

CDM

MONITORING REPORT #1-Rev4 of "N2O Emission Reduction in Nitric Acid Plant at Paulínia, SP - Brazil" UNFCCC 1011

From: July 28, 2007 To: March 3, 2008

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1 Introduction

The purpose of this monitoring report is to calculate and clarify GHG emission reduction quantity achieved by this project for periodic verification.

This monitoring report covers the project campaign 1 from July 28, 2007 to March 3, 2008.

Duration of the project activity period: Registration Date: 02 Jun 07 Crediting Period: 28 July 07 – 27 July 2014 (renewable)

2. Reference

Approved Baseline and Monitoring methodology:

AM0028 version 4 - Catalytic N2O destruction in the tail gas of Nitric Acid or Caprolactam Production Plants AM0034 version 2 - Catalytic reduction of N2O inside the ammonia burner of nitric acid plants

Project Design Document:

N2O Emission Reduction in nitric acid plant Paulínia, SP, Brazil. Version number of the document: 4 Date: January 23rd, 2007

CDM registration number:

"N2O Emission Reduction in nitric acid plant Paulínia, SP, Brazil" – UNFCCC ref number 1011

3. Definition

- n : Project campaign (in this report, see dates \S 1)
- PDD : Project Design Document of this project "N2O Emission Reduction in nitric acid plant Paulínia, SP, Brazil." Version number of the document: 4, issued on January, 23rd, 2007

4. General description of project

4.1 Project activity

Nitrous oxide (N_2O) is a by-product of nitric acid production. It is of low toxicity but is a greenhouse gas (GHG), whose GWP is large (GWP=310 in the IPCC $2nd$ Assessment Report). Emissions of $N₂O$ will be controlled under the Kyoto Protocol. As far as we are aware, there are however no national or regional regulations or restrictions on the emission of N_2O in Brazil. There are in fact no governmental regulations with quantified emission limits in any non-Annex I countries at this point.

In this project, Rhodia Energy Brazil Ltda. additionally installed a secondary catalyst for the abatement of N_2O emissions in the existing nitric acid plant of Paulínia. This installation reduces the GHG emissions, which would otherwise be released to the atmosphere if the project were not implemented.

The N2O abatement catalyst was installed in the factory site of Paulínia Rhodia Poliamida e Especialidades Ltda. in July, 2007 and the destruction of N_2O started in July 28, 2007.

This project activity was registered at UNFCCC on June $2nd$, 2007 with the number 1011.

4.2 Location of the project activity

The N2O abatement catalyst was installed in the nitric acid plant of Rhodia Poliamida e Especialidades Ltda in Paulínia, SP, Brazil.

4.3 Technology employed by the project activity

The basic Ostwald process involves 3 chemical steps:

A) Catalytic oxidation of ammonia with atmospheric oxygen, to yield Nitrogen Monoxide (or Nitric Oxide). (1) 4 NH3 + 5 O2 \rightarrow 4 NO + 6 H2O

B) Oxidation of the Nitrogen Monoxide to Nitrogen Dioxide or Dinitrogen Tetroxide (2) 2 NO + O2 \rightarrow 2 NO2 <-> N2O4

C) Absorption of the Nitrogen Oxides with water to yield Nitric Acid (3) 3 NO2 + H2O \rightarrow 2 HNO3 + NO

Reaction 1 is favored by lower pressure and higher temperature. Nevertheless, at too high temperature, secondary reactions take place that lower yield (affecting nitric production); then, an optimal is found between 850-950 C, affected by other process conditions and catalyst chemical composition.

Reactions 2 and 3 are favored by higher pressure and lower temperatures. The way in which these three steps are implemented, characterizes the various Nitric Acid processes found throughout the industry. In single pressure (our case) processes ammonia combustion and nitrogen oxide absorption take place at the same working pressure. In dual

pressure or split pressure plants the absorption pressure is higher than the combustion pressure.

Nitrous Oxide formation

Nitrous oxide is formed during the catalytic oxidation of Ammonia. Over a suitable catalyst, typically 90-99% of the fed Ammonia is converted to Nitric Oxide (NO) according to reaction (1) above. The remainder participates in undesirable side reactions that lead to Nitrous Oxide (N2O), among other compounds.

Possible side reactions during oxidation of Ammonia: (4) 4 NH3 + 4 O2 \rightarrow 2 N2O + 6 H2O (Nitrous Oxide formation). (5) 4 NH3 + 3 O2 \rightarrow 2 N2 + 6 H2O (6) 2 NO \rightarrow N2 + O2 (7) 4 NH3 + 6 NO \rightarrow 5 N2 + 6 H2O

N2O abatement technology classification

The potential technologies (proven and under development) to treat N2O emissions at Nitric acid plants, have been classified as follow, based on the process location of the treatment device:

Primary: N2O is prevented from forming in the oxidation gauzes.

Secondary: N2O once formed, is eliminated anywhere between the outlet of the ammonia oxidation gauzes and the inlet of the absorption tower.

Tertiary: N2O is removed at the tail gas, after the absorption tower and previous to the expansion turbine.

Quaternary: N2O is removed following the expansion turbine, and before the stack.

Selected technology for the project

The technology applied at Paulínia nitric acid plant involves the installation of a new catalyst, not previously installed, below the oxidation gauzes ("secondary catalyst") with the purpose of decomposing N_2O .

This choice has the following advantages:

- Catalyst does not consume electricity, steam, fuels or reducing agents (all sources of leakage) to eliminate N_2O emissions. Therefore, operating costs are reduced to the cost of the catalyst itself.
- Installation is extremely simple and does not require new process unit or redesign of existing one. The main investment consists in the implantation of the measurement equipments (analyzer, flow meter, etc.).
- Installation can be simultaneously done with the primary gauze changing; without loss in production due to incrementing downtime.

This "secondary catalyst" decomposes N₂O without affecting Nitric Acid production. Typically the catalyst has a very high activity for N_2O decomposition; in a typical medium pressure plant. Basically, high level (more than 80%) of N₂O abatement can be reached. The catalyst selected as secondary catalyst has showed the following specific advantages:

- No measurable effect on ammonia to nitric oxide yield.
- Low level of N_2O in tail gas is achievable by adjusting the catalyst bed thickness.

• No additional greenhouse gases or other emissions are generated by the reactions on the N₂O abatement catalyst.

The Nitric Acid Plant at Paulínia uses a basket structure that gives support to the nitric acid generation gauze. For creating space to insert the new catalyst, some layers of Raschig rings were removed from the basket. Once the secondary catalyst is installed, the primary gauzes are placed on top of the basket, as usual. Then, the secondary catalyst acts as support system for the primary gauze pack and both catalysts are in close contact.

The N₂O abatement catalyst supplier is obliged by Rhodia Energy Brazil Ltda. to take back the catalyst at the end of their useful life and refine, recycle or dispose of them according to the prevailing EU standards and hence fulfill sustainability standards.

5. Project Boundary

The project boundary encompasses the complete process equipment for the nitric acid production.

The only GHG emission important to the project activity is N_2O contained in the waste stream exiting the stack.

An overview of all emission sources inside the project boundary can be verified below:

6. Baseline and monitoring methodology applied to the project activity

The baseline has been established through continuous monitoring of both $N₂O$ concentration and gas flow volume in the stack of the nitric acid plant for one complete campaign prior to project implementation.

6.1 Determination of the permitted operating conditions of the nitric acid plant to avoid overestimation of baseline emissions:

In order to avoid the possibility that the operating conditions of the nitric acid production plant are modified in such a way that increases N_2O generation during the baseline campaign, the normal ranges for operating conditions have been determined for the following parameters:

- (i) oxidation temperature;
- (ii) oxidation pressure;
- (iii) ammonia gas flow rate, and
- (iv) air input flow rates.

The permitted range has been established using the procedures described below. Note that data for these parameters are routinely logged in the process control system of the plant.

i. Oxidation temperature and pressure:

Process parameters monitored are the following:

 $\overline{\text{O}}$ T_h $\overline{\text{O}}$ Oxidation temperature for each hour (\degree C)

 OP_h Oxidation pressure for each hour (kgf/cm² gauge)

 $\text{OT}_{\text{normal}}$ Normal range for oxidation temperature (°C)

OP_{normal} Normal range for oxidation pressure (kgf/cm^2 gauge)

The "permitted range" for oxidation temperature and pressure has been determined using historical data for the operating range of temperature and pressure from the five (5) campaigns previous to the baseline campaign.

ii. Ammonia gas flow rates and ammonia to air ratio input into the ammonia oxidation reactor (AOR):

Parameters monitored:

AFR Ammonia gas flow rate to the AOR $(tNH₃/h)$

 AFR_{max} Maximum ammonia gas flow rate to the AOR (tNH₃/h)

AIFR Ammonia to air ratio (%)

AIFR_{max} Maximum ammonia to air ratio $\binom{9}{0}$

The upper limits for ammonia flow and ammonia to air ratio have been determined using historical maximum operating data for hourly ammonia gas and ammonia to air ratio for the five (5) campaigns previous to the baseline campaign.

6.2 Determination of baseline emission factor: measurement procedure for N2O concentration and gas volume flow

N₂O concentration and gas volume flow have been monitored throughout the baseline campaign. The monitoring system is installed using the European Norm 14181 (2004). This

monitoring system provides separate readings for N_2O concentration (NCSG) and gas flow volume (VSG) at the stack for every two seconds during operation of the plant. Error readings due downtime or malfunction and extreme values are to be automatically eliminated from the output data series by the monitoring system.

Measurement results can be distorted before and after periods of downtime or malfunction of the monitoring system and can lead to mavericks. To eliminate such extremes and to ensure a conservative approach, the following statistical evaluation has been applied to the complete data series of N_2O concentration as well as to the data series for gas volume flow. The statistical procedure has been applied to data obtained after eliminating data measured for periods where the plant operated outside the permitted ranges:

a) Calculate the sample mean (x)

- b) Calculate the sample standard deviation (s)
- c) Calculate the 95% confidence interval (equal to 1.96 times the standard deviation)
- d) Eliminate all data that lie outside the 95% confidence interval
- e) Calculate the new sample mean from the remaining values (volume of stack gas (VSG) and N_2O concentration of stack gas (NCSG)).

The average mass of N_2O emissions per hour is estimated as product of the NCSG and VSG. The N_2O emissions per campaign are estimates product of N_2O emission per hour and the total number of complete hours of operation of the campaign (OH) using the following equation:

$BE_{BC} = VSG_{BC}$ x $NCSG_{BC}$ x 10^{-9} x OH_{BC}

where:

 BE_{BC} : total N₂O emissions during the baseline campaign (t N₂O)

VSG_{BC}: mean gas volume flow rate at the stack in the baseline measurement period (Nm³/h) NCSG_{BC}: mean concentration of N₂O in stack gas in the baseline campaign (mg N₂O /Nm³) OH_{BC} : operating hours of the baseline campaign (h)

The plant specific baseline emissions factor representing the average $N₂O$ emissions per tonne of nitric acid over the baseline campaign has been derived by dividing the total mass of N_2O emissions by the total output of 100% concentrated nitric acid for that period. The overall uncertainty of the monitoring system (UNC) has been determined and the measurement error has been expressed as a percentage.

The N₂O emission factor per tonne of nitric acid produced in the baseline period (EF_{BL}) is reduced by the estimated percentage error as follows:

$EF_{BL} = (BE_{BC} / NAP_{BC}) (1 - UNC/100)$

where:

EF_{BL} : baseline N₂O emissions factor (t N₂O /t HNO₃)

 BE_{BC} : total N₂O emissions during the baseline campaign (t N₂O)

 NAP_{BC} : nitric acid production during the baseline campaign (t $HNO₃$)

UNC : overall uncertainty of the monitoring system (%), calculated as the combined uncertainty of the applied monitoring equipment

In the absence of any national or regional regulations for N_2O emissions in Brazil, the resulting EF_{BL} has been used as the baseline emission factor.

The gauze supplier and gauze composition during the baseline campaign have been the same as used during the historic campaigns when the permitted operating conditions were established. As a consequence, the E_{BL} derived is valid.

As the plant operated within the permitted range of normal operating conditions for more than 50% of the time, the baseline campaign can be considered valid and the resulting EF_{BI} can be used to calculate the resulting emission reduction of the project.

6.3 Baseline Campaign Length

In order to take into account the variations in campaign length and its influence on $N₂O$ emission levels, the historic campaign lengths and the baseline campaign length are to be determined and compared to the project campaign length. Campaign length is defined as the total number of metric tonnes of nitric acid at 100% concentration produced with one set of gauzes.

The average historic campaign length (CL_{normal}) defined as the average campaign length for the historic campaigns used to define operating condition (the previous five campaigns), has been used as a cap on the length of the baseline campaign described in the PDD.

If Baseline Campaign Length (CL_{BL} **)** $\leq CL_{normal}$ **, all N₂O values measured during the** baseline campaign can be used for the calculation of E_{BL} (subject to the elimination of data that was monitored during times where the plant was operating outside of the "permitted range").

If $CL_{BL} > CL_{normal}$, N₂O values that were measured beyond the length of CL_{normal} during the production of the quantity of nitric acid (i.e. the final tonnes produced) are to be eliminated from the calculation of E_{BL} .

At Paulínia nitric acid plant the value obtained for CL_{normal} was 29 695 t HNO₃. The baseline campaign was conducted from September 15, 2006 to April 05, 2007 and achieved a production bigger than that value. Therefore, according to the rules indicated above the CL_{BL} is 29 695 t HNO₃, which was reached on March 20, 2007.

6.4 Statistical Tests comparing Baseline Campaign with "normal" operating conditions

In accordance with AM0034, statistical tests were performed to compare the average values of the permitted operating conditions with the average values obtained during the baseline campaign.

If the mean values of OT_h and OP_h of the baseline campaign fall within the 95% confidence interval of normal operating conditions, and if the mean values of AFR and AIFR of the baseline campaign are lower than AFR_{max} and $AIFR_{\text{max}}$, respectively, then the baseline campaign is considered to be representative of a normal campaign ,

According to these tests the baseline campaign was found to be representative of a normal campaign.

6.5 Leakage

As defined in AM0034, no leakage emission calculation is required since no leakage emissions have occurred as a result of the project activity now nor are expected in the future.

6.6 Project emissions

During the project activity, N_2O concentration, gas volume flow in the stack of the nitric acid plant together with temperature and pressure of ammonia gas flow and ammonia-to-air ratio are measured continuously.

The statistical evaluation described below was applied to the baseline data and to this project campaign.

- a) Calculate the sample mean (x)
- b) Calculate the sample standard deviation (s)
- c) Calculate the 95% confidence interval (equal to 1.96 times the standard deviation)
- d) Eliminate all data that lie outside the 95% confidence interval
- e) Calculate the new sample mean from the remaining values

The emissions due to the project activity in a given campaign (PE_n) are the total emissions of N₂O during the nth campaign:

$PE_n = VSG \times NCSG \times 10^{-9} \times OH$ (t N₂O)

In order to take into account possible long-term emissions trends over the duration of the project activity and to take a conservative approach a moving average emission factor shall be estimated as follows:

Step1: estimate campaign specific emissions factor for each campaign during the project's crediting period is obtained by dividing the total mass of $N₂O$ emissions during that campaign (PE_n) by the total production of 100% concentrated nitric acid (NAP) during that same campaign.

For example, for campaign n the campaign specific emission factor would be:

$EF_n = PE_n / NAP_n$ (t $N_2O/t HNO_3$)

Step 2: estimate a moving average emissions factor (EF_{ma}) at the end of a campaign n as follows:

$EF_{ma, n} = (EF_1 + EF_2 + ... + EF_n) / n (t N_2O/t HNO_3)$

This process is repeated for each campaign so that a moving average, EF_{man} , is established over time, becoming more representative and precise with each additional campaign.

To calculate the total emission reductions achieved in a campaign the higher of the two values EF_{man} and EF_{n} shall be applied as the emission factor relevant for the particular campaign to be used to calculate emissions reductions (EF_p) . Thus:

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If $EF_{\text{ma,n}} > EF_n$ **then** $EF_p = EF_{\text{ma,n}}$ **If** $EF_{\text{man}} < EF_{\text{n}}$ **then** $EF_{\text{n}} = EF_{\text{n}}$

As this is the first project campaign, then $n=1$ and $EF_{ma,1} = EF_1$

6.7 Minimum project emission factor

A campaign-specific emissions factor shall be used to cap any potential long-term trend towards decreasing N_2O emissions that may result from a potential built up of platinum deposits. After the first ten (10) campaigns of the crediting period of the project, the lowest EF_n observed during those campaigns will be adopted as a minimum (EF_{min}). If any of the later project campaigns results in a EF_n that is lower than EF_{min} , the calculation of the emission reductions for that particular campaign shall use EF_{min} and not EF_n .

Not applicable for the moment as this is the first project campaign.

6.8 Project Campaign Length

If the length of each individual project campaign CL_n is longer than or equal to the average historic campaign length CL_{normal} , then all N₂O values measured during the baseline campaign can be used for the calculation of EF (subject to the elimination of data from the Ammonia/Air analysis, see above).

If $CL_n < CL_{normal}$, recalculate EF_{BL} by eliminating those N₂O values that were obtained during the production of tonnes of nitric acid beyond the CL_n (i.e. the last tones produced) from the calculation of EF_n .

The length of the first project campaign was longer than CL_{normal} , so all N_2O values measured during the baseline campaign can be used for the calculation of EF.

6.9 Emission Reductions

The emission reductions for the project activity over a specific campaign are determined by deducting the campaign-specific emission factor from the baseline emission factor and multiplying the result by the production output of 100% concentrated nitric acid over the campaign period and the GWP of N_2O :

$ER = (EF_{BL} - EF_P)$ x NAP x GWP_{N2O} (tCO₂e)

As stated in AM0034, the nitric acid production (NAP) during the project campaign shall not exceed the design capacity of the nitric acid plant on a yearly basis.

The nameplate capacity of the Paulínia Nitric Acid Plant is 55 900 metric tonnes per year of 100% nitric acid and the product is sent to storage as a 60% solution. Therefore, the nitric acid plant shall not be eligible to earn CERs for any tonnes of nitric acid produced exceeding that value on a yearly basis.

In order to verify the compliance with such production cap for the calculation of CERs, in this project activity the yearly production is calculated based on the anniversary date of the project. The N2O emissions reduction of this project started up on July 28, 2007 when the first load of secondary catalyst initiated the first project campaign. Thus for any project campaign it is verified whether the accumulated production since the last date July 28 has exceeded 55 900 tonnes. If that limit is exceeded then no CERs are claimed on the nitric acid production made from the day the yearly cap is achieved until the new date July 28. This verification is automatically made in the "Workbook ER_Nitric-Paulínia.xls" which is used to store and calculate all the data pertinent to the project campaigns.

6.10 Data and parameters of baseline campaign – Annex 1

6.11 Data and parameters of the present project campaign – Annex 2

7. Monitoring plan:

7.1 General description

The overall responsibility, including the publication of the monitoring report, is with Rhodia Energy SAS represented by the CO2 operations director.

The monitoring process is under the responsibility of the Nitric Acid Plant Manager. The description of these activities is made at the Data Handling Protocol. This document is included in the plant quality system and is available to audit.

The monitoring procedures for baseline and project campaigns are described below.

7.1.1 Data collection

The production supervisor and/or plant operations technician are responsible by data collection during plant operation.

7.1.2 Data processing

These data are processed, validated, adjusted, if necessary, and recorded. The nitric acid plant process engineer is in charge of programming all formulae in the spreadsheets which are used. The plant operations technician processes the data, checks the data for consistency, validates them, and records them every day as an electronic file. In case of failure of an instrument, or inconsistency of the data, he adjusts the data according to the Data Handling Protocol. In case the failure is not covered by the procedure, the nitric acid plant Manager makes the decision to correct the figures or to abandon the data.

7.1.3 Data archiving

The nitric acid plant Production Engineer or Process Engineer is responsible for archiving the data. Once validated, the data are input in an electronic folder and protected against any modification. A backup of all the data is made every day on the plant server. Both original document and the backup file are kept for the project crediting period.

7.1.4 Calculation of Emission Reductions

Calculation of emission reductions is done after each campaign by the nitric acid plant Production Engineer or Process Engineer, based on the campaign data, and validated by the nitric acid plant Manager. This last one is responsible, too, by declaring Emission Reductions.

7.1.5 Training

As Paulínia nitric acid plant is certified in ISO 9001:2000, the requirement 6.2.2 Competence, Awareness and Training of ISO 9001:2000 is met. There is a training procedure for the nitric acid plant (ISAL-EQ-002) and the changes introduced due to this project were done according to that procedure for the operation team. For the lab team, which is responsible for the adjustments, calibration and operation of the N2O analyzer, the corresponding training was done according to the procedure PIP-DCA-RH-013.

7.2 Good monitoring practice and performance characteristics

The nitric acid plant on Rhodia site at Paulínia is ISO9001 and ISO14000 certified.

All measured variables to be collected for the baseline and on project activity campaigns are considered critical process variable, The critical variables instruments calibration plan follow the critical variables procedures, and are included in the scope the yearly ISO9001 audit.

The European Norm EN 14181:2004 is recommended as guidance regarding the selection, installation and operation of the Automatic Measuring System (AMS) under Monitoring Methodology AM0034, and stipulates three levels of Quality Assurance Levels (QAL):

QAL1: Suitability of the AMS for the specific measuring task.

The EN 14181: 2004 QAL1 report was provided by the equipment manufacturer considering the performance characteristics as measured by a qualified Technical Inspection Authority. The QAL1 report confirmed that N2O analyzer (an AO 2000- URAS 14 NDIR supplied by ABB GmbH) is suitable to perform the indicated analysis (N2O concentration). The equipment manufacture report was handed to the DOE for verification.

QAL2: Validation of the AMS following the installation.

QAL2 describes a procedure for the determination of the calibration function and its variability, by means of certain number of parallel measurements, performed with a Standard Reference Method (SRM). The testing performing the measurements with the SRM shall have an accredited quality assurance system according to EN ISO/IEC 17025 or relevant (national) standards.

QAL2 tests were performed for N_2O Analyzer on October 2006 and on August 2007. QAL2 test for stack gas flow meter was performed on June 2007. The QAL2 reports were made available for verification of DOE.

QAL3: Ongoing quality assurance during operation.

According to EN 14181: 2004 drift and precision are checked in order to demonstrate that the AMS is in control during its operations so that it continues to function within the required specification for uncertainty. This is achieved by conducting periodic zero and span checks on the AMS, and evaluating results obtained using CUSUM (Cumulative Sum) control charts as recommended in Annex C of EN 14181:2004. All monitoring equipment has been serviced and maintained according to the manufacturer's instructions and international standards by qualified personnel. Calibration and maintenance records are well kept at site and available for auditing purposes.

8. GHG emission reductions calculations

8.1 Baseline emissions

For baseline emission factor determination, the N_2O concentration and the gas volume flow rate were monitored throughout the baseline campaign. Hourly average readings for N₂O concentration and gas flow rate were calculated from every 2-second raw data. Error readings (e.g. downtime or malfunction) and extreme values were eliminated from the output data series.

Determination of the normal operating conditions

To ensure that data obtained during baseline campaign are representative of the actual GHG emissions from the source plant, a set of process parameters known to affect N_2O generation have been set based on plant historical operating conditions and plant design data. Those parameters, called by the methodology normal operating conditions, are: oxidation temperature, oxidation pressure, ammonia flow to the reactor and ammonia-to-air flow ratio.

The normal operating conditions which are in the PDD are the technical operating limits of the nitric acid plant in Paulínia. The upper limits for oxidation temperature and oxidation pressure are given by safety criteria, while for the lower limit corresponds to operation limit, and is part of the safety system of the plant. Both the lower limit and the upper limit are recorded in the Plant Operating Manual (a document controlled in the Rhodia Quality System) and are also in the plant operators log sheet. The ammonia flow to the reactor and ammonia-to-air flow ratio values are based on the maximum value of each one taking into account the five (5) operational campaigns.

Normal operating conditions determined for nitric acid plant at Paulínia are:

In compliance with the methodology, the PDD states in paragraph B.6.1.1.i that "The "permitted range" for oxidation temperature and pressure is to be determined using historical data for the operating range of temperature and pressure from the previous five campaigns". In consequence, Rhodia used this criterion to determine the "permitted range" which is the range of operating parameters that should be used to determine the valid N2O data for estimating the baseline emission factor.

According to the criterion selected, the permitted range is determined through a statistical analysis of the historical data in which the time series data is to be interpreted as a sample for a stochastic variable. All data that falls within the upper and lower 2.5% percentiles of the sample distribution is defined as abnormal and shall be eliminated. The permitted range of operating temperature and pressure is then assigned as the historical minimum (value of parameter below which 2.5% of the observation lie) and maximum operating conditions (value of parameter exceeded by 2.5% of observations). For complementing, as for normal operation conditions, ammonia flow to the reactor and ammonia-to-air flow ratio values are based on the maximum value of each one taking into account also the five (5) operational campaigns.

Permitted range operating conditions determined for nitric acid plant at Paulínia are:

Only those N_2O measurements taken when the plant was operating within the permitted range were considered in the calculation of baseline emissions.

After eliminating data measured when the plant was operating outside the permitted conditions, the following statistical procedure was applied.

a) Calculated the sample mean (x)

b) Calculated the sample standard deviation (s)

c) Calculated the 95% confidence interval (equal to 1.96 times the standard deviation)

d) Eliminated all data that lied outside the 95% confidence interval

e) Calculated the new sample mean from the remaining values (volume of stack gas (VSG) and N_2O concentration of stack gas (NCSG))

The baseline emissions are calculated using the following formulae:

$BE_{BC} = VSG_{BC}$ x $NCSG_{BC}$ x 10^{-9} x OH_{BC}

$EF_{BL} = (BE_{BC} / NAP_{BC}) (1 - UNC/100)$

where:

UNC : overall uncertainty of the monitoring system $(\%)$, calculated as the combined uncertainty of the applied monitoring equipment

Another parameter that is measured and must be compared with the normal value is the campaign length.

Normal campaign (CL_{normal}) length value obtained for nitric acid plant at Paulínia was 29 695 t.

According to AM0034:

If Baseline Campaign Length (CL_{BL} **)** $\leq CL_{normal}$ **, all N₂O values measured during the** baseline campaign can be used for the calculation of E_{BL} (subject to the elimination of data that was monitored during times where the plant was operating outside of the "permitted range").

If $CL_{BL} > CL_{normal}$, N₂O values that were measured beyond the length of CL_{normal} during the production of the quantity of nitric acid (i.e. the final tonnes produced) are to be eliminated from the calculation of E_{BL} .

At Paulínia plant, baseline campaign took place from September 15, 2006 to April 05, 2007. The production achieved during that period was $32\,330$ t which is bigger than CL_{normal} (29) 695 t). Therefore, according to the rules indicated above the CL_{BL} is 29 695 t HNO₃, which was reached on March 20, 2007.

As the $CL_{BL} > CL_{normal}$ then was used the CL_{normal} as NAP_{BC} .

The values obtained in the baseline campaign are:

The emission factor for the baseline campaign (EF_{BL}) is then calculated as follow:

 $BE_{BC} = VSG_{BC}$ x $NCSG_{BC}$ x 10^{-9} x OH_{BC}

 $BE_{BC} = 23\,456 \times 1756 \times 10^{-9} \times 4\,424.6 = 182.278 \text{ t N}_2\text{O}$

 $E\mathbf{F}_{BL} = (B\mathbf{E}_{BC} / NAP_{BC}) \mathbf{x} (1 - \text{UNC}/100)$

 $EF_{BL} = (182.278 / 29695)$ x $(1 - 6.12/100) = 0.005763$ t N₂O/t HNO₃

The actual value of BE_{BC} is slightly different from the value obtained by direct calculation shown above due to a rounding effect. The value of E_{BL} is more accurate calculated in the workbook.

The plant baseline campaign was valid since for more than 50% of the duration of the campaign, the plant was operated within the normal operating conditions. The value obtained was 82.37% for both NCGS and VSG.

8.2 Project emissions

The monitoring system is installed according to the guidance document EN 14181 and provides separate readings for N_2O concentration and gas flow volume for a defined period of time (e.g. every hour of operation, i.e. an average of the measuring values of the past 60 minutes). Error readings (e.g. downtime or malfunction) and extreme values are eliminated from the output data series.

The emissions due to project activity in a campaign (PE_n) are the total emissions of N₂O during the nth campaign were obtained from the following formulae (equations 3 and 4 from AM0034):

$PE_n = VSG \times NCSG \times 10^{-9} \times OH$

$EF_n = PE_n / NAP_n$

where:

- PE_n : total Project emissions of the nth campaign (t N₂O)
- VSG : mean stack gas volume flow rate for the nth project campaign (Nm^3/h)
- NCSG : mean concentration of N₂O in the stack gas for the project campaign (mg N₂O/Nm³)
- OH : number of operating hours in the project campaign (h)
- EF_n : emission factor calculated for the nth campaign (t N₂O/t HNO₃)
- NAP_n : nitric acid production in the nth campaign (t 100% HNO₃)

The following values were obtained in this project campaign:

The emission factor for this project campaign (EF_n) is then calculated as follow:

$PE_n = VSG \times NCSG \times 10^{-9} \times OH$

 $PE_n = 23\,442 \times 165 \times 10^{-9} \times 5\,237.5 = 20.237 \text{ t N}_2\text{O}$

 $EF_n = PE_n / NAP_n$

$EF_n = 20.237 / 35838 = 0.000565 t N_2O/t HNO₃$

The actual value of PE_n is slightly different from the value obtained by direct calculation shown above due to a rounding effect. The value of EF_n is more accurate calculated in the workbook.

Since this is the 1_{st} project campaign then n=1 and $EF_{ma,1} = EF_1$. The value of EF_n can be used as such for the emission reduction calculation of this campaign.

8.3 Emission reductions

The emission reductions for the project activity over a specific campaign is determined by deducting the campaign-specific emission factor from the baseline emission factor and multiplying the result by the production output of 100% concentrated nitric acid over the campaign period and the GWP of N_2O , as according to AM0034 version 2:

 $ER = (EF_{BL} - EF_P)$ x NAP x GWP_{N2O}

where:

ER : emission reductions of the project for the specific campaign (t $CO₂e$)

 NAP : nitric acid production for the project campaign (t $HNO₃$). The maximum value of NAP shall not exceed the design capacity.

 EF_{BL} : baseline emissions factor (t N₂O/t HNO₃)

 EF_P : emissions factor used to calculate the emissions from this particular campaign (i.e. the higher of $EF_{ma,n}$ and EF_n)

 GWP_{N2O} : global warming potential of N₂O set as 310 t CO₂e/t N₂O by the IPCCC

The total emission reduction achieved by this project activity during this campaign is therefore

$ER = (EF_{BL} - EF_{P})$ x NAP x GWP_{N2O}

ER = $(0.005763 - 0.000565)$ x 35 838 x 310 = 57 751 t CO₂e

The actual value of ER is slightly different from the value obtained by direct calculation shown above due to a rounding effect. The value of ER is more accurate calculated in the workbook.

The above emission reduction covers the generation of N2O in the nitric acid production during this campaign.

Annex 1 – Data and parameters of baseline campaign

Annex 2 – Data and parameters of the present project campaign

