze that is common practice in the region or has been used in the nitric acid or caprolactam production plant during the last three years without limitation of N_2O baseline emissions.

16. In case where the nitric acid or caprolactam production plant operator decides to use a primary gauze that is not common practice in the region and not reported as being in use in the relevant literature, the project applicant has to demonstrate (either by economic or other arguments) that the choice of the new composition was based on considerations other than an attempt to increase the rate of N_2O production. If the project applicant can demonstrate appropriate and verifiable reasons, the plant operator is allowed to use new primary gauzes without limitation of N_2O baseline emissions.

17. This means that baseline emissions are not limited as long as it is demonstrated that the primary gauze is in use. If the plant operators fail to provide the proper justification, baseline emissions are limited to the maximum specific N_2O emissions of previous periods.

18. In summary, in AM0028 there is no impediment to change the primary gauze. However, a change to a primary gauze that results in lower N_2O formation would result in lower baseline emissions and thus in lower CER revenues. In this regard, the methodology provides a disincentive to use new technologies that result in lower N_2O formation. So far, among the 19 projects already registered, none of them have reported that they changed their ammonia oxidation catalyst.

B. AM0034

<u>Operating conditions</u>

19. In order to avoid the possibility that the operating conditions of the nitric acid production plant are modified in a way that increases N_2O generation during the baseline campaign, the normal ranges for operating conditions shall be determined over a period of five campaigns for the following parameters: (i) Oxidation temperature; (ii) Oxidation pressure; (iii) Ammonia gas flow rate; (iv) Air input flow rates.

<u>Ammonia gauze</u>

20. If the composition of the primary gauze used after the implementation of the project is different to that used in the campaign for setting the operating conditions (previous five campaigns), the project proponent should repeat the baseline campaign to determine a new baseline emissions factor, and:

(a) Compare the new baseline emission factor to the previous baseline emission factor and adopt the lower figure as emission factor for the baseline; or

(b) Set the baseline emissions factor to the IPCC default emission factor, adjusted conservatively for uncertainty, for N_2O from nitric acid plants which have not installed N_2O destruction measures and which use the least GHG intensive technology (4.5 $kgN_2O/tHNO_3$).

21. As in AM0028, there is no impediment to use different primary gauzes in AM0034. However, the methodology provides disincentives to adopt primary gauzes that result in lower N_2O formation:

(a) The requirement to repeat the baseline campaign does not allow the project proponent to claim any CERs for the duration of the campaign;

(b) The resulting N_2O baseline emission factor from the new campaign may be lower than the previously used emission factor, resulting in lower baseline emissions and fewer CERs for the remainder of the crediting periods.

VII. N_2O emission factors

22. Table 1 provides an overview of the emission factors for plants not applying secondary or tertiary abatement of N_2O included in the 2006 IPCC Guidelines and other relevant sources in the literature. Table 2 provides an overview of the baseline emission factors of registered CDM project activities.

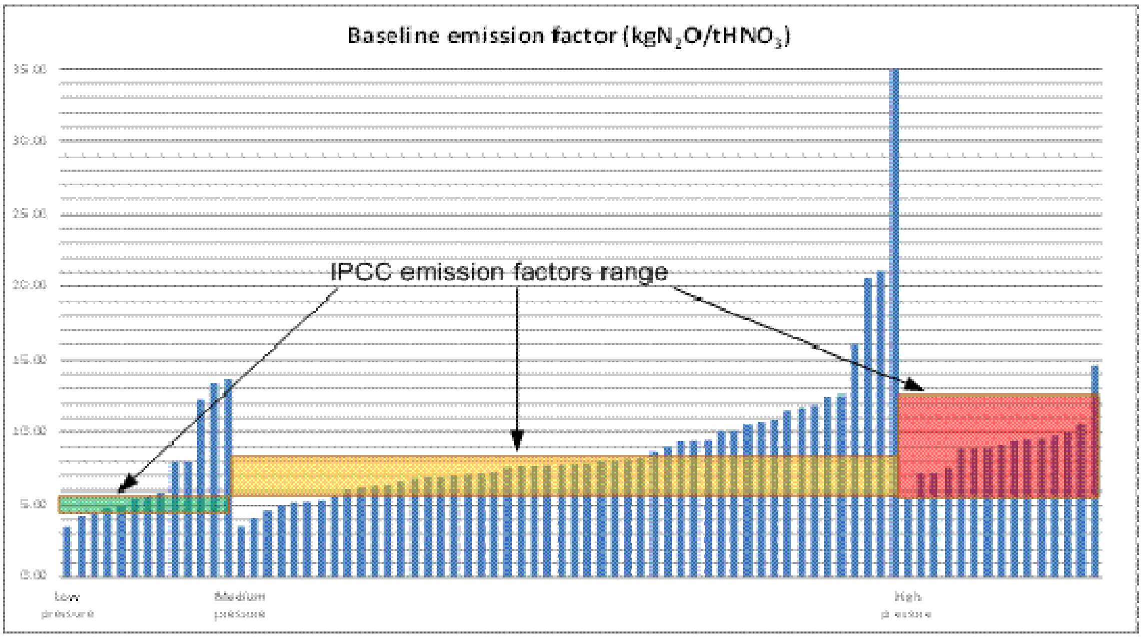
Table 1: Default emission factors for nitric acid production

Production process in the ammonia burner	(kg N_2O / t HNO_3)
Low pressure plants	4.5 – 5.5
Medium pressure plants	5.6 – 8.4
High pressure plants	5.4 – 12.6

Table 2: Information on the baseline emission factors of the 72 registered CDM project activities using methodologies AM0028 or AM0034

Emission factor	(kg N_2O / t HNO_3)
Lowest emission factor	3.47
Highest emission factor	37.01
Median emission factor	7.94
Average emission factor of the top 20% performing plants	4.85

Figure 2: Emission factors of 72 registered CDM projects[7]



---

[7] The 72 CDM project activities include a total of 78 nitric acid plants.

23. Figure 2 shows a wide variety of emission factors. Except from some outliers, most plants have emission factors in the range of emissions described by the IPCC. Higher emission factors beyond the uncertainty range of the default emission factors provided in the 2006 IPCC Guidelines indicate that the plants may not be operated properly. An emission factor of 12 kg N_2O per ton HNO_3 implies N_2O selectivities approaching and possibly exceeding 3%. The analysis of the existing monitoring reports also shows that plants with high emission factors also have low nitric acid production rates (expressed in terms of nitric acid produced per unit of ammonia consumed) reinforcing the assumption that those plants may not be working appropriately. The existing monitoring parameters listed in both methodologies, AM0028 and AM0034, do not provide sufficient information to determine whether the plant is operating properly or not.

24. A nitric acid plant could use an improved primary ammonia oxidation catalyst but without an optimized production process the emission levels could remain high. The same could apply to a plant that uses an optimized production process but does not use improved primary gauzes.

VIII. Introduction of technologies with lower N_2O formation

25. To assess the implications of the provisions in AM0028 and AM0034, the following questions are important:

(a) Would the project participants in the absence of the incentives from the CDM introduce technologies with lower N_2O formation at some point during their crediting periods?

(b) Do the provisions in the methodologies AM0028 and AM0034 constitute sufficiently strong incentives not to introduce technologies with lower N_2O formation?

26. If both apply, then the emission reductions would likely be overestimated. In this case, the baseline emissions would be calculated based on a technology that results in a higher N_2O formation, while in the absence of the CDM a technology that results in lower N_2O formation would be used.

27. With regard to the first question the available information and data suggests that the discussed new technologies are over time increasingly taken up in the market. This suggests that it is possible that some plants which currently do not yet use these technologies would start to use them in the future. In addition, new technologies may emerge in the future.

IX. Conclusions

28. The data above showed that several options (gauze's materials and geometry) for technological improvements in the production of nitric acid emerged over the past years. These technologies can possibly result in a lower N_2O formation but may not lead to such a reduction in each plant. The market uptake of these technologies varies by region but is generally increasing since their introduction. Given the ongoing innovation observed in the sector, it is possible that the currently available technologies will be further developed and new technologies with lower N_2O formation emerge in the near future.

29. The approved methodologies AM0028 and AM0034 provide disincentives to introduce new types of primary gauzes or to change the operating conditions in a way that may result in lower N_2O formation and reduce the specific ammonia consumption. AM0034 provides stronger disincentives than AM0028. It is possible that the incentives from the CDM are sufficiently strong in order not to introduce new technologies that may have lower N_2O formation, in particular in the case of AM0034 where crediting may be interrupted for significant time in such cases.

30. Given the increased uptake of improved technologies in the market and the ongoing development of new technologies it is possible that some nitric acid plants would in the absence of the CDM install improved ammonia gauzes or optimize their operating conditions at some point during their remaining crediting period, while the CDM provides them incentives not do so. This may, in some situations, lead to an overestimation of the emission reductions.

31. In addition, the panel identified that some nitric acid plants operated in their baseline campaign at conditions which resulted in a level of N_2O formation that is well beyond the uncertainty range of the default emission factors provided in the 2006 IPCC Guidelines (up to 37 kg N_2O per ton of nitric acid). Such high N_2O emission factors indicate that these plants are not operated appropriately with a very high specific consumption (observed values of 1.8 kg HNO_3/kg NH_3 while the average expected is 3.6 kg HNO_3/kg NH_3).

X. Recommendations

32. Based on these considerations, the Meth Panel considers that it is necessary to revise the approved methodologies in order to remove any requirements that currently discourage or provide disincentives to use technologies that result in lower N_2O formation or that could provide incentives to operate plants in a way that maximize N_2O formation during a baseline campaign. This holds in particular for the use of improved primary gauzes and the possible improvement in operating conditions.

33. The Meth Panel identified different options to remove such incentives and came to the conclusion that the use of a cap (default baseline emission factors) is the most appropriate way to address this issue. The use of a default value to determine baseline emissions is the simplest way to ensure that project proponents do not receive more CERs due to a poor operation of a plant during a baseline campaign. The use of default values also ensures that plant operators do not have any disincentives to switch to new technologies that may result in lower N_2O formation. Finally, the use of default values can simplify the methodologies and lower transaction costs considerably.

34. With regard to the choice of the default baseline emission factors, the panel has the view that less conservative emission factors can be used for existing plants than the emission factors provided in the approved methodology ACM0019. In this regard, the panel recommends using an emission factor for each type of technology of the ammonia burner - divided by low, medium and high pressure – calculated using the information of existing CDM projects using methodologies AM0028 and AM0034.

(a) The pane considers more appropriate to use information from CDM projects than IPCC because the uncertainty ranges of IPCC are too wide and because it includes data from plants in Annex I and Non-Annex I countries;

(b) The determination of the proposed emission factors was done by removing outlier nitric acid plants from the set of data to ensure 95% confidence level in the analysis and then the final emission factor was calculated as the average emission factor for each technology minus one standard deviation;

(c) The emission factors will start with the values of 4.4, 5.9 and 8.2 kgN_2O/tHNO_3 for low, medium and high pressure ammonia burners and decrease every year by 0.2;

(d) The reason to include a yearly decrease in the emission factors is to take into account the technological development in the sector.

35. The Meth Panel further concluded that such an improvement to the approved methodologies AM0028 and AM0034 would result in a methodology that is similar to the approved consolidated methodology ACM0019 "N_2O abatement from nitric acid production". The only substantial difference would be that the emission factors for existing plants may be different from the values used in ACM0019.

36. The Meth Panel considers that the improvement in methodology ACM0019 provides incentives to reduce N_2O emissions to the atmosphere, considerably simplifies the monitoring requirements and also allows to project proponents to claim emission reductions from the total production of nitric acid by removing any cap on the eligible amount of nitric acid.

37. For this reason, the Meth Panel recommends to revise the approved methodology AM0028 to limit its applicability to caprolactam plants, to withdraw approved methodologies AM0034 and AM0051 and to revise the methodology ACM0019 with the view to provide the project participants more flexibility and to introduce a cap (default emission factors) for existing plants, while still ensuring that the overall emission reductions are real and additional.

- - - - -

History of the document

Version	**Date**	**Nature of revision**
01.0	21 September 2012	EB 69, Annex # To be considered at EB 69.
Decision Class: Regulatory **Document Type**: Information note **Business Function**: Methodology		