

## CDM MONITORING REPORT #2-Rev.02 of "N2O Emission Reduction in Nitric Acid Plant at Paulínia, SP - Brazil" UNFCCC 1011

From: March 4, 2008 To: September 14, 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 2 from March 4 (production campaign started on March 8), 2008 to September 14, 2008 (end of production campaign).

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:**

<u>AM0028 version 4</u> - Catalytic N<sub>2</sub>O destruction in the tail gas of Nitric Acid or Caprolactam Production Plants <u>AM0034 version 2</u> - Catalytic reduction of N<sub>2</sub>O 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 23<sup>rd</sup>, 2007

#### **CDM registration number:**

"N<sub>2</sub>O Emission Reduction in nitric acid plant Paulínia, SP, Brazil" – UNFCCC ref number 1011

#### 3. Definition

- n : Project campaign (in this report, see dates § 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 23<sup>rd</sup>, 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 2<sup>nd</sup> Assessment Report). Emissions of N<sub>2</sub>O 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<sub>2</sub>O 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 2<sup>nd</sup>, 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).

 $(1) 4 \text{ NH}_3 + 5 \text{ O}_2 \rightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$ 

B) Oxidation of the Nitrogen Monoxide to Nitrogen Dioxide or Dinitrogen Tetroxide (2) 2 NO +  $O_2 \rightarrow 2 NO_2 \Leftrightarrow N_2O_4$ 

C) Absorption of the Nitrogen Oxides with water to yield Nitric Acid (3)  $3 \text{ NO}_2 + \text{H}_2\text{O} \rightarrow 2 \text{ HNO}_3 + \text{NO}$ 

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 (N<sub>2</sub>O), among other compounds.

Possible side reactions during oxidation of Ammonia: (4) 4 NH<sub>3</sub> + 4 O<sub>2</sub>  $\rightarrow$  2 N<sub>2</sub>O + 6 H<sub>2</sub>O (Nitrous Oxide formation). (5) 4 NH<sub>3</sub> + 3 O<sub>2</sub>  $\rightarrow$  2 N<sub>2</sub> + 6 H<sub>2</sub>O (6) 2 NO  $\rightarrow$  N<sub>2</sub> + O<sub>2</sub> (7) 4 NH<sub>3</sub> + 6 NO  $\rightarrow$  5 N<sub>2</sub> + 6 H<sub>2</sub>O

#### 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: N<sub>2</sub>O is prevented from forming in the oxidation gauzes.

Secondary:  $N_2O$  once formed, is eliminated anywhere between the outlet of the ammonia oxidation gauzes and the inlet of the absorption tower.

Tertiary:  $N_2O$  is removed at the tail gas, after the absorption tower and previous to the expansion turbine.

Quaternary: N<sub>2</sub>O 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<sub>2</sub>O 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  $N_2O$  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  $N_2O$  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<sub>2</sub>O 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 N<sub>2</sub>O 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  $N_2O$  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:

	Source	Gas	Included?	Justification/Explanation
ne	Nitric Acid Plant (Burner Inlet to Stack	CO <sub>2</sub>	No	The process does not lead to any $CO_2$ and $CH_4$ emissions
aseliı		CH <sub>4</sub>	No	
		N <sub>2</sub> O	Yes	
Activity	Nitric Acid Plant (Burner Inlet to Stack)	CO <sub>2</sub>	No	The process does not lead to any CO <sub>2</sub> and CH <sub>4</sub> emissions
		CH <sub>4</sub>	No	
		N <sub>2</sub> O	Yes	
ject	Leakage emissions from	CO <sub>2</sub>	No	
Pro	production, transport, operation and decommissioning of the catalyst	CH <sub>4</sub>	No	No leakage emissions are expected
		N <sub>2</sub> O	No	1



## 6. Baseline and monitoring methodology applied to the project activity

The baseline has been established through continuous monitoring of both  $N_2O$  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:

OT<sub>h</sub> Oxidation temperature for each hour (°C)

- OP<sub>h</sub> Oxidation pressure for each hour (kgf/cm<sup>2</sup> gauge)
- $OT_{normal}$  Normal range for oxidation temperature (°C)
- OP<sub>normal</sub> Normal range for oxidation pressure (kgf/cm<sup>2</sup> 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 (tNH<sub>3</sub>/h)

AFR<sub>max</sub> Maximum ammonia gas flow rate to the AOR (tNH<sub>3</sub>/h)

AIFR	Ammonia to air ratio (%)
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AIFR<sub>max</sub> Maximum ammonia to air ratio (%)

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 $N_2O$ concentration and gas volume flow

 $N_2O$  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<sub>2</sub>O 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 the 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:

#### $BE_{BC} = VSG_{BC} \times NCSG_{BC} \times 10^{-9} \times OH_{BC}$

where:

 $BE_{BC}$  : total N<sub>2</sub>O emissions during the baseline campaign (t N<sub>2</sub>O)

 $VSG_{BC}$ : mean gas volume flow rate at the stack in the baseline measurement period (Nm<sup>3</sup>/h) NCSG<sub>BC</sub>: mean concentration of N<sub>2</sub>O in stack gas in the baseline campaign (mg N<sub>2</sub>O /Nm<sup>3</sup>) OH<sub>BC</sub> : total operating hours of the baseline campaign (h)

The plant specific baseline emissions factor representing the average  $N_2O$  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 the baseline campaign (see also item 6.3) during that period. The overall uncertainty of the monitoring system (UNC) has been determined and the measurement error has been expressed as a percentage.

The  $N_2O$  emission factor per tonne of nitric acid produced in the baseline period (EF<sub>BL</sub>) is reduced by the estimated percentage error as follows:

#### $\mathbf{EF}_{BL} = (\mathbf{BE}_{BC} / \mathbf{NAP}_{BC}) (1 - \mathbf{UNC}/100)$

where:

 $EF_{BL}$  : baseline N<sub>2</sub>O emissions factor (t N<sub>2</sub>O /t HNO<sub>3</sub>)

- $BE_{BC}$ : total N<sub>2</sub>O emissions during the baseline campaign (t N<sub>2</sub>O)
- NAP<sub>BC</sub>: total nitric acid production of the baseline campaign (t HNO<sub>3</sub>)
- 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  $EF_{BL}$  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  $EF_{BL}$  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  $N_2O$  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 tons 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 N<sub>2</sub>O values (NCSG and VSG) measured during the baseline campaign can be used for the calculation of EF<sub>BL</sub> (subject to the elimination of data that were monitored during times when the plant was operating outside of the "permitted range").

If  $CL_{BL} > CL_{normal}$ , the calculation of the baseline N<sub>2</sub>O emission factor needs to include the nitric acid production values measured beyond the normal campaign length while N<sub>2</sub>O values (NCSG and VSG) measured during the same period should be eliminated, following the guidance issued by EB45 (EB45 report, agenda sub-item 3 (f): Matters relating to the issuance of CERs and the CDM registry, article 62.0.i)

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

In accordance with AM0034 version 2, 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<sub>max</sub> and AIFR<sub>max</sub>, 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 version 2, 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<sub>2</sub>O 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 N<sub>2</sub>O during the nth campaign:

## $PE_n = VSG \times NCSG \times 10^{-9} \times OH (t N_2O)$

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  $N_2O$  emissions during that campaign (PE<sub>n</sub>) 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,  $EF_{ma,n}$ , 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  $EF_{ma,n}$  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:



If  $EF_{ma,n} > EF_n$  then  $EF_p = EF_{ma,n}$ If  $EF_{ma,n} < EF_n$  then  $EF_p = EF_n$ 

As this is the second project campaign, n is equal "2", then as defined by methodology, it will be evaluated the obtained values of  $EF_{ma,2}$  and  $EF_2$  and established which value will be used for calculating the emission reduction.

#### 6.7 Minimum project emission factor

A campaign-specific emissions factor shall be used to cap any potential long-term trend towards decreasing N<sub>2</sub>O 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<sub>min</sub> and not EF<sub>n</sub>.

Not applicable for the moment as this is the second 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<sub>normal</sub>, then all N<sub>2</sub>O 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 N<sub>2</sub>O values that were obtained during the production of tons of nitric acid beyond the CL<sub>n</sub> (i.e. the last tons produced) from the calculation of  $EF_n$ .

The length of the second project campaign will be compared with CL<sub>normal</sub> for verifying if it will be necessary recalculate  $EF_{BL}$ .

#### **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<sub>2</sub>O:

#### $ER = (EF_{BL} - EF_P) \times NAP \times GWP_{N2O} (tCO_2e)$

As stated in AM0034 version 2, 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 tons 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 tons 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 N<sub>2</sub>O 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 tons. 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 CO<sub>2</sub> operations director.

The monitoring process is under the responsibility of the Nitric Acid Plant Manager. The description of these activities is made in 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 or the Production 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. The Workbook is saved both electronically and on paper.

#### 7.1.4 Calculation of Emission Reductions

Calculation of emission reductions is done after each campaign by the nitric acid plant Production Engineer or the 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 N<sub>2</sub>O 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 version 2, and stipulates three levels of Quality Assurance Levels (QAL) and an Annual Surveillance Test (AST):

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  $N_2O$  analyzer (an AO 2000- URAS 14 NDIR supplied by ABB GmbH) is suitable to perform the indicated analysis ( $N_2O$  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.

The last QAL2 tests were performed for  $N_2O$  Analyzer on March 2008 . The QAL2 report was 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.

#### AST: Annual validation of AMS

Taking into account EN 14181:2004 this test is to be done with the goal to evaluate whether the measured values obtained from AMS still meet the uncertainty criteria – as demonstrated in the previous QAL2 test. It also verifies if the calibration function obtained during the previous QAL2 test is still valid. The validity of the measured values obtained with the AMS is checked by means of a series of functional tests as well as by the performance of a limited number of parallel measurements using a appropriate SRM.



Until the end of this period it was not necessary to perform the AST for  $N_2O$  analyzer since the time between QAL2 tests has not reached one year.

#### 7.3 Environmental Impact

Rhodia has created the procedure SG-014 as part of its ISO9001 and ISO14000 systems requirements and therefore to continually track and evaluate any modification in national or regional regulations that could modify the emission limits for  $NO_x$  and  $N_2O$ . According to that procedure Rhodia has hired an external company, which is responsible for following the evolution of regulations concerning environment and safety standards. GSIMAP (a department of the Paulínia Industrial Platform, in charge of safety, security and environmental issues) receives a quarterly report that allows anticipating any change in  $N_2O$  and  $NO_x$  emission limits. This report is analyzed by GSIMAP and the results are shared with all plants on site.

Monitoring of the NO<sub>x</sub> content in the waste gas is required by local environmental legislation stated in the Commitment Agreement (TAC) signed with the Public Attorney of the State of São Paulo. NOx in the gaseous effluent can be randomly checked by the environmental agency Cetesb through sampling and analysis by an external laboratory. Analytical data show that the plant complies with the established environmental standard.

Online analysis of the  $NO_x$  content in the gaseous effluents is carried out to verify such discharge from the Nitric Acid plant.

Parameter	Unit	Value as per	Analytical results in
		applicable standard	this campaign
NO <sub>x</sub>	vppm	200 max	Average of 176 and
		at least 95% of time	Less than 200
			for 100% of time

#### Table showing analysis of Gaseous Emission of the Nitric Acid plant

Those data, which confirm the information above and cover the project campaign 2 from March 4<sup>th</sup>, 2008 to September 14<sup>th</sup>, 2008, were provided to the environmental agency Cetesb and DOE auditors.



### 8. GHG emission reductions calculations

#### 8.1 Baseline emissions

At Paulínia plant, the baseline campaign took place from September 15, 2006 to April 13, 2007.

If Baseline Campaign Length ( $CL_{BL}$ )  $\leq CL_{normal}$ , all N<sub>2</sub>O values (VSG and NCSG) measured during the baseline campaign can be used for the calculation of EF<sub>BL</sub> (subject to the elimination of data that was monitored during times where the plant was operating outside of the "permitted range").

If  $CL_{BL} > CL_{normal}$ , the calculation of baseline N<sub>2</sub>O emission factor need to include the nitric acid production values measured beyond the normal campaign length while N<sub>2</sub>O values (NCSG and VSG) measured during the same period should be eliminated, following the guidance issued by EB45 (EB45 report, agenda sub-item 3 (f): Matters relating to the issuance of CERs and the CDM registry, article 62.0.i).

The production achieved during that period was 33 518 tons which is bigger than  $CL_{normal}$  (29695 tons). CLnormal was reached on March 20, 2007. Therefore, according to the rules indicated above the N<sub>2</sub>O values (VSG and NCSG) measured after the date when CLnormal was reached were eliminated from the calculation of the baseline parameters VSG<sub>BC</sub> and NCSG<sub>BC</sub>

The baseline emissions are calculated using the following formulae:

## $BE_{BC} = VSG_{BC} \times NCSG_{BC} \times 10^{-9} \times OH_{BC}$

 $\mathbf{EF}_{BL} = (\mathbf{BE}_{BC} / \mathbf{NAP}_{BC}) (1 - \mathbf{UNC}/100)$ 

where:

 $\begin{array}{lll} BE_{BC} & : \mbox{total } N_2O \mbox{ emissions during the baseline campaign (t $N_2O$)} \\ VSG_{BC} & : \mbox{ mean gas volume flow rate at the stack in the baseline measurement period ($Nm^3/h$)} \\ NCSG_{BC} & : \mbox{ mean concentration of } N_2O \mbox{ in stack gas in the baseline campaign (mg $N_2O$ /Nm^3$)} \\ OH_{BC} & : \mbox{ total operating hours of the baseline campaign (h} \\ EF_{BL} & : \mbox{ baseline } N_2O \mbox{ emissions factor (t $N_2O$ /t $HNO_3$)} \\ NAP_{BC} & : \mbox{ total nitric acid production during the baseline campaign (t $HNO_3$)} \\ UNC & : \mbox{ overall uncertainty of the monitoring system (%), calculated as the combined uncertainty of the applied monitoring equipment \\ \end{array}$ 



The values obtained in the baseline campaign are:

Parameter	Data unit	Value
VSG <sub>BC</sub>	Nm <sup>3</sup> /h	23 456
NCSG <sub>BC</sub>	mg N <sub>2</sub> O/Nm <sup>3</sup>	1 756
OH <sub>BC</sub>	h	5 012.8
NAP <sub>BC</sub>	t HNO <sub>3</sub>	33 518
UNC	%	6.12

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

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

 $BE_{BC} = 23\ 456\ x\ 1\ 756\ x\ 10^{-9}\ x\ 5\ 012.8 = 206.508\ t\ N_2O$ 

 $\mathbf{EF}_{BL} = (\mathbf{BE}_{BC} / \mathbf{NAP}_{BC}) \times (1 - \mathbf{UNC}/100)$ 

 $EF_{BL} = (206.508 / 33518) \times (1 - 6.12/100) = 0.005784 \times 10^{-10} \text{ km}^{-1}$ 

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  $EF_{BL}$  is more accurately 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 82.60% for both NCGS and VSG.

The above calculations were verified by the DOE after the project campaign 1.

The value of  $EF_{BL}$  has been used as the baseline emission factor since there are currently no national or regional regulations for N<sub>2</sub>O emissions in Brazil.

#### 8.2 Project emissions of project campaign 2

The emissions due to project activity in a campaign ( $PE_n$ ) are the total emissions of  $N_2O$  during the nth campaign were obtained from the following formulae (equations 3 and 4 from AM0034 version 2):

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

 $\mathbf{EF_n} = \mathbf{PE_n} / \mathbf{NAP_n}$ 

where:

 $PE_n$  : total Project emissions of the nth campaign (t N<sub>2</sub>O)

VSG : mean stack gas volume flow rate for the nth project campaign  $(Nm^3/h)$ 

NCSG : mean concentration of  $N_2O$  in the stack gas for the project campaign (mg  $N_2O/Nm^3$ )



OH : number of operating hours in the project campaign (h)

 $EF_n$  : emission factor calculated for the nth campaign (t N<sub>2</sub>O/t HNO<sub>3</sub>)

 $NAP_n$  : nitric acid production in the nth campaign (t 100% HNO<sub>3</sub>)

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. In the event that the monitoring system is down or when there is acquisition failure for those parameters, the highest measured value of the emission factor in the campaign is applied for calculating the conservative values of the missing VSG and/or NCSG, which are used for the calculation of the campaign emission factor.

Parameter	Data unit	Value
VSG	Nm <sup>3</sup> /h	24 485
NCSG	mg N <sub>2</sub> O/Nm <sup>3</sup>	183
ОН	h	4 464.4
NAP <sub>2</sub>	t HNO <sub>3</sub>	31 660

The following values were obtained in this second project campaign (n = 2):

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

## $PE_2 = VSG \times NCSG \times 10^{-9} \times OH$

#### $PE_2 = 24\ 485\ x\ 183\ x\ 10^{-9}\ x\ 4\ 464.4 = 19.983\ t\ N_2O$

 $\mathbf{EF}_2 = \mathbf{PE}_2 / \mathbf{NAP}_2$ 

#### $EF_2 = 19.983 / 31 \ 660 = 0.000631 \ t \ N_2O / t \ HNO_3$

The actual value of  $PE_2$  is slightly different from the value obtained by direct calculation shown above due to a rounding effect. The value of  $EF_2$  is more accurately calculated in the Workbook.

As this is the 2<sup>nd</sup> project campaign and in order to take into account the methodology will be calculated the moving average emissions factor as follows:

 $EF_{ma, 2} = (EF_1 + EF_2) / 2$  (t N<sub>2</sub>O/t HNO<sub>3</sub>)

Where: EF<sub>1</sub>: emission factor of  $1^{st}$  project campaign EF<sub>2</sub>: emission factor of  $2^{nd}$  project campaign 2: number of project campaigns



Considering the data of emission factor of each project campaign below:

Campaign (n)	Emission Factor
$1^{st}$	0.000565
$2^{nd}$	0.000631

The  $EF_{ma,n}$  value will be:

 $EF_{ma, 2} = (EF_1 + EF_2) / 2 = (0.000565 + 0.000631) / 2$ 

 $EF_{ma, 2} = 0.001196 / 2$ 

 $EF_{ma. 2} = 0.000598$  $(t N_2O/t HNO_3)$ 

Further considering the methodology:

If  $EF_{ma,2} > EF_2$  then  $EF_2 = EF_{ma,2}$ If  $EF_{ma,2} < EF_2$  then  $EF_2 = EF_2$ 

As  $EF_{ma,2} \le EF_2$  then  $EF_2 = 0.000631$  will be used for emission reduction calculation.

According to methodology AM0034 version 2 "if the length of each individual project campaign CL<sub>n</sub> is longer than or equal to the average historic campaign length CL<sub>normal</sub>, then all N<sub>2</sub>O 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)". In this campaign the campaign length was 31 660 tons which is higher than CL<sub>normal</sub> (29 695 tons). Therefore the baseline emission factor can be used without any change. The calculation of the baseline emission factor was verified by the DOE after project campaign 1.

#### **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<sub>2</sub>O, as according to AM0034 version 2:

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

where:	
ER	: emission reductions of the project for the specific campaign (t $CO_2e$ )
NAP	: nitric acid production for the project campaign (t HNO <sub>3</sub> ). The maximum value of
	NAP shall not exceed the design capacity.
EF <sub>BL</sub>	: baseline emissions factor (t $N_2O/t$ HNO <sub>3</sub> )
EF <sub>P</sub>	: emissions factor used to calculate the emissions from this particular campaign (i.e.
	the higher of $EF_{ma,2}$ and $EF_2$ )
GWP <sub>N20</sub>	: global warming potential of N <sub>2</sub> O set as 310 t CO <sub>2</sub> e/t N <sub>2</sub> O by the IPCCC

N2O • ıg l



According to AM0034 version 2, the applicability of this methodology "is limited to the existing production capacity measured in tons of nitric acid where the commercial production had begun no later than 31 December 2005." The PDD states that it is applied only for the installed capacities of the plant (measured in tons of nitric acid per year) that exist before project implementation. The nameplate capacity of the Paulínia plant established in 2005 is 55 900 t of HNO3 / year.

In order to comply with this applicability criterion it is necessary to verify whether the yearly production of nitric acid has exceeded the cap or not. If the yearly production is above the cap then the emissions reduction calculation shall only be applied up to that limit. This verification is performed by taking as reference the project anniversary date (start date of the 1<sup>st</sup> project campaign, i.e., 28 July 2007):

Start date campaign 1	28 July 2007
End date of campaign 1	3 March 2008
Nitric acid production in campaign 1, tons	35 838
Date when production cap was achieved	7 July 2008
Nitric acid production on campaign 2 until 7 July 2008 included, tons	20 043
Nitric acid production from July 8 to July 27, 2008 (excess above the cap), tons	3 389
Nitric acid production in campaign 2, in the current year (from 28 July, 2008 included), tons	8 227
Total nitric acid production in campaign 2 (tons)	31 660
Nitric acid in campaign 2 eligible for emissions reduction calculation, tons	28 270

As can be verified the nitric acid production used for emissions reduction calculation in the production year, encompassing all campaign 1 and part of the campaign 2 is:

From 28 July 2007 to 7 July 2008 = 35 838 + 20 043 = 55 881 tons

This is below the plant nameplate capacity (55 900 tons) as required by the PDD and the methodology.

Therefore the nitric acid production which shall be used for emissions reduction calculation in project campaign 2 is:  $(31\ 660\ -3\ 389) = 28\ 270$  tons. This calculation is slightly different from the more accurate value given by the Workbook due to a rounding effect.

Thus: NAP for campaign  $2 = 28\ 270$  tons.

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

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

ER = (0.005784 - 0.000631) x 28 270 x 310 = 45 160 t CO<sub>2</sub>e



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 accurately calculated in the Workbook.

The above emission reduction covers the generation of  $N_2O$  in the nitric acid production during this campaign.



Annex 1 – Data and	parameters	of baseline	campaign
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Data / Parameter:	NCSG <sub>BC</sub>
Data unit:	mg/Nm <sup>3</sup>
Description:	$N_2O$ concentration in the stack gas
Source of data used:	N <sub>2</sub> O analyzer
Value monitored:	1 756
Description of measurement methods and procedures applied:	ABB Infrared analyzer model AO2040 URAS 14. The Measurement Principle is a non-dispersive infrared absorption in the $\lambda = 2.5-8 \mu m$ wavelength range Because of analyzer technology, water has to be removed. So, this is a dry-basis measurement. The direct measurement is corrected to compensate the water removal allowing to a good N <sub>2</sub> O flow rate evaluation.
QA/QC procedures applied:	Paulínia nitric acid plant is ISO 9001 certified. This measurement is considered as a critical measurement on the ISO 9001, so calibration routines and periodic check-up is followed-up by the quality system
Any comment:	

Data / Parameter:	VSG <sub>BC</sub>
Data unit:	Nm <sup>3</sup> /h
Description:	Volume flow rate of the stack gas
Source of data used:	Gas volume flow meter
Value monitored:	23 456
Description of	Venturi flow meter built according to standard ISO 5167 - 2003 Edition.
measurement	
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is followed-up by the quality system.
Any comment:	

Data / Parameter:	OH <sub>BC</sub>
Data unit:	Hours
Description:	Total operating hours
Source of data used:	Production log
Value monitored:	5 012.8
Description of	The value is obtained from operational log and can be compared with on-
measurement	line instruments data. The responsible people for this data is informed on
methods and	Data Handling Protocol and these information can be checked by the
procedures applied:	auditors on document during audits
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	



Data / Parameter:	BE <sub>BC</sub>
Data unit:	t N <sub>2</sub> O
Description:	Total N <sub>2</sub> O for baseline campaign
Source of data used:	Calculated : $\mathbf{BE}_{BC} = VSG_{BC} \times NCSG_{BC} \times 10^{-9} \times OH_{BC}$
Value obtained:	206.508
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	NAP <sub>BC</sub>
Data unit:	t HNO <sub>3</sub>
Description:	Nitric acid (100% concentrated) over baseline campaign
Source of data used:	Production log
Value monitored:	33 518
Description of	Flow meter (totalizer) and plant accounting system
measurement	
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

Data / Parameter:	TSG
Data unit:	°C
Description:	Temperature of stack gas during baseline campaign
Source of data used:	Probe (part of the gas volume flow meter)
Value monitored:	137.9
Description of	Temperature measured, each 2 sec, by probe installed in the Venturi flow
measurement	meter to correct the flow.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Value shown was obtained as average from baseline campaign data.



Data / Parameter:	PSG
Data unit:	bar abs
Description:	Pressure of stack gas during baseline campaign
Source of data used:	Probe (part of the gas volume flow meter)
Value monitored:	0.91
Description of	Pressure measured, each 2 sec, by probe installed in the Venturi flow
measurement	meter to correct the flow.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Value shown was obtained as average from baseline campaign data.

Data / Parameter:	UNC
Data unit:	%
Description:	Overall measurement uncertainty of the monitoring system
Source of data used:	Calculated of the combined uncertainty of the applied monitoring
	equipment
Value applied:	6.12
Description of	The overall uncertainty is determined as the combined uncertainty of the
measurement	flow meter and uncertainty of the N2O concentration measurement.
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	EF <sub>BL</sub>
Data unit:	t N <sub>2</sub> O / t HNO <sub>3</sub>
Description:	Emissions factor for baseline period
Source of data used:	Calculated : $\mathbf{EF}_{BL} = \mathbf{BE}_{BC} / \mathbf{NAP}_{BC} \times (1 - \mathbf{UNC}/100)$
Value obtained:	0.005784
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	



Data / Parameter:	AFR
Data unit:	kg NH <sub>3</sub> /h
Description:	Ammonia gas flow rate
Source of data used:	Flow meter
Value monitored:	Not applicable: AFR values are used to determine if plant is operating
	outside AFR <sub>max</sub>
Description of	NH3 mass flow by a Venturi flow meter with temperature and pressure
measurement	automatic correction.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

Data / Parameter:	AFR <sub>max</sub>
Data unit:	kg NH <sub>3</sub> /h
Description:	Maximum Ammonia flow rate
Source of data used:	Flow meter
Value monitored:	1 960
Description of	NH3 mass flow by a Venturi flow meter with temperature and pressure
measurement	automatic correction.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Maximum value of five (5) operational campaigns before baseline
	campaign

Data / Parameter:	AIFR
Data unit:	% mass
Description:	Ammonia to air ratio
Source of data used:	Ratio of NH3 mass flow per (NH3 mass flow + Air mass flow)
Value obtained:	Not applicable: AIFR data are used to determine if plant was
	operating outside AIFR <sub>max</sub>
Description of	NH3 mass flow and air mass flow measured by two Venturi flow meters
measurement	with temperature and pressure automatic correction.
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	



Data / Parameter:	AIFRmax
Data unit:	% mass
Description:	Maximum ammonia to air ratio
Source of data used:	Calculated : Ratio of NH3 mass flow per (NH3 mass flow + Air mass
	flow)
Value monitored:	7.1
Description of	NH3 mass flow and air mass flow measured by two Venturi flow meters
measurement	with temperature and pressure automatic correction.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Maximum value of five (5) operational campaigns before baseline
	campaign

Data / Parameter:	CL <sub>BL</sub>
Data unit:	t HNO <sub>3</sub>
Description:	Campaign length of baseline campaign
Source of data used:	Calculated from nitric acid production data
Value monitored:	33 518
Description of	Flow meter (totalizer) and plant accounting system
measurement	
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

Data / Parameter:	CL <sub>normal</sub>
Data unit:	t HNO <sub>3</sub>
Description:	Normal campaign length
Source of data used:	Calculated from nitric acid production data (average historical campaign
	length during the operation condition campaign)
Value monitored:	29 695
Description of	Flow meter (totalizer) and plant accounting system
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	The value reported in the PDD (32 444 tons) was an indicative ex-ante
	estimation



Data / Parameter:	OT <sub>h</sub>
Data unit:	°C
Description:	operating temperature for each hour
Source of data used:	Thermocouple
Value monitored:	Not applicable; OT <sub>h</sub> values are used to determine if the plant was
	operating outside OT <sub>normal</sub>
Description of	Three temperature probes under the catalyst gauzes are able to measure an
measurement	average temperature.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

Data / Parameter:	OT <sub>normal</sub>
Data unit:	°C
Description:	Normal operating temperature
Source of data used:	Thermocouple
Value monitored:	880 - 902
Description of	Three temperature probes under the catalyst gauzes are able to measure an
measurement	average temperature.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Calculated according to the methodology definition of the "permitted
	range". The ex-ante values 920-840 which are in the PDD are the technical
	operating limits of the nitric acid plant in Paulínia

Data / Parameter:	OP <sub>h</sub>
Data unit:	kgf/cm <sup>2</sup> gauge
Description:	Oxidation pressure for each hour
Source of data used:	Pressure probe
Value monitored:	Not applicable; OP <sub>h</sub> values are used to determine if the plant was
	operating outside OP <sub>normal</sub>
Description of	
measurement	A manometer, installed on the reactor, give to the control room reliable
methods and	pressure measurement, accurate enough for the operation purposes.
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	



Data / Parameter:	<b>OP</b> <sub>normal</sub>
Data unit:	kgf/cm <sup>2</sup> gauge
Description:	Normal operating pressure
Source of data used:	Pressure probe
Value monitored:	3.66 - 3.93
Description of	A manometer, installed on the reactor, give to the control room reliable
measurement	pressure measurement, accurate enough for the operation purposes.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Calculated according to the methodology definition of the "permitted
	range". The ex-ante values (3.26-4.28 kgf/cm <sup>2</sup> or 320 000-420 000 Pa)
	which are in the PDD are the technical operating limits of the nitric acid
	plant in Paulínia

Data / Parameter:	GS <sub>normal</sub>
Data unit:	Name of supplier
Description:	Normal gauze supplier for the operation condition campaign
Source of data used:	certificate of analysis /invoices
Value monitored:	Umicore
Description of	Umicore provides catalyst gauzes and technical assistance to Rhodia.
measurement	Umicore is a traditional supplier of kind of gauzes.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. The gauze supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	OM Group was the gauze supplier to Rhodia until 2003 when its precious
	metal activity were acquired by Umicore

Data / Parameter:	GS <sub>BL</sub>
Data unit:	Name of supplier
Description:	Gauze supplier for baseline campaign
Source of data used:	certificate of analysis/invoices
Value monitored:	Umicore
Description of	Umicore provides catalyst gauzes and technical assistance to Rhodia.
measurement	Umicore is a traditional supplier of kind of gauzes.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. The gauze supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	

![](_page_28_Picture_0.jpeg)

Data / Parameter:	GC <sub>normal</sub>
Data unit:	%
Description:	Gauze composition during the operation campaign
Source of data used:	Certificate of analysis
Value monitored:	95% mass Pt 5% mass Rh
Description of	The supplier sends the gauzes with a certificate of analysis that is kept in
measurement	the plant files.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This gauzes supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	

Data / Parameter:	GC <sub>BL</sub>
Data unit:	%
Description:	Gauze composition during the Baseline campaign
Source of data used:	Certificate of analysis
Value monitored:	95% mass Pt 5% mass Rh
Description of	The supplier sends the gauze with a composition analytical certificate that
measurement	is kept in the plant files.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This gauzes supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	

![](_page_29_Picture_0.jpeg)

Data / Parameter:	EF <sub>reg</sub>
Data unit:	
Description:	Emissions level set by incoming policies or regulations
Source of data used:	
Value monitored:	Not existent in Brazil
Description of	At date of introducing or change of regulation.
measurement	Rhodia follows the evolution of Brazilian legislation about N2O emissions
methods and	that could affect the project Emission Reduction through the parameter
procedures applied:	EF <sub>reg</sub> as part of the ISO 14000 requirements.
	Rhodia has hired an external company specialized in regulations. It sends
	to GSIMAP (Rhodia Industrial Platform) all the changes in regulations
	that may impact Rhodia. GSIMAP team evaluates the changes and
	discusses the applicability to the Rhodia operations in a steering
	committee. The conclusions from this steering committee are then
	presented to the Quality representatives of all plant units in a formal
	meeting that happens every three months. Furthermore GSIMAP experts
	on environmental issues participate on meetings held on external
	organizations (such as ABIQUIM - Brazilian Association of Chemical
	Industries, CETESB - local environmental agency) that discuss draft
	regulations. Those experts know in advance what comes next in terms of
	environmental laws.
QA/QC procedures	Paulínia nitric acid plant is ISO 14000 certified. Existing procedures
applied:	assure the follow-up of any evolution of EFr <sub>eg</sub> .
Any comment:	

![](_page_30_Picture_0.jpeg)

Data / Parameter:	NCSG
Data unit:	mg/Nm <sup>3</sup>
Description:	N <sub>2</sub> O concentration in the stack gas
Source of data used:	N <sub>2</sub> O analyzer
Value monitored:	183
Description of	ABB Infrared analyzer model AO2040 URAS 14. The Measurement
measurement	Principle is a non-dispersive infrared absorption in the $\lambda = 2.5-8 \ \mu m$
methods and	wavelength range
procedures applied:	Because of analyzer technology, water has to be removed. So, this is a
	dry-basis measurement. For the project campaigns, Rhodia keeps the dry
	basis data as a conservative approach (the value for water content in the
	waste gas is considered to be zero)
QA/QC procedures	This monitoring equipment is serviced, calibrated and maintained
applied:	according to the manufacture's instructions.
	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

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

Data / Parameter:	VSG
Data unit:	Nm <sup>3</sup> /h
Description:	Volume flow rate of stack gas
Source of data used:	Gas volume flow meter
Value monitored:	24 485
Description of	Venturi flow meter built according standard ISO 5167 - 2003 Edition. It's
measurement	considered a critical variable, so included in the ISO-9001 Nitric Acid
methods and	Plant procedures.
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

![](_page_31_Picture_0.jpeg)

Data / Parameter:	ОН
Data unit:	Hours
Description:	Operating hours
Source of data used:	Production log
Value monitored:	4 464.4
Description of	The value is obtained from operational log and can be compared with on-
measurement	line instruments data. The responsible people for this data is informed on
methods and	Data Handling Protocol and these information can be checked by the
procedures applied:	auditors on document during audits
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This data is considered as
applied:	a critical data on the ISO 9001 quality system
Any comment:	

Data / Parameter:	PE <sub>2</sub>
Data unit:	t N <sub>2</sub> O
Description:	N <sub>2</sub> O emissions of nth project campaign
Source of data used:	Calculated : $PE_2 = VSG \times NCSG \times 10^{-9} \times OH$
Value obtained:	19.983
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	NAP
Data unit:	t HNO <sub>3</sub>
Description:	Nitric acid production (100% concentrate)
Source of data used:	Production log
Value monitored:	$NAP_2 = 31\ 660$ (used for EF <sub>2</sub> calculation)
	$NAP = 28\ 270$ (used for ER calculation)
Description of	Flow meter (totalizer). Plant accounting
measurement	
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This data is considered as
applied:	a critical measurement on the ISO 9001, so calibration routines and
	periodic check-up is follow-up by the quality system
Any comment:	* NAP <sub>2</sub> : corresponds to the Nitric Acid total production on the 2 <sup>nd</sup>
	campaign. That value is used to calculate the campaign emission factor as
	defined in the methodology.
	* NAP: is the Nitric Acid production on the 2 <sup>nd</sup> campaign that is eligible
	for calculation of emission reduction by taking into account the nameplate
	yearly capacity of the plant (55 900 tons).

![](_page_32_Picture_0.jpeg)

Data / Parameter:	TSG
Data unit:	°C
Description:	temperature of stack gas during project campaign
Source of data used:	Probe (part of gas volume flow meter)
Value monitored:	137.4
Description of	Temperature measured, each 2 sec, by probe installed in the Venturi flow
measurement	meter to correct the flow
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Value shown was obtained as average from project campaign data.

Data / Parameter:	PSG
Data unit:	bar abs
Description:	pressure of stack gas during project campaign
Source of data used:	Probe (part of gas volume flow meter)
Value monitored::	0.94
Description of	Pressure measured, each 2 sec, by probe installed in the Venturi flow
measurement	meter to correct the flow
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	Value shown was obtained as average from project campaign data.

Data / Parameter:	AFR
Data unit:	kg NH <sub>3</sub> /h
Description:	Ammonia gas flow rate
Source of data used:	Flow meter
Value monitored:	Not applicable: AFR values are used to determine if plant is operating
	outside AFR <sub>max</sub>
Description of	NH3 mass flow by a Venturi flow meter with temperature and pressure
measurement	automatic correction.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

![](_page_33_Picture_0.jpeg)

Data / Parameter:	AIFR
Data unit:	% mass
Description:	Ammonia to air ratio
Source of data used:	Ratio of NH3 mass flow per (NH3 mass flow + Air mass flow)
Value obtained:	Not applicable
Description of	NH3 mass flow and air mass flow measured by two Venturi flow meters
measurement	with temperature and pressure automatic correction.
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	OT <sub>h</sub>
Data unit:	°C
Description:	operating temperature for each hour
Source of data used:	Thermocouple
Value monitored:	Not applicable
Description of	Three temperature probes under the catalyst gauzes are able to measure an
measurement	average temperature.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

Data / Parameter:	OP <sub>h</sub>
Data unit:	kgf/cm <sup>2</sup> gauge
Description:	Oxidation pressure for each hour
Source of data used:	Pressure probe
Value monitored:	Not applicable
Description of	A manometer, installed on the reactor, give to the control room reliable
measurement	pressure measurement, accurate enough for the operation purposes.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This measurement is
applied:	considered as a critical measurement on the ISO 9001, so calibration
	routines and periodic check-up is follow-up by the quality system
Any comment:	

![](_page_34_Picture_0.jpeg)

Data / Parameter:	EF <sub>2</sub>
Data unit:	t N <sub>2</sub> O / t HNO <sub>3</sub>
Description:	Emissions factor calculated for nth campaign
Source of data used:	Calculated : $\mathbf{EF}_2 = \mathbf{PE}_2 / \mathbf{NAP}_2$
Value obtained:	0.000631
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	EF <sub>ma,2</sub>
Data unit:	t N <sub>2</sub> O / t HNO <sub>3</sub>
Description:	Moving average emissions factor
Source of data used:	Calculated from campaign emissions factors
Value obtained:	0.000598
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	CL <sub>2</sub>
Data unit:	t HNO <sub>3</sub>
Description:	Campaign length
Source of data used:	Calculated from nitric acid production data
Value monitored:	31 660
Description of	Calculated from monitored data
measurement	
methods and	
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

![](_page_35_Picture_0.jpeg)

Data / Parameter:	EFp
Data unit:	t N <sub>2</sub> O / t HNO <sub>3</sub>
Description:	Emissions factor used to determine emissions reductions
Source of data used:	Calculated : EF <sub>p</sub> function of EF <sub>2</sub> and EF <sub>ma,2</sub>
Value obtained:	0.000631
Description of	Calculated from monitored data
measurement	If $EF_{ma,2} > EF_2$ then $EF_p = EF_{ma,2}$
methods and	If $EF_{ma,2} < EF_2$ then $EF_p = EF_2$
procedures applied:	
QA/QC procedures	QA/QC not applicable
applied:	
Any comment:	

Data / Parameter:	GSproject
Data unit:	Name of supplier
Description:	Gauze supplier for the project campaign
Source of data used:	certificate of analysis/invoices
Value monitored:	Umicore
Description of	Umicore provides catalyst gauzes and technical assistance to Rhodia.
measurement	Umicore is a traditional supplier of kind of gauzes.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. The gauze supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	

Data / Parameter:	GCproject
Data unit:	%
Description:	Gauze composition during project campaigns
Source of data used:	Certificate of analysis
Value monitored:	95% mass Pt 5% mass Rh
Description of	The supplier sends the gauze with a composition analytical certificate that
measurement	is kept in the plant files.
methods and	
procedures applied:	
QA/QC procedures	Paulínia nitric acid plant is ISO 9001 certified. This gauzes supplier
applied:	complies with standards of the Rhodia Quality System.
Any comment:	