



**QUANTIFICATION PROTOCOL
FOR NITROUS OXIDE ABATEMENT FROM
NITRIC ACID PRODUCTION**

Submitted to:

Alberta Environment
Protocol Development

Submitted by:

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1.0 Project and Methodology Scope and Description

This quantification protocol for nitrous oxide abatement from nitric acid production is written for the nitric acid production operator or nitric acid N₂O abatement project developer. Some familiarity with, or general understanding of the operation of a nitric acid production facility is assumed.

The opportunity for generating carbon offsets with this protocol arise from the quantification of reductions in greenhouse gas (GHG) emissions resulting from the installation of a dedicated N₂O abatement catalyst inside the ammonia burner of a nitric acid plant that catalytically reduces N₂O, once it has been formed in the Ammonia Oxidation Reactor.

1.1 Protocol Scope and Description

This protocol quantifies emission reductions created by the abatement of nitrous oxide during the production of nitric acid through the oxidization of ammonia on precious metal catalyst gauze in the ammonia burner of a nitric acid plant. The project boundary encompasses the physical and geographical site of the plant and the equipment for the entire production process. The only GHG emission relevant to the project activity is N₂O in the waste stream to stack. **Figure 1.1** is a process flow diagram for a typical project.

Protocol Approach:

This protocol applies to projects where the nitrous oxide would otherwise have been released into the atmosphere during the production of nitric acid as it does not have any economic value or toxicity at emission levels typical of nitric acid manufacture.

This protocol serves as a generic ‘recipe’ for project developers to follow in order to meet the measurement, monitoring and GHG quantification requirements.

The baseline condition has been identified as the release of the greenhouse gases created during the production of nitric acid through the oxidation of ammonia on precious metal catalyst gauze in the ammonia burner of a nitric acid plant for one campaign or primary catalyst run before project implementation. For illustration purposes, the process flow diagrams **Figure 1.1** and **1.2** for the baseline and project condition.

Figure 1.1: Process flow diagram for Project SS's

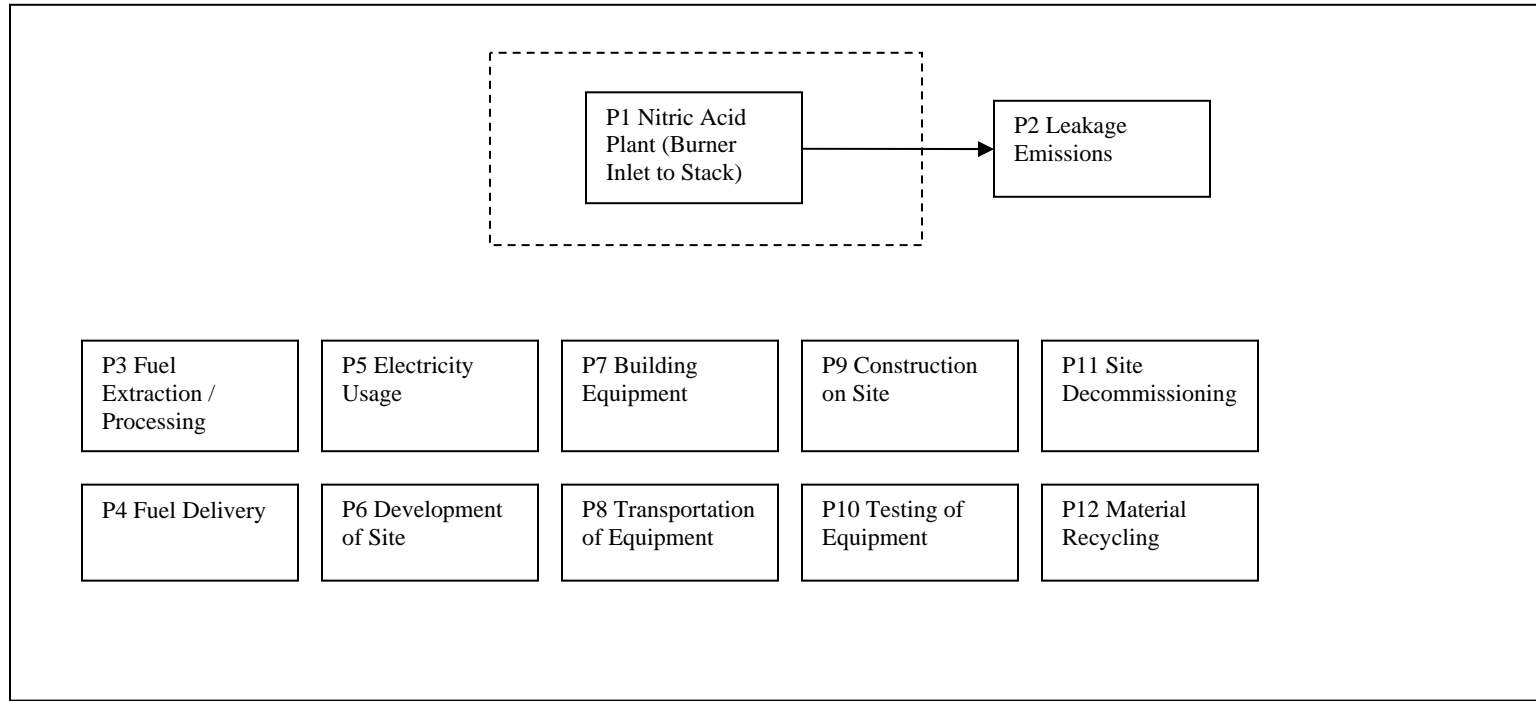
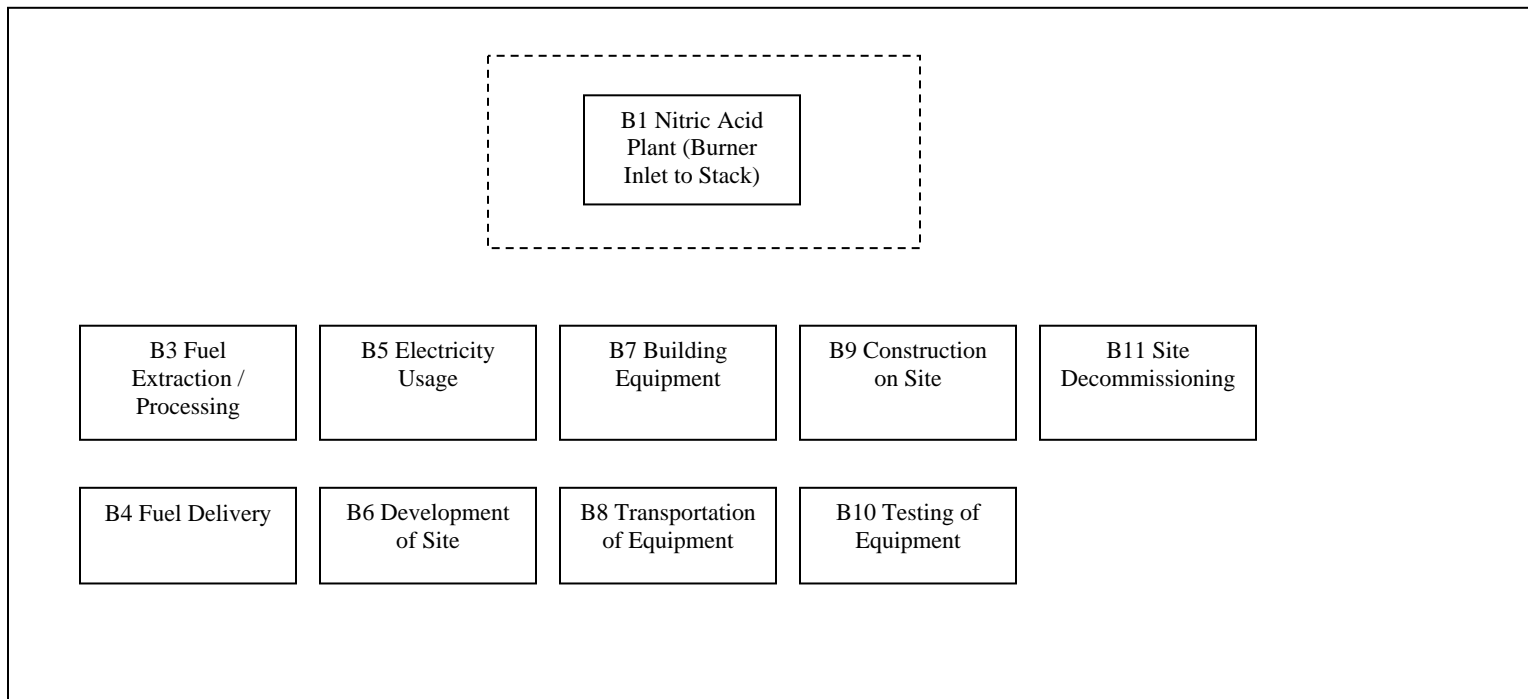


Figure 1.2: Process flow diagram for Baseline SS's



Protocol Applicability:

To demonstrate that a project meets the requirements under this protocol, the project developer must provide evidence that:

1. The abatement process is carried out under controlled conditions as demonstrated by a description of technology in use;
2. The quantification of reductions achieved by the project is based on actual measurement and monitoring (except where indicated in this protocol) as indicated by the proper application of this protocol; and
3. The project must meet the requirements for offset eligibility as specified in the applicable regulation and guidance documents for the Alberta Offset System.
4. The project activity will not result in the shutdown of any existing N₂O destruction or abatement facility or equipment in the plant;
5. The project activity shall not affect the level of nitric acid production
6. Continuous real-time measurements of N₂O concentration and total gas volume flow can be carried out in the stack:
 - a. Prior to the installation of the secondary catalyst for one campaign, and
 - b. After the installation of the secondary catalyst throughout the project activity

Protocol Flexibility:

Flexibility in applying the quantification protocol is provided to project developers in the following ways:

1. Project developers may use alternative monitoring methodologies and/or equipment rather than the methodologies and/or equipment described in this protocol. The proponent must justify that the chosen methodology and/or equipment provides equivalent, more accurate or more conservative data than the specified methodology and/or equipment;

If applicable, the proponent must indicate and justify why flexibility provisions have been used.

1.2 Glossary of New Terms

Campaign

The length of one campaign is defined as the total number of metric tonnes of nitric acid at 100% concentration produced with one set of primary gauze. A campaign can run between 60-365 days prior to changing out the catalyst.

Catalyst Gauze

Typically a material composed of precious metals (platinum, palladium, rhodium), but may consist of other catalytic materials, such as cobalt, used in the production of nitric acid.

Continuous Emission Monitoring Systems (CEMS)

The equipment and procedures required to analyze, measure, and provide, on a continuous basis, a permanent record of emission and other parameters as established by this code.

European Norm 14181 (2004)

Stationary Source Emissions – The European standard for the quality assurance procedures required to ensure that automated measurement systems (AMS), installed to measure emissions to air, are capable of meeting legislative requirements arising out of EU Directives.

Nitrous Oxide (N₂O)

Greenhouse gas with a global warming potential of 310 as defined in the 2007 Intergovernmental Panel on Climate Change (IPCC) Assessment Report 4

2.0 Quantification Development and Justification

The following sections outline the quantification development and justification.

2.1 Identification of Sources and Sinks (SS's) for the Project

Based on the process flow diagrams provided in **FIGURE 1.1**, the project SS's were organized into life system categories in **FIGURE 2.1**. Descriptions of each of the SS's and their classification as 'controlled', 'related', or 'affected' are provided in **TABLE 2.1**.

FIGURE 2.1: Project Element Life Cycle Chart

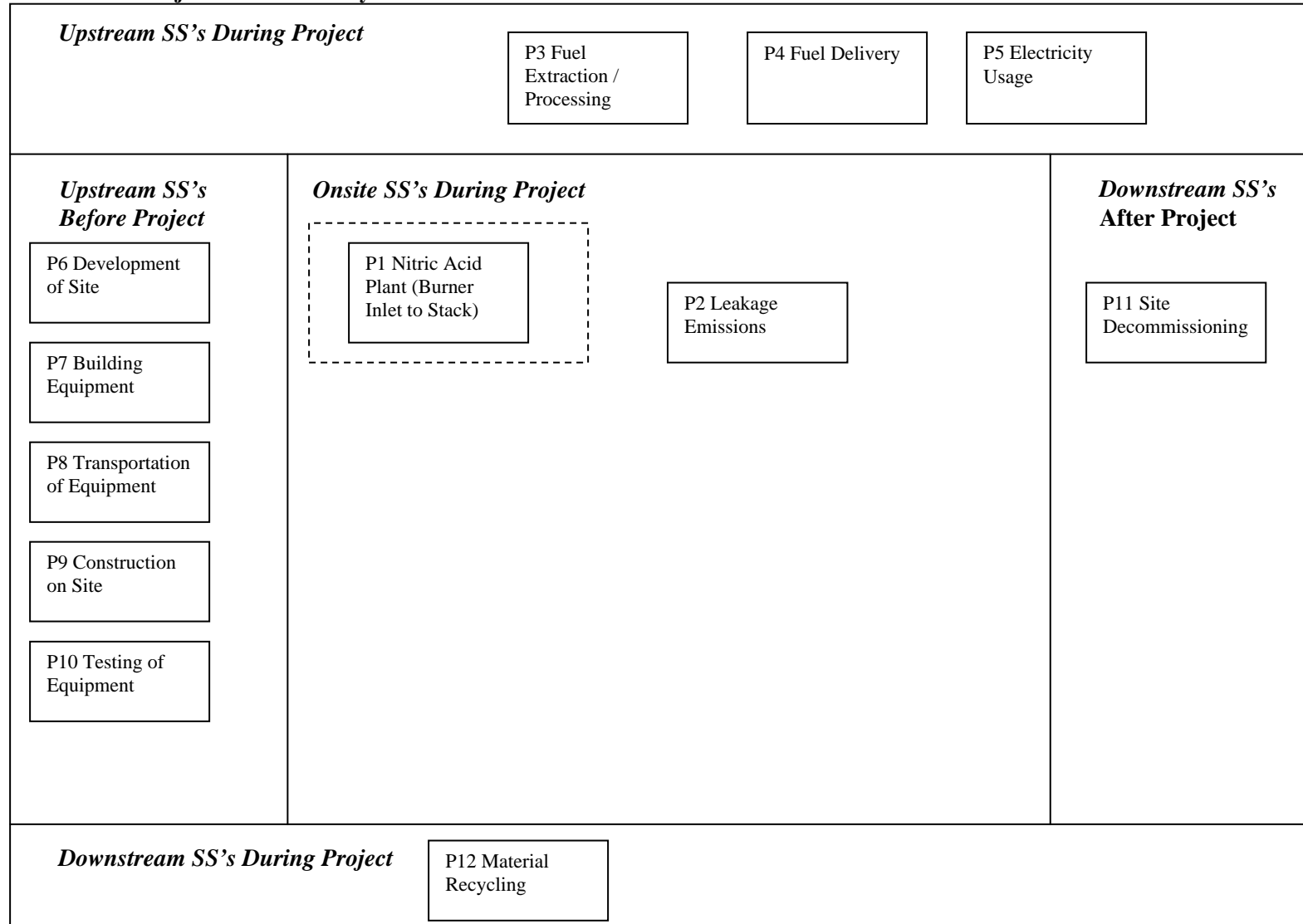


TABLE 2.1: Project SS's

1. SS	2. Description	3. Controlled, Related, or Affected
Upstream SS's during Project Operation		
P3 Fuel Extraction/Processing	Each of the fuels used throughout the on-site component of the project will need to be sourced and processed. The total volumes of fuel for each of the on-site SS's are considered under this SS. Volumes and types of fuels are the important characteristics to be tracked.	Related
P4 Fuel Delivery	Each of the fuels used throughout the on-site component of the project will need to be transported to the site. This includes the delivery of liquid ammonia, which may be shipped by rail, or tanker, resulting in emissions of greenhouse gases. It is reasonable to exclude fuel sourced by taking equipment to an existing commercial fuelling station as the fuel used to take the equipment to the site is captured under other SS's.	Related
P5 Electricity Usage	Electricity may be produced off-site. Measurement of the quantity of electricity required by the facility would need to be tracked.	Related
On-site SS's during Project Operation		
P1 Nitric Acid Plant (Burner Inlet to Stack)	The spatial extent of the project boundary shall cover the facility and equipment for the complete nitric acid production process from the inlet to the ammonia burner to the stack. This includes all compressors, tail gas expander turbines and any N ₂ O abatement equipment installed. Volumes, flow rates, temperatures and pressures must all be monitored and tracked.	Controlled
P2 Leakage Emissions	Leakages that occur from the replacement of the used catalyst with the new catalyst.	Related
Downstream SS's during Project Operation		
P12 Material Recycling	The end of life of the N ₂ O abatement catalyst will require the used catalyst to be refined, recycled and properly disposed of according to prevailing standards.	Related
Other		
P6 Development of Site	Development of the site could include clearing, grading, building access roads as well as civil infrastructure such as access to electricity, gas, water supply and water treatment. Building and structures on the site including offices, storage facilities, storm water drainage, and structures to enclose, support and house equipment may need to be developed. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment required to develop the site.	Related
P7 Building Equipment	Equipment may need to be built either on-site or off-site. This includes all of the components of the storage, handling, processing, combustion, air quality control, and system control and safety systems. These may be sourced as pre-made standard equipment or custom built to specification. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment for the extraction of the raw materials, processing, fabricating and assembly.	Related

<p>P8 Transportation of Equipment</p>	<p>Equipment may need to be built either on-site or off-site. This includes all of the components of the storage, handling, processing, combustion, air quality control, and control and safety systems. These may be sources as pre-made standard equipment or custom built to specification. Greenhouse gas emission would be primarily attributed to the use of fossil fuels and electricity used to power equipment for the extraction or implementation of the raw material, processing, fabricating and assembly. Also included may be the transportation of the replacement gauze required for each new campaign, and replacement raschig rings.</p>	<p>Related</p>
<p>P9 Construction on Site</p>	<p>The process of construction at the site will require a variety of heavy equipment, smaller power tools, cranes and generators. The operation of this equipment will have associated greenhouse gas emissions from the use of fossil fuels and electricity.</p>	<p>Related</p>
<p>P10 Testing of Equipment</p>	<p>Equipment may need to be tested to ensure that it is operational. This may result in running the equipment using fossil fuels in order to ensure that the equipment runs properly. These activities will result in greenhouse gas emissions associated with the combustion of fossil fuels and the use of electricity.</p>	<p>Related</p>
<p>P11 Site Decommissioning</p>	<p>Once the facility is no longer operational, the site may need to be decommissioned. This may involve the disassembly of the equipment, demolition of on-site structures, disposal of some materials, environmental restoration, re-grading, planting or seeding, and transportation of materials off-site. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment required to decommission the site.</p>	<p>Related</p>

2.2 Identification of Baseline

The baseline condition for projects applying this protocol is defined as the operating condition prior to the implementation of the N₂O abatement project. Baseline Emissions are determined by measuring nitrous oxide concentration and total flow rate in the tail gas of the nitric acid plant. The measurements are for the duration of one entire campaign prior to the implementation of the N₂O abatement project, and are used to determine a plant-specific baseline emission factor. A permitted range of parameters that influence the level of N₂O formation is established during the baseline campaign which must be demonstrated to be within the specifications of the plant.

2.3 Identification of SS's for the Baseline

According to the baseline scenario identified above and on the process flow diagrams provided in **FIGURE 1.2**, the project SS's were organized in life system categories in **FIGURE 2.2**. Descriptions of each of the SS's and their classification as 'controlled', 'related', or 'affected' is provided in **TABLE 2.2**.

FIGURE 2.2: Baseline Element Life Cycle Chart

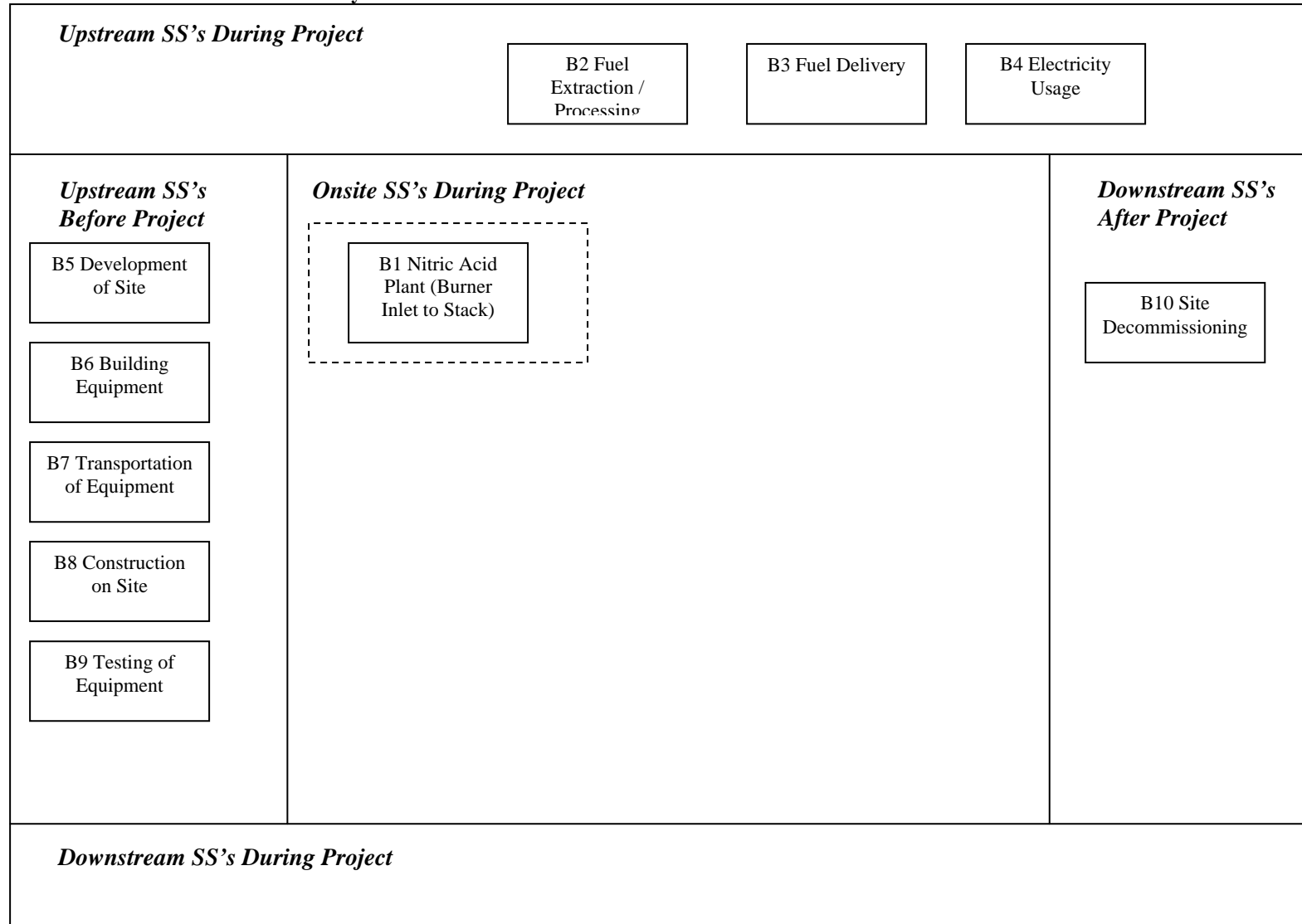


Table 2.2: Baseline SS's

1. SS	2. Description	3. Controlled, Related, or Affected
Upstream SS's during Project Operation		
B2 Fuel Extraction/Processing	Each of the fuels used throughout the on-site component of the project will need to be sourced and processed. The total volumes of fuel for each of the on-site SS's are considered under this SS. Volumes and types of fuels are the important characteristics to be tracked.	Related
B3 Fuel Delivery	Each of the fuels used throughout the on-site component of the project will need to be transported to the site. This includes the delivery of liquid ammonia, which may be shipped by rail, or tanker, resulting in emissions of greenhouse gases. It is reasonable to exclude fuel sourced by taking equipment to an existing commercial fueling station as the fuel used to take the equipment to the site is captured under other SS's.	Related
B4 Electricity Usage	Electricity may be produced off-site. Measurement of the quantity of electricity required by the facility would need to be tracked.	Related
On-site SS's during Project Operation		
B1 Nitric Acid Plant (Burner Inlet to Stack)	The spatial extent of the project boundary shall cover the facility and equipment for the complete nitric acid production process from the inlet to the ammonia burner to the stack. This includes all compressors, tail gas expander turbines and any N ₂ O abatement equipment installed. Volumes, flow rates, temperatures and pressures must all be monitored and tracked.	Controlled
Downstream SS's during Project Operation		
	NONE	
Other		
B5 Development of Site	Development of the site could include clearing, grading, building access roads as well as civil infrastructure such as access to electricity, gas, water supply and water treatment. Building and structures on the site including offices, storage facilities, storm water drainage, and structures to enclose, support and house equipment may need to be developed. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment required to develop the site.	Related
B6 Building Equipment	Equipment may need to be built either on-site or off-site. This includes all of the components of the storage, handling, processing, combustion, air quality control, and system control and safety systems. These may be sourced as pre-made standard equipment or custom built to specification. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment for the extraction of the raw materials, processing, fabricating and assembly.	Related
B7 Transportation of Equipment	Equipment may need to be built either on-site or off-site. This includes all of the components of the storage, handling, processing, combustion, air quality control, and system control and safety	Related

	<p>systems. These may be sources as pre-made standard equipment or custom built to specification. Greenhouse gas emission would be primarily attributed to the use of fossil fuels and electricity used to power equipment for the extraction or implementation of the raw material, processing, fabricating and assembly. Also included may be the transportation of the replacement gauze required for each new campaign, and replacement raschig rings.</p>	
B8 Construction on Site	<p>The process of construction at the site will require a variety of heavy equipment, smaller power tools, cranes and generators. The operation of this equipment will have associated greenhouse gas emission from the use of fossil fuels and electricity.</p>	Related
B9 Testing of Equipment	<p>Equipment may need to be tested to ensure that it is operational. This may result in running the equipment using fossil fuels in order to ensure that the equipment runs properly. These activities will result in greenhouse gas emissions associated with the combustion of fossil fuels and the use of electricity.</p>	Related
B10 Site Decommissioning	<p>Once the facility is no longer operational, the site may need to be decommissioned. This may involve the disassembly of the equipment, demolition of on-site structures, disposal of some materials, environmental restoration, re-grading, planting or seeding, and transportation of materials off-site. Greenhouse gas emissions would be primarily attributed to the use of fossil fuels and electricity used to power equipment required to decommission the site.</p>	Related

2.4 Selection of Relevant Project and Baseline SS's

Each of the SS's from the project and baseline condition were compared and evaluated as to their relevancy using the guidance provided in Canada's Offset System for Greenhouse Gases – Guide to Protocol Developers (August 2008 – Draft version), and the guidance of the approved Clean Development Mechanism methodology AM0034v3.1 “Catalytic reduction of N₂O inside the ammonia burner of nitric acid plants. The justification for the inclusion, exclusion, or conditions upon which SS's may be excluded is provided in **TABLE 2.3** below.

TABLE 2.3 Comparison of SS's

1. Identified SS	2. Baseline (C, R, A)	3. Project (C, R, A)	4. Included or Excluded from Quantification	5. Justification for Exclusion
Upstream SS's				
B2 Fuel Extraction/Processing	Related	N/A	Excluded	Excluded as emissions from fuel extraction/processing are not impacted by the implementation of the project and as such baseline and project conditions for this SS are similar.
P3 Fuel Extraction/Processing	N/A	Related	Excluded	
B3 Fuel Delivery	Related	N/A	Excluded	Excluded as emissions from fuel delivery are not impacted by the implementation of the project and as such baseline and project conditions related to this SS are similar.
P4 Fuel Delivery	N/A	Related	Excluded	
B4 Electricity Usage	Related	N/A	Excluded	Excluded as these SS's activity levels are not impacted by the implementation of this project and as such baseline and project conditions for this SS are similar.
P5 Electricity Usage	N/A	Related	Excluded	
Onsite SS's				
B1 Nitric Acid Plant (Burner Inlet to Stack)	Controlled	N/A	Included	N/A
P1 Nitric Acid Plant (Burner Inlet to Stack)	N/A	Controlled	Included	
P2 Leakage Emissions	N/A	Related	Excluded	Excluded as no leakage emissions are expected. Existing good practice guidance (CDM methodology AM0034 / Version 3.1 "Catalytic reduction of N2O inside the ammonia burner of nitric acid plants") excludes this source.
Downstream SS's				
P12 Material Recycling	N/A	Related	Excluded	Excluded as these emissions are not material to the life of the project, and the minimal change outs of the catalyst.
Other				
B5 Development of Site	Related	N/A	Excluded	Excluded as emissions from site development are not material to the implementation of this project, as no changes to the site are required to implement this project.
P6 Development of Site	N/A	Related	Excluded	
B6 Building Equipment	Related	N/A	Excluded	Emissions from building equipment are not material given the

P7 Building Equipment	N/A	Related	Excluded	long project life, and the minimal building equipment typically required. In this case, the only difference in building equipment between the baseline and the project is the catalyst. GHG emissions associated with catalyst transportation were calculated and demonstrated to be not significant, supporting documentation submitted to AENV.
B7 Transportation of Equipment	Related	N/A	Excluded	Emissions from transportation of equipment are not material given the long project life, and the minimal transportation of equipment typically required. GHG emissions associated with catalyst transportation were calculated and demonstrated to be not significant, supporting documentation submitted to AENV.
P8 Transportation of Equipment	N/A	Related	Excluded	
B8 Construction on Site	Related	N/A	Excluded	Excluded as emissions from site development are not material to the implementation of this project, as no changes to the site are required to implement this project.
P9 Construction on Site	N/A	Related	Excluded	
B9 Testing of Equipment	Related	N/A	Excluded	Emissions from testing of equipment are not material given the minimal testing of equipment typically required.
P10 Testing of Equipment	N/A	Related	Excluded	
B01 Site Decommissioning	Related	N/A	Excluded	Emissions from decommissioning are not material given the long project life, and the minimal decommissioning typically required (catalyst only). GHG emissions associated with catalyst transportation were calculated and demonstrated to be not significant, supporting documentation submitted to AENV.
P11 Site Decommissioning	N/A	Related	Excluded	

2.5 Quantification of Reductions, Removals, and Reversals of Relevant SS's

2.5.1 Quantification Approaches

Quantification of the reductions, removals and reversals of relevant SS's for each of the greenhouse gases will be completed using the methodologies outlined in **TABLE 2.4**, below. The quantification methodologies are based on guidance from the UNFCCC approved CDM methodology AM0034 Version 3.1. The quantification approach presented in this protocol differs from the CDM methodology AM0034 Version 3.1 in the following two areas:

1. The CDM methodology AM0034 requires that the monitoring installed must follow the European Norm 14181 (2004). In this protocol the monitoring system installed will follow an independently validated N₂O Meter Code based on the Alberta CEMS Code 1998 and the Canadian EPS 1/PG/7.
2. The CDM methodology AM0034 requires users to derive a moving average emission factor, after each project campaign and a project emission factor for the campaign. The lowest value between the campaign project emission factor and the moving average emission factor must be used when performing the GHG quantification for that specific project period. This protocol requires that the GHG quantification be performed using the calculated project emission factor for the relevant period, no moving average project emission factor is required.

The calculation methodologies presented in CDM methodology AM0034 serve to complete the following three equations for calculating the emission reductions from the comparison of the baseline and project conditions.

$$\text{Emission Reduction} = (\text{Emissions}_{\text{Baseline}} - \text{Emissions}_{\text{Project}})$$

$$\text{Emissions}_{\text{Baseline}} = \text{Emissions Factor}_{\text{Baseline}} * \text{NAP} * \text{GWP}_{\text{N}_2\text{O}}$$

$$\text{Emissions}_{\text{Project}} = \text{Emissions Factor}_{\text{Project}} * \text{NAP} * \text{GWP}_{\text{N}_2\text{O}}$$

Where:

Emissions_{Baseline} = the sum of the GHG emissions under the baseline condition (tCO₂e)

Emissions Factor_{Baseline} = calculated emissions factor under the baseline conditions (tN₂O/tHNO₃)

NAP = Nitric acid production for the baseline campaign (tHNO₃).

GWP_{N₂O} = Global Warming Potential of N₂O (tCO₂e/tN₂O)

Emissions_{Project} = the sum of the GHG emissions under the project condition (tCO₂e)

Emissions Factor_{Project} = calculated emissions factor under the project conditions (tN₂O/tHNO₃)

NAP = Nitric acid production for the project campaign (tHNO₃).

GWP_{N₂O} = Global Warming Potential of N₂O (tCO₂e/tN₂O)

Table 2.4: Quantification Procedures

1.0 Project SS	2. Parameter/ Variable	3. Unit	4. Measured/ Estimated	5. Method	6. Frequency	7. Justify measurement or estimation and frequency
Project SS's						
P1 Nitric Acid Plant (Burner Inlet to Stack)	Emissions Factor_{Project} = [(VSG_{Project} * NCSG_{Project} * 10⁻⁹ * OH_{Project}) / Project NAP] * (1 - Uncertainty/100);					
	Where: Emissions Factor is calculated leveraging the UNFCCC approved CDM methodology AM0034 v.3.1					
	Emissions Factor _{Project}	tN ₂ O/tHNO ₃	N/A	Modified from the UNFCCC approved CDM methodology AM0034 v.3.1	N/A	Emission Factor calculated on project emissions factor and not on the moving average project emission factor
	VSG = Mean stack gas volume flow rate	m ³ /hr	Measured	Sick Flow Sick Model 107	Continuous Monitoring 5-10 Second Intervals	Measured using an Analyzer meeting the Alberta CEMS Code
	NCSG = Mean concentration of N ₂ O emissions	mg N ₂ O/m ³	Measured	N2O Analyzer Procal P-200	Continuous Monitoring 5-10 Second Intervals	Measured using an Analyzer meeting the N ₂ O Meter Code (Appendix B) or the EN14181 Standard
	OH = operating hours in nth project campaign	hrs	Measured	Measure by the time clock, DCS, and plant NH3 flow rate.	Daily, compiled for entire campaign	Hours of production creating emissions
	Uncertainty	kg/h	Estimated	European Norm 14181	Calculated at implementation of monitoring system	Uncertainty Calculation Using EN14181 – Supported in Appendix A
Project NAP	tonnes of HNO ₃	Measured	Measure using a mass flow meter.	Daily, compiled for entire campaign	Total output quantity in nth project campaign	

1.0 Baseline SS	2. Parameter/ Variable	3. Unit	4. Measured/ Estimated	5. Method	6. Frequency	7. Justify measurement or estimation and frequency
Baseline SS's						
B1 Nitric Acid Plant (Burner Inlet to Stack)	Emissions Factor $\text{Emissions Factor}_{\text{Baseline}} = [(VSG_{\text{Baseline}} * NCSG_{\text{Baseline}} * 10^{-9} * OH_{\text{Baseline}}) / \text{Baseline NAP}] * (1 - \text{Uncertainty}/100)$					
	Where: Emissions Factor is calculated leveraging the UNFCCC approved CDM methodology AM0034 v.3.1					
	Emissions Factor $\text{Emissions Factor}_{\text{Baseline}}$	tN ₂ O/tHNO ₃	N/A	From the UNFCCC approved CDM methodology AM0034 v.3.1	N/A	Emission Factor calculated based on one full campaign prior to project implementation.
	VSG = Mean stack gas volume flow rate	m ³ /hr	Measured	Sick Flow Sick Model 107	Continuous Monitoring 5-10 Second Intervals	Measured using an Analyzer meeting the Alberta CEMS Code
	NCSG = Mean concentration of N ₂ O emissions	mg N ₂ O/m ³	Measured	N2O Analyzer Procal P-200	Continuous Monitoring 5-10 Second Intervals	Measured using an Analyzer meeting the N ₂ O Meter Code (Appendix B) or the EN14181 Standard
	OH = operating hours in baseline campaign	hrs	Measured	Measure by the time clock, DCS, and plant NH3 flow rate.	Daily, compiled for entire campaign	Hours of production creating emissions
	Uncertainty	kg/h	Estimated	European Norm 14181	Calculated at implementation of monitoring system	Uncertainty Calculation Using EN14181 – Supported in Appendix A
Baseline NAP	tonnes of HNO ₃	Measured	Measure using a mass flow meter.	Daily, compiled for entire campaign	Total output quantity	

2.5.2 Contingent Data Approaches

Contingent means for calculating or estimating the required data for the equations outlined in section 2.5.1 are included in the N20 Meter Code. More specifically the following section applies to contingent data approaches.

Section 2.4.4 of the N20 Meter Code states:

2.4.4. Backfilling and Substitution for Missing Data

Emission data that are missing due to a malfunction of the CEMS may be substituted for a period up to 120 hours for any single episode by averaging 120 hours of representative continuous data during stable operations of the nitric acid plant. Reference Method test data or data obtained from a monitor previously certified for the application may also be used for substituting data.

The technique used to obtain substitute data must be fully described in the QAP developed for each CEMS.

When a CEMS malfunction extends beyond 120 hours for any single episode, data must be generated by another authorized CEMS or valid Reference Method.

Other CEMS used for this purpose must meet all design and performance specifications given in this Code. When using another system, the effluent stream sample shall be extracted from the sample port used for the Reference method during certification of the installed CEMS.

Data substitution shall be limited to a maximum of 120 hours per calendar month

2.6 Management of Data Quality

In general, data quality management must include sufficient data capture such that the mass and energy balances may be easily performed with the need for minimal assumptions and use of contingency procedures. The data should be of sufficient quality to fulfill the quantification requirements and be substantiated by company records for the purpose of verification.

The project proponent shall establish and apply quality management procedures to manage data and information. Written procedures should be established for each measurement task outlining responsibility, timing and record location requirements. The greater the rigour of the management system for the data, the more easily an audit will be to conduct for the project.

2.6.1 Record Keeping

Record keeping practises should include:

- a. Electronic recording of values of logged primary parameters measurement interval;
- b. Printing of monthly back-up hard copies of all captured data;
- c. Written logs of operations and maintenance of the project system notation of all shut-downs, start-ups and process adjustments;
- d. Retention of copies of logs and all logged data for a period of 7 years;
- e. Keeping all records available for review by a verification body.

2.6.2 Quality Assurance/Quality Control (QA/QC)

QA/QC can also be applied to add confidence that all measurements and calculations have been made correctly. These include, but are not limited to:

- a. Protecting monitoring equipment;
- b. Protecting records of monitored data (hard copy and electronic storage);
- c. Checking data integrity on a regular and periodic basis (manual assessment, comparing redundant metered data, and detection of outstanding data/records);
- d. Automatically zeroing N₂O meters on a daily basis
- e. Comparing current estimates with previous estimates as a 'reality check';
- f. Provide sufficient training to operators to perform maintenance and calibration of monitoring devices;
- g. Establish minimum experience and requirements for operators in charge of project and monitoring; and
- h. Performing recalculations to make sure no mathematical errors have been made.

Appendix A

Uncertainty Calculation Methodology

UNCERTAINTY CALCULATION USING EN14181

Introduction

This document describes the estimation of uncertainty for the measurement of the nitrous oxide (N₂O) emission rate from the Number 1 Nitric Acid Plant (NAP1) at Orica Canada's Carseland works.

This measurement will provide evidence of the level of N₂O emission before and after the installation of abatement technology. A methodology document, 'Catalytic Nitrous Oxide Abatement Project Orica – Carseland, Alberta'¹, describes the data collection and retention requirements for this measurement. This document requires the calculation of the uncertainty of the N₂O emission rate for use in the calculation of the amount of carbon emission reduction credits awarded to the plant.

Measurement System

Overview of Measurement System

The measurement system provides a measure of the emission rate of N₂O from the stack (the measurand). The measurement system expresses the measurand in kg/h.

The measurement system consists of three independent instruments:

1. in-situ gas analyser (analyser);
2. ultrasonic flow meter (flowmeter); and
3. temperature probe;

Analyser

The analyser, by Procal (U.K.), measures the volume fraction of N₂O in the tail gas passing through its sample chamber. The result is expressed as N₂O in parts per million volume (ppmv) (or volume N₂O x 10⁶ per volume all components at standard temperature and pressure).

The sample chamber is located within the stack (in-situ). The sample is continuously heated to maintain a constant sample temperature. There is no other sample conditioning. The unit uses internal pressure and temperature probes to compensate for variations in these conditions in the sample gas.

Analyser calibration involves passing N₂O gas of known concentration through the analyser sample chamber. Cylinder Gas Audits (CGA) regularly check that the calibration gas composition matches the stated concentration.

¹ Orica, June 2007.

The analyser has certification to EN14181 standard for many gases (including NO_x). Procal (U.K.) are in the process of obtaining certification for N₂O.

Flowmeter

The ultrasonic flow meter, by SickMaihak (Germany) model Flowsic 107, measures the actual rate of gas flow in the stack. The result is expressed in m/h (meters per hour). This instrument completes a self zero and span every 24 hours.

Temperature

The temperature probe provides temperature information for the calculation of the flow rate at standard conditions. The temperature probe expresses results in °C.

Typical Readings

Table 1 provides typical readings for the instruments described in sections 0, 0, and 0. This document will use these typical readings as the test value for the uncertainty estimate.

Table 1: Typical readings for the instruments in the measurements system.

PPD Tag	Variable	Source	Expected/ Typical Reading	Units
ppmv	N2O Meter	Analyser	900	ppm
VEL	Flowrate	Flowmeter	127800	m/h
TEMP	Temperature	Temperature probe	117	°C
	Stack Area	Design Document	1.131	m ²

Conclusions of Measurement System

The measurement system consists of four independent instruments. The site’s DCS (distributed control system) collects the measures from the four instruments. The DCS calculates the measurand using Equation 1.

$$\begin{aligned}
 BE &= \frac{VSG \times NCSG}{1000000} \\
 &= \frac{\left(\frac{(VEL)(stack\ area)(PRESS)(273.15)}{1000(273.15 + TEMP)} \right) \left(\frac{(ppmv)(MW_{N_2O})}{Std.V} \right)}{1000000}
 \end{aligned}$$

Equation 1

where:

- BE = the measurand
- ppmv = N₂O concentration (ppmv)
- VEL = gas velocity (m/h)
- stack area = stack area (m²)

PRESS = gas pressure (mbar) = 1000 mbar
 TEMP = gas temperature (°C)

Collecting the constants leaves:

$$BE = \frac{c_1(\text{VEL})(\text{stack area})(\text{PRESS})(\text{ppmv})}{(c_2 + \text{TEMP})}$$

Equation 2

where:

$$c_1 = \frac{\left(\frac{273.15}{1000}\right)\left(\frac{\text{MW}_{\text{N}_2\text{O}}}{\text{Std.V}}\right)}{1000000} = \frac{\left(\frac{273.15}{1000}\right)\left(\frac{44.0126}{22.4}\right)}{1000000}; \text{ and}$$

$$c_2 = 273.15$$

Using the typical readings in Table 1, gives a value of BE of 179 kg/h.

Calculation of Uncertainty

Basis for Calculation

The basis for the calculation of uncertainty for this project is the recommendation of the European Norm 14181 (EN14181) as this represents the highest standard available for the calculation of uncertainty. EN14181 states that QAL1 (of EN ISO 14956) is used to establish the uncertainty of the measurement system is within required bounds. Of the QAL1 process, EN14181 states²:

‘In QAL1 the total uncertainty required by the applicable regulation is calculated by summing in an appropriate manner all the relevant uncertainty components arising from the individual performance characteristics.’

For continuing monitoring of uncertainty, EN14181 states³:

‘The standard deviation, s_{AMS} shall be derived from the information obtained for the QAL1 calculations. s_{AMS} shall be calculated considering plant conditions and not the test conditions during QAL1’

Consequently, the basis of this calculation is Section 8 of ISO 14956⁴.

² European Committee for Standardisation (2004), EN14181-Stationary Source Emissions-Quality Assurance of Automated Measuring Systems, European Committee for Standardisation, Section 5.1.

³ *ibid.* Section 7.2.

⁴ ISO (2002), ISO14956-Air Quality-Evaluation of the suitability of a measurement procedure by comparison with a required measurement uncertainty, ISO.

Uncertainty Equation

ISO 14956 provides the following equation to calculate uncertainty in a measurand (Equation 4, pg. 8).

$$u_c^2 = \sum_i w_i^2 u^2(y_i) + \sum_j b_j^2 u^2(\Delta x_j)$$

Equation 3

where:

c = the measurand = BE

u_c = the combined standard uncertainty of c

i = the index of an input quantity (to the equation of c) with an uncertainty

w_i = the weighting factor of y_i ; first derivative $w_i = \frac{\partial c(y_1, \dots, y_n)}{\partial y_i}$

$u(y_i)$ = the standard uncertainty (deviation) of y_i

y_i = an input quantity to the measurand

j = the index of a non-ideal influence during calibration (i.e. differences between the calibration temperature and the actual temperature attained during calibration)

b_j = the sensitivity of the measurand to x_j

$u(\Delta x_j)$ = the standard uncertainty (deviation) of x_j

Δx_j = non-ideal influence during calibration (i.e. differences between the calibration temperature and the actual temperature attained during calibration)

Uncertainty of BE

Equation 2 shows the calculation method for the measurand, BE.

Thus y_i for this measurand are:

$y_{\text{ppmv}} = \text{N}_2\text{O concentration (ppmv) (analyser)}$

$y_{\text{VEL}} = \text{gas velocity (m/h) (flowmeter)}$

$y_{\text{stack area}} = \text{stack area (m}^2\text{)}$

$y_{\text{TEMP}} = \text{gas temperature (}^\circ\text{C)}$

For ease of estimating the partial derivative, gas temperature is converted to absolute:

$\text{TEMPA} = (c_2 + \text{TEMP}) = \text{gas temperature (K)}$

The weighting factors, w_i , for these y_i are:

$$w_{\text{ppmv}} = \frac{\partial c}{\partial \text{ppmv}} = \frac{c_1(\text{stack area})(\text{PRESS})(\text{VEL})}{(c_2 + \text{TEMP})} = 0.201$$

$$w_{\text{VEL}} = \frac{\partial c}{\partial \text{VEL}} = \frac{c_1(\text{stack area})(\text{PRESS})(\text{ppmv})}{(c_2 + \text{TEMP})} = 0.00141$$

$$w_{\text{stack area}} = \frac{\partial c}{\partial \text{stack area}} = \frac{c_1(\text{VEL})(\text{PRESS})(\text{ppmv})}{(c_2 + \text{TEMP})} = 160$$

$$w_{\text{TEMPA}} = \frac{\partial c}{\partial \text{TEMPA}} = - \frac{c_1 (\text{stack area})(\text{PRESS})(\text{VEL})(\text{ppmv})}{(c_2 + \text{TEMP})^2} = 0.463$$

$u(y_{\text{ppmv}})$ = uncertainty in N₂O concentration (ppmv) (analyser)

Basis: The basis for this uncertainty calculation should be the uncertainty calculation made to obtain QAL1 under EN14181 (e.g. ISO14956). Actual data from site would then be included to update the analysis. However, the vendor, Procal, is in the process of MCERTS testing (MCERTS is the equivalent certification to EN14181 for the UK). Consequently, none of the input and influence factors are known for this instrument. Orica should update this uncertainty calculation following the completion of the certification process and delivery by Procal of the certification report.

For the moment, the uncertainty calculation will assume that the two most significant sources of uncertainty are: reproducibility and the uncertainty in the calibration gas composition.

The instrument calibration by Procal shows the instrument measured 4932 ppm for N₂O gas of composition 4955 ppm⁵. Thus, the value of the partial uncertainty is:

$$u_{\text{rep}} = 1.(4955 - 4932) = 24 \text{ ppmv}$$

The calibration gas certificates show the uncertainty of calibration gas is 2 %. Thus, the value of the partial uncertainty is:

$$u_{\text{cal}} = 1. \frac{(0.02)(\text{ppmv})}{\sqrt{3}} = 1. \frac{(0.02)(900)}{\sqrt{3}} = 10.4 \text{ ppmv}$$

The combined uncertainty for the analyser is:

$$u(y_{\text{ppmv}}) = \sqrt{(u_{\text{rep}})^2 + (u_{\text{cal}})^2} = \sqrt{(23.0)^2 + (10.4)^2} = 25.2 \text{ ppmv}$$

$u(y_{\text{VEL}})$ = gas velocity (m/h) (flow meter)

Basis: Manufacture specification sheet for Flowsic 107⁶

Error is ±1% of full scale (30 m/s) = ±0.3 m/s = ±1080 m/hr

⁵ Procal (2007), 'Certificate of Calibration', attached.

⁶ Flowsic 107 'Technical Specifications', attached.

$$u(y_{VEL}) = 1 \cdot \frac{(1080)(m/h)}{\sqrt{3}} = 624 m/h$$

$$u(y_{stack\ area}) = \text{stack area (m}^2\text{)}$$

Basis: Design Documents – Pipe Specifications

$$u(y_{stack\ area}) = 1 \cdot \frac{(0.00005)(\text{stack area})}{\sqrt{3}} = 1 \cdot \frac{(0.00005)(1.131)}{\sqrt{3}} = 0.000033 \text{ m}^2$$

$$u(y_{TEMP}) = \text{gas temperature (}^\circ\text{C)} \text{ (temperature probe)}$$

Basis: Relative accuracy test results (Table 2)

Table 2: Summary of Previous Relative Accuracy Test Audit results

Rata Date	Temperature (+/- Deg C)
Oct-07	3.2
Apr-07	1.1
Aug-06	2.0
Apr-06	2.0
Oct-05	0.2
Average	1.7

$$u(y_{TEMP}) = 1 \cdot \frac{1.7}{\sqrt{3}} = 0.98 \text{ }^\circ\text{C}$$

None of this information includes confidence limits for these uncertainties. It is assumed that the distribution is symmetric. Consequently, ISO14956 Equation 8 is used to convert the uncertainty range into a standard uncertainty.

Estimation of the combined uncertainty is through application of Equation 3:

$$u_c^2 = \sum_i w_i^2 u^2(y_i) + \sum_j b_j^2 u^2(\Delta x_j)$$

It is assumed that the input parameter uncertainties, $u^2(y_i)$, include all significant influence parameter uncertainties, $u^2(\Delta x_j)$.

$$u_c^2 = w_{ppmv}^2 u^2(y_{ppmv}) + w_{VEL}^2 u^2(y_{VEL}) + w_{stack\ area}^2 u^2(y_{stack\ area}) + w_{TEMP}^2 u^2(y_{TEMP})$$

$$u_c = \sqrt{(0.201)^2 (25.2)^2 + (0.00141)^2 (624)^2 + (160)^2 (0.000033)^2 + (0.463)^2 (0.98)^2}$$

$$= 5.2 \text{ kg/h}$$

Estimation of the expanded uncertainty uses Equation 17 of ISO 14956:

$$U_c = k \cdot u_c = 2.6.8 \\ = 10.4 \text{ kg/h}$$

Conclusions of Calculation of Uncertainty

Section 3 shows that the measurand at the typical readings shown in Table 1 was 179 kg/h. Thus, the uncertainty of the measurand is 179 ± 10.4 kg/h.

Conclusions and Recommendations

The uncertainty of the measurement system was found to be 179 ± 10.4 kg/h using the typical readings shown in Table 1.

The uncertainty estimation for the analyser was limited as the QAL1 results for the analyser are not yet available. The instrument vendor is in the process of obtaining this certification. It is recommended that Orica update this calculation following the completion of the QAL1 and the delivery by Procal of the certification report.

Appendix B

N₂O Meter (CEMS) Code

N₂O METER (CEMS) CODE

October 24, 2008

Background to this Document

The Alberta CEMS Code 1998 was used as the base document for creation of this Code for managing the N₂O meter to be installed as part of a project for catalytic nitrous oxide abatement from nitric acid production.

Canadian EPS 1/PG/7 was reviewed and some features were incorporated into this document.

The sections on NO_x, temperature, pressure and flow instrument have been retained in this document for completeness and reference only. The Alberta CEMS code will be used to manage these instruments since they are used in common for the NO_x analyzer and N₂O analyzer.

Section 4.5.8 is for reference only since N₂O does not have a standard reference method. SRC has designed a method for measuring N₂O based on FTIR unit.

1.0 INTRODUCTION

1.1 General

This code establishes requirements for the installation, operation, maintenance, and certification of a continuous emission monitoring system for nitrous oxide. These requirements will ensure effective measurement, recording, and standardized reporting of specified emissions and other parameters. In addition, the code establishes requirements for alternative monitoring systems and for the quality assurance and quality control of continuous emission monitoring data.

1.2 Purpose and Intent

The Alberta Continuous Emissions Monitoring System Code (CEMS Code) is largely based on methodology developed and used by both the U.S. Environmental Protection Agency and Environment Canada. This document uses the 1998 Alberta CEMS code as a basis for the development of a CEMS Code for N₂O to be used in the “*Quantification Protocol for Nitrous Oxide Abatement from Nitric Acid Production*” under Alberta’s Specified Gas Emitters Regulation. This CEMS Code for N₂O contains performance specifications for N₂O continuous emission monitoring system requirements.

1.3 CEMS Data Use

The CEMS data generated will be used for verification and validation of GHG offsets generated by abatement on a nitric acid plant.

1.4 Application of CEMS Code New and Existing CEMS Installations

1.4.1 Code Requirements for New Installations

All new CEMS required after the issuance of this Code must comply with all design, installation, performance, and quality control requirements of this Code. All new CEMS will be required to conduct the initial performance specification testing as contained in this CEMS Code and be certified in accordance with Section 4.0 of this code.

1.4.2 Code Requirements for Existing Installations

All existing CEMS required after the issuance of this Code must comply with all design, installation, performance, and quality control requirements of this Code. All existing CEMS will be required to conduct the initial performance specification testing as contained in this CEMS Code and be certified in accordance during or prior to the project baseline campaign, in accordance to Section 4.0 of this code.

1.5 CEMS Technology

In general, monitoring techniques are based on the direct measurement of both physical and chemical properties of the component of interest. The method selected for the gas analysis depends primarily upon the characteristics of the subject gas, but it can also be affected by other parameters such as regulatory requirements and stack conditions. Commonly used analytical techniques include those of spectroscopic absorption, luminescence, electroanalysis, electro-chemical analysis and paramagnetism.

The specifications of this Code address the use of independent certified gases for calibration and audit for CEMS that accept calibration gases.

1.6 CEMS Data Retention Requirements

Each facility shall maintain "raw" data for a period of at least 3 years and "summary" data for a period of at least 10 years. "Raw" data must be consistent with the definition of continuous as defined in Appendix A and should provide for "satisfactory demonstration" of quality control activities as defined in the CEMS Code and the facility Quality Assurance Plan (QAP). The media for storage of "raw" data shall be designated by the facility and documented in the facility QAP. Raw data shall be made available for inspection if requested.

2.0 DESIGN SPECIFICATIONS

Continuous Emission Monitoring Systems for monitoring gases consists of the following four subsystems:

- ❑ Sample Interface/Conditioning;
- ❑ Gas Analyzers;
- ❑ Data Acquisition;
- ❑ Flow monitor (where applicable).

The acceptability of emission monitoring systems is in general, performance based; however minimal design specifications are specified for gas analyzers, and flow monitoring systems. These specifications have been established either to ensure the overall stability of the CEMS once the analyzers are incorporated into the system, or to ensure that accurate readings will be obtained for the parameter being measured. Procedures for the verification of design specifications are given in Section 4.0.

The chosen range for the N₂O monitor is specified in Table 1. If the average monthly parameter of any analyzer should fall outside these limits, the analyzer span should be adjusted so that the average is brought back within these limits. Data that fall outside the range of an analyzer are considered to be missing.

2.1 Design Specifications for Gas Analyzers

Design specifications for gas analyzers for monitoring nitrous oxide is given in Table 1;

Table 1 Design Specifications for CEM system gas analyzers

Design Specifications	N ₂ O Analyzers
Lower detection limit	≤ 2% of span
Interference rejection (sum total)	≤ ± 4% of span
Response time (95%)	200 s (Max.)
Temperature-responsive zero drift ^a	≤ ± 2% of span
Temperature-responsive span drift ^a	≤ ± 4% of span
Analyzer Range	≥ 1.5 times the maximum of the

^a for every 10°C change in analyzer operating temperature.

2.1.1 Interference Rejection

Each analyzer shall exhibit a response of less than that specified in Tables 1 for the sum of all interferences due to other gas constituents as measured by the procedures given in Section 4.0.

2.1.2 Temperature-Responsive Drifts

Each pollutant gas analyzer used in the system must exhibit a zero drift less than 2% of the full-scale setting for any 10°C change over the temperature range of 5° to 35°C. Additionally, each analyzer must exhibit a span drift of less than 4% of the full-scale setting for any 10°C change in temperature from 5° to 35°C. Both the zero and span drift tests are to be carried out within the acceptable temperature operating range of the analyzer, as specified by the manufacturer. Follow the procedures outlined in Section 4.4.2 of the 1998 Alberta CEMS Code or alternatively confirm that Section 4.4.3 1998 Alberta CEMS Codes has been complied with to determine the temperature-responsive drift.

2.1.3 Cycle-time/Response Time

The cycle-time/response-time specification applies to systems, as opposed to analyzers. One complete measurement or cycle of measurements of all effluent streams must be completed in 15 minutes or less.

2.2 Design Specifications for Flow Monitors

Refer to the 1998 Alberta CEMS Code Section 2.3

2.3 Design Specifications for Temperature Sensors

Refer to the 1998 Alberta CEMS Code Section 2.4

2.4 Specifications for the Data Acquisition System

Refer to the 1998 Alberta CEMS Code Section 2.5

2.4.4 Backfilling and Substitution for Missing Data

Emission data that are missing due to a malfunction of the CEMS may be substituted for a period up to 120 hours for any single episode by averaging 120 hours of representative continuous data during stable operations of the nitric acid plant. Reference Method test data or data obtained from a monitor previously certified for the application may also be used for substituting data.

The technique used to obtain substitute data must be fully described in the QAP developed for each CEMS.

When a CEMS malfunction extends beyond 120 hours for any single episode, data must be generated by another authorized CEMS or valid Reference Method.

Other CEMS used for this purpose must meet all design and performance specifications given in this Code. When using another system, the effluent stream sample shall be extracted from the sample port used for the Reference method during certification of the installed CEMS.

Data substitution shall be limited to a maximum of 120 hours per calendar month

3.0 INSTALLATION SPECIFICATIONS

This Section contains guidelines for selecting a suitable sampling site on the flue, duct, or stack and determining the representativeness of the desired location with respect to the homogeneity of the effluent stream.

3.1 Location of the Sampling Site

Refer to the 1998 Alberta CEMS Code Section 3.1.

3.2 Representativeness

The sampling probe or in-situ analyzer must be installed in a location where effluent gases are completely mixed or at a location authorized by the Project. Flowing gases are generally well mixed, but stratification can occur when there are differing temperatures or when dissimilar gas streams intersect or where the duct/flue geometry changes. The degree of stratification in a duct or stack can be quantified. One method of quantification has been proposed (U.S. EPA 1979) that involves traversing the stack or duct and obtaining gas concentrations and comparing those concentrations to the target gas at a fixed concentration.

Gas stratification testing may be conducted on another gas species, O₂ or NO_x; if the degree of stratification is acceptable, then the entire gas stream degree of stratification is also acceptable.

3.2.1 Stratification Test Procedure

A minimum of nine (9) traverse points are required for this test. Locate the points in a balanced matrix of equal area on the stack or duct, using the procedures of Method 1 of the Alberta Stack Sampling Code.

For determining flow stratification, a pitot tube may be used (instead of automated gas monitoring systems) following the procedures of Method 2 of the Alberta Stack Sampling Code.

If the concentration of the gas measured or the velocity of the effluent stream at the fixed location varies by more than +/-10% of the average concentration for longer than one minute during this test, retest for stratification when more stable conditions prevail.

Alternately, if the stability of the emission source has been demonstrated at a chosen load, using the output of a chosen automated analyzer withdrawing a sample from a fixed point, the single automated analyzer may be used to measure the degree of stratification.

The concentration of a target gas or the velocity of the effluent stream shall be measured at each of the sampling points in the matrix. At the conclusion of the traverses, repeat the measurement of the concentration at the initial measurement point. If the concentrations differ by more than +/-10% for the pre- and post-test values at this point, retest for stratification when more stable conditions prevail.

The degree of stratification at each sampling point can be calculated as:

$$\% \text{ of stratification at point } i = \frac{(C_i - C_{ave})}{C_{ave}} \times 100$$

where:

C_i = concentration of target gas at point i

C_{ave} = average of target gas concentration

The sampling plane across the stack or duct is considered stratified if any of the calculated values are greater than +/- 10%.

4.0 PERFORMANCE SPECIFICATIONS and TEST PROCEDURES

4.1 General

This section addresses how to evaluate the acceptability of a CEMS at the time of installation and whenever specified in the CEMS Code. The specifications are not designed to evaluate CEMS performance over an extended period of time, nor do they identify detailed calibration procedures to assess CEMS performance. It is the responsibility of the source owner or operator to properly calibrate, maintain, and operate the CEMS.

Performance specifications and test procedure requirements for each specific CEMS are detailed in this section.

4.1.1 Initial Certification Requirements and Test Procedures

Subject to Section 1.5.1, the owner or operator of the facility shall demonstrate that the CEMS meets all the applicable system performance specifications within six (6) months of the installation of a new CEMS, upon recertification, or as specified otherwise by the Director. The satisfactory demonstration by the approval holder of meeting all of these performance specifications, along with notice of such to the Director, shall constitute certification of the CEMS.

4.2 Performance Specifications

Performance specifications for continuous emission monitoring systems are given in Table 2 and referenced 1998 Alberta CEMS Code Sections. .

4.2.1 Performance Specifications for Nitrous Oxide Emission Monitoring Systems.

Any owner or operator, shall install, calibrate, maintain, and operate N₂O monitoring systems and record the output of the systems.

Table 2 provides a summary of the general performance specifications of N₂O emission monitoring systems. These specifications are not meant to limit the types of technologies that can be used or prevent the use of equivalent methods.

Table 2. Performance specifications for N₂O emission monitoring systems.

Performance Specifications	N₂O Systems
Analyzer linearity	$\leq \pm 2\%$ of span from cal. curve
Relative accuracy ^(a)	$\leq \pm 10\%$ of RM
Zero drift - 24 hr	$\leq \pm 2\%$ of span
Span drift - 24 hr	$\leq \pm 4\%$ of span

If the reference method value is less than 50% of the analyzer full scale, then use 2% of full scale for relative accuracy for N₂O.

4.2.2 Performance Specifications for Volumetric Flow/Velocity Monitoring Systems.

Refer to the 1998 Alberta CEMS Code Section 4.2.5

4.2.3 Performance Specifications for Temperature Sensors

Refer to the 1998 Alberta CEMS Code Section 4.2.6

4.3 Test Procedures – Administrative

Refer to the 1998 Alberta CEMS Code Section 4.3.

4.4 Test Procedures for Verifying Design Specifications

4.4.1 Manufacturer's Certificate of Conformance

It may be considered that specifications for both interference rejection and temperature responsive drift have been met if the analyzer meets the international performance standard, MCERTS Performance Standards for Continuous Emissions Monitoring Systems, Version 2 Revision 1 (April 2003).

TEST	MCERTS Specification
Cross Sensitivity to: H ₂ O (5%) and CO ₂	<±4%
Response Time	<200s
Detection Limit	<±2%
Availability	>95%
Maintenance Interval	To Be Reported

Refer to the 1998 Alberta CEMS code Section 4.4 for alternative certification methods.

4.5 Performance Specification Test Procedures

4.5.1 Conditioning Test Period

Refer to the 1998 Alberta CEMS Code section 4.5.1

4.5.2 Operational Test Period

When the Conditioning Test Period has been successfully completed, the CEMS must be operated for an additional 168-hour period during which the emission source is operating under typical conditions. The Operational Test Period need not immediately follow the Conditioning Test Period.

During the Operational Test Period, the CEMS must continue to analyze the gases without interruption and produce a permanent record, using the data acquisition system, of the emission data. Sampling may be interrupted during this test period only to carry out system calibration checks and specified procedures as contained in the QAP.

During this period, no unscheduled maintenance, repairs, or adjustments should be carried out. Calibration adjustments may be performed at 24-hour intervals or more frequently, if specified by the manufacturer and stated in the QAP. Automatic zero and calibration adjustments made without operator intervention may be carried out at any time, but these adjustments must be documented by the data acquisition system.

If the test period is interrupted because of process shutdown, the times and dates of this period should be recorded, and the test period continued when the process continues operation. If the test period is interrupted as a result of CEMS failure, the entire test period must be restarted after the problem has been rectified.

The Performance Specifications tests outlined in Section 4.5 are carried out during the Operational Test Period, with the exception of the relative accuracy tests, which may be conducted during the Operational Test Period or during the 168-hour period immediately following the Operational Test Period. These tests are to be carried under conditions that typify the day-to-day operation of the CEMS and should be described in the QAP.

4.5.3 Calibration Drift Test Protocol for Gas and Flow Monitoring Systems

Refer to the 1998 Alberta CEMS Code section 4.5.3

4.5.4 Linearity

Refer to the 1998 Alberta CEMS Code section 4.5.4

4.5.5 Flow Monitor Calibration Drift

Refer to the 1998 Alberta CEMS Code section 4.5.5

4.5.6 Flow Monitor Orientation Sensitivity

Refer to the 1998 Alberta CEMS Code section 4.5.6.

4.5.7 System Cycle Time/Response Time Test

Refer to the 1998 Alberta CEMS Code section 4.5.7.

4.5.8 Relative Accuracy and Bias Tests for Gas Monitoring Systems

Perform a Relative Accuracy Test audit (RATA) for each CEMS. Record the CEMS output from the data acquisition system. For each CEMS, calculate bias as well as relative accuracy for each test.

Plant Operating Conditions - For new CEMS installations, complete the RATA test. Perform the test for each CEMS at a normal rate for the unit.

CEMS Operating Conditions - Do not perform corrective maintenance, repairs, replacements or adjustments on the CEMS during the RATA other than as required in the operation and maintenance portion of the QAP.

Note: Since a specific Standard Reference Method (SRM) for N₂O does not exist, EPA Method 320 and 40 CFR, Part 60, Appendix B Performance Specification 15 will be used for measurement of N₂O. The two paragraphs below are for reference only.

Reference Method Sampling Points - When the absence of stratified flow has not been verified, or if the gas flow has been found to be stratified, the Reference Method samples must be collected at a number of points in the effluent stream. Establish a "measurement line" that passes through the centroidal area of the flue or duct. This line should be located within 30 cm of the CEM sampling system cross section. Locate three (3) sampling points at 16.7, 50, and 83.3% along the length of the measurement line. Other sample points may be selected if it can be demonstrated that they will provide a representative sample of the effluent flow over the period of the test. A tip of the Reference Method probe must be within 3 cm of each indicated traverse point, but no closer than 7.5 cm to the wall of the stack or duct.

Where two or more probes are in the same proximity, care should be taken to prevent probes from interfering with each other's sampling.

Reference Method Sampling Conditions - Conduct the Reference Method tests in accordance with the Alberta Stack Sampling Code, and in such a manner that they will yield results representative of the pollutant concentration, emission rate, moisture content, temperature, and effluent flow rate from the unit and can be correlated with the CEMS measurements. Conduct the diluent (O_2 or CO_2) measurements and any moisture measurements that may be needed simultaneously with the pollutant concentration measurements. To properly correlate individual CEMS data, with the Reference Method data, mark the beginning and end of each Reference Method test run (including the exact time of day) on the data acquisition system, individual chart recorder(s) or other permanent recording device(s).

(e) Consistency - Confirm that the CEMS and Reference Method test results are based on consistent moisture, pressure, temperature, and diluent concentration and in the same units. In addition, consider the response times of the CEMS to ensure comparison of simultaneous measurements.

For each RATA conducted, compare the measurements obtained from the monitor via the data acquisition system (in ppm, % CO_2 , lb./M Btu, or other units as appropriate) against the corresponding Reference Method values. Display the paired data in a table.

Sampling Strategy - Perform a minimum of nine sets of paired monitor (or monitoring system) and Reference Method test data for every required (i.e., certification, semiannual, or annual) relative accuracy or Bias Test audit. Each test shall take a minimum duration of thirty (30) minutes, sampling for equal periods at the three (3) sampling points for stratified flow testing, or at the single point for nonstratified flow.

NOTE: the tester may choose to perform more than nine sets of Reference Method tests up to a total of 12 tests. If this option is chosen, the tester may reject a maximum of three sets of the test results, if an appropriate statistical test applied to the data demonstrates that these results are outliers, and as long as the total number of test results used to determine the relative accuracy or bias is greater than or equal to nine. All data must be reported, including the outliers, along with all calculations.

Calculations - Analyze the test data from the Reference Method and CEMS tests for the applicable CEMS.

Summarize the results on a data sheet. Calculate the mean of the monitor or monitoring system measurement values. Calculate the mean of the Reference Method values. Using

data from the automated data acquisition system, calculate the arithmetic differences between the Reference Method and monitor measurement data sets. Then calculate the arithmetic mean of the difference, the standard deviation, the % confidence coefficient, and the monitor or monitoring system relative accuracy using the following procedures and equations.

The absolute value of the average difference, \bar{d} , is calculated using the equation:

$$\bar{d} = \frac{1}{n} \sum_{i=1}^n (X_i - Y_i)$$

Where: n = number of data points

X_i = concentration from the Reference Method

Y_i = concentration from the CEMS

The standard deviation, S_d , is calculated using the equation:

$$S_d = \sqrt{\frac{\sum_{i=1}^n d_i^2 - \frac{1}{n} \left(\sum_{i=1}^n d_i\right)^2}{n - 1}}$$

Where: d_i = difference between individual pairs

The 2.5% error confidence coefficient, $t_{0.025}$, is calculated using the equation:

$$|CC| = t_{0.025} \frac{S_d}{\sqrt{n}}$$

Where: $t_{0.025}$ = t - table value from Table 3.

Table 3. Range of t-values applicable for calculating confidence coefficients in Relative Accuracy Tests of CEMS.

<u>t-VALUES</u>			
n	$t_{0.025}$	n	$t_{0.025}$
2	12.706	10	2.262
3	4.303	11	2.228
4	3.182	12	2.201
5	2.776	13	2.179
6	2.571	14	2.160
7	2.447	15	2.145
8	2.365	16	2.131
9	2.306		

The Relative Accuracy (RA) is calculated using the equation:

$$RA = \frac{|d| + |cc|}{\overline{RM}} \times 100$$

Where:

|d| = Absolute value of the mean difference

|cc| = Absolute value of the confidence coefficient RM =

Average Reference Method value

(h) The Bias Test

A bias, or systematic error is considered to be present if:

$$|d| \geq |cc|$$

(i) Acceptance Criteria for Analyzer Bias-

For each pollutant and diluent gas analyzer in the CEMS, calculate |d| and |cc|, in the units of the analyzer. If

$$|d| - |cc| \leq 2\% \text{ of FS}$$

the analyzer has significant bias. The cause of the bias must be determined and rectified. After corrections have been made, the Relative Accuracy Tests must be repeated to determine if the systematic error has been eliminated or reduced to an acceptable level.

4.5.9 Relative Accuracy Test for Flow Monitors

Refer to the 1998 Alberta CEMS Code section 4.5.9

4.5.10 Relative Accuracy Test for Temperature Sensors

Refer to the 1998 Alberta CEMS Code section 4.5.10

5.0 QUALITY ASSURANCE AND QUALITY CONTROL

The Quality Assurance (QA) procedures consist of two distinct and equally important functions. One function is the assessment of the quality of the CEMS data by estimating accuracy. The other function is the control and improvement of the quality of the CEMS data by implementing Quality Control (QC) policies and corrective actions. These two functions form a control loop. When the assessment function indicates that the data quality is inadequate, the control effort must be increased until the data quality is acceptable.

To provide high-quality data on a continuing basis a good QA program is necessary. The approval holder shall develop a QAP for each installed CEMS to ensure the quality of the CEMS measurements.

A "Quality Assurance" program is defined as a management program to ensure that the necessary quality control activities are being adequately performed, whereas "Quality Control" activities are those that detail the day-to-day operation of the system. The program shall be fully described in a Quality Assurance Plan (QAP) that is specific to the CEMS for N₂O.

5.1 Quality Assurance Plan (QAP) for CEMS

The QAP must include and describe a complete program of activities to be implemented to ensure that the data generated by the CEMS will be complete, accurate, and precise. As a minimum, the manual must include QA/QC procedures specified in this code. The recommended Table of Contents for a QAP is shown in Table 4.

5.1.1 Section 1 - Quality Assurance Activities

This section of the manual describes the CEM system QAP, and describes how the QA program is managed, provide personnel qualifications, and describe the QA reporting system. It must describe the CEMS, how it operates, and the procedures for calibration and inspection. It must also include preventative maintenance and performance evaluation procedures.

5.1.2 Section 2 - Quality Control Activities

This section of the manual provides the detailed descriptions of the step-by-step procedures, the standard operating procedures required to operate and evaluate the system, including details about daily calibration procedures, CGAs, Relative Accuracy Tests, and tests for system bias. Minimum criteria and procedures for these activities are provided in Section 4.2, Section 4.4, and Section 4.5 of this document.

Table 4. Example Table of Contents for facility CEMS QAP for N₂O.

SECTION	SUBSECTION	CONTENTS
I		The Quality Assurance Plan
	1	Assurance Policy and Objectives
	2	QAP Distribution
	3	Quality Requirement of CEM System
	4	Document Revision and Control
	5	CEMs Description
	6	Organization and Responsibilities
	7	Equipment and Spare Parts
	8	Data Handling: Methods and Procedures
	9	System Calibrations and Quality Control Checks
	10	Preventative Maintenance and System Evaluations
	11	Performance Evaluations
	12	Corrective Maintenance
	13	Reports
14	Data Back Filling Procedures	
II		Quality Control Procedures
	1	Installation and Start-up
	2	Daily CEMS Operation
	3	Calibration Procedures
	4	Preventative Maintenance Procedures
	5	Corrective Maintenance Procedures
	6	Evaluation Procedures - Cylinder Gas Audits
	7	Evaluation Procedures - Relative Accuracy Tests
	8	System and Subsystem Evaluation Procedures
	9	Data Backup Procedures
	10	Training
	11	CEMS Security
12	Data Reporting Procedures	
III		Appendices
	1	Facility Approval
	2	CEMS Specifications
	3	Reference Method Procedures
	4	Blank Forms

5.1.3 Inspection, Verification, and Calibration

Inspection, verification and calibration (when required) of the CEMS performance are among the most important aspects of the QA/QC program. The following summarizes the requirements for inspection, verification and calibration, all of which must appear in the QAP.

The method of verifying the accuracy of a CEMS component is to compare the value of the reference standard (e.g., reference gas or dead weight tester output) to the value displayed by the data acquisition system.

Frequency - All CEMS components shall be inspected periodically (approval holder shall identify frequency in the QAP) to verify that individual components have not failed and are operating within prescribed guidelines (e.g., sample system flow rates are appropriate). The use of system components with integral fault detection diagnostics is highly desirable.

The minimum verification frequency for individual CEMS components (e.g., analyzers and temperature transmitters) performance shall be as specified in Table 6. The minimum frequency may be reduced provided the operator can demonstrate (using historical data) that a lower verification frequency will not affect system performance at the 95% confidence level.

(a) Accuracy of Verification/Calibration Equipment and Materials - The minimum accuracy requirement for verification/calibration equipment and materials shall be a factor of two or better than the performance requirement specified for that system component in Section 4.2 of this document. (For example, if a performance specification requires an accuracy of $\pm 2\%$ then the verification/calibration equipment shall be accurate to within $\pm 1\%$.)

For analyzers, the use of certified reference gases is acceptable for routine analyzer system performance verifications. Protocol 1 gases are required for a CGA. All other calibration equipment such as test pressure gauges, dead weight testers and multi-meters must be calibrated at least every 2 years in a manner that is traceable either through the Canadian Standards Association (CSA) or the U.S. National Institute of Standards and Technology (NIST).

For parameters for which cylinder gases are not available at reasonable cost, are unstable, or are unavailable, alternative calibration techniques are acceptable.

Calibration Adjustment - A CEMS component must be calibrated (i.e., output adjusted) whenever the observed inaccuracy exceeds the limits for that system component accuracy as specified in the Performance Specifications. A CEMS component need not be calibrated after each verification, only when it exceeds the specified tolerance.

(b) Out-of-Control Conditions - Only quality assured data may be used to determine CEMS availability. When an analyzer or system is out-of-control, the data generated by the specific analyzer or system are considered missing and does not qualify for meeting the requirement for system availability.

An out-of-control period occurs if either the low level (zero) or high level calibration results exceed twice the applicable Performance Specification. The criteria that pertain to out-of-control periods for specific CEMS are illustrated in Table 5.

Table 5. Criteria for out-of-control periods^e.

Instrument	Acceptable		2X ^(a,b)		4X ^(c)	
	Zero drift	Span drift	Zero drift	Span drift	Zero drift	Span drift
N ₂ O ^g	±2%	±4%	±4%	±8%	±8%	±16%

- a) Corrective action must be taken, at a minimum, whenever the daily zero calibration drift or daily span calibration drift exceeds two times the limits stated above.
- b) If either the zero or span calibration drift results exceeds twice the above stated calibration drift for five consecutive daily periods, the CEMS is out-of-control beginning on the fifth day of error.
- c) If either the zero or span calibration drift results exceeds four times the applicable calibration drift, the CEMS is out-of-control back to the previous calibration drift found to be within tolerance unless a decisive point error occurrence can be defined.
- d) If the CO₂/O₂ CEMS is defined as being out-of-control, the TRS/SO₂/NO_x will also be out-of-control, until the CO₂/O₂ CEMS is defined as being within acceptable limits.
- e) If the CEMS is out-of-control, assess and identify the cause of the excessive drift and correct accordingly. Once the appropriate corrective action has been implemented, repeat the calibration drift test in order to demonstrate the CEMS is back within acceptable limits.
- f) Values are given as a % of gas concentration.
- g) Values are given as a % of full scale reading.

In addition, an out-of-control period also occurs if any of the quarterly, semiannual, or annual performance evaluations exceed the applicable performance specification criteria (i.e., Relative Accuracy, Bias, etc.). In this case, the out-of-control period begins with the hour when this condition occurred and ends with the hour after this condition ends.

(c) Verification/Calibration—Data Logging, and Tabulation - The "as found" values for each verification point shall be recorded before any calibration occurs. The "as left" values for each verification point shall also be recorded after any component is calibrated (i.e., adjustment). For systems capable of automated calibrations, the data system shall record the "as found" and "as left" values including a time stamp (date and time). If strip chart recorder data are reported, any automatic calibration adjustments must be noted on the strip chart recorder.

All verification data must be time-stamped and tabulated on a daily (where applicable) and monthly basis. The use of quality control charts is recommended.

The approval holder must retain the results of all performance evaluations including raw test data as well as all maintenance logs, corrective action logs and the QAP (including sample calculations) for a period of at least 3 years.

(d) Gas Analyzer/ System Verification - For all CEMS, the system is calibrated rather than the analyzer.

System performance shall be verified in accordance with the procedures specified in the facility QAP.

For systems amenable to verification through the use of standard reference gases, the standard reference gas must be introduced at the probe inlet or in the vicinity of the probe inlet. A calibration filter may be used for daily system zero and span verification for path in-situ CEMS only.

Ensure enough time passes to allow the system to attain a steady output, as shown by the data acquisition system, before recording.

For CGAs, the process and analyzer system must be operating at normal conditions (e.g., pressure, temperature, flow rate, pollutant concentration). The analyzer system must be challenged three times with each gas, but not in succession. To do this, alternate the gases presented to the system. Calculate the average response of the system as indicated by the data acquisition system or chart recorder to the three challenges of each concentration of reference gas.

For analyzers not amenable to verification/calibration through the use of reference gases, the operator shall detail verification/calibration procedures in the facility's QAP.

(e) Flow Element Subsystem Verification - For pitot tube or similar systems visual inspection at turnaround (or at least once per year) and as opportunities present themselves for visible signs of plugging or damage. Wind tunnel calibration of pitot tubes should be carried out before initial installation, when visible damage has occurred, or when flow system inaccuracy exceeds acceptable tolerances and inaccuracy cannot be attributed to any component other than the flow element. For pitot tube systems, if, when compared to the stack survey data, $d > \pm 15\%$, then pitot tubes must be pulled and recalibrated unless the source of the error is found to be in the transmitter. (d refers to absolute difference.)

Backpurging (as necessary) of the primary flow measuring elements at an appropriate frequency is acceptable to ensure accurate data (and remove any build up of materials) but should be done when analyzer is being calibrated (or zeroed) so that actual complete sampling time of both flow and pollutant concentration is maximized.

For other flow methods such as ultrasonic meters, anemometers, etc., the QA/QC procedures and frequency shall be specified in the facility QAP and be followed accordingly.

Table 6. Minimum frequency for CEM system component Quality Assurance/Quality Control (QA/QC) requirements.

CEMS COMPONENT	Frequency of Performance Verification Parameter				
	Inspection	Zero Drift	Span Drift	Cylinder Gas Audit ^a	Relative Accuracy Test Audit ^a
Analyzers					
N ₂ O	Daily	Daily	Daily	1/campaign	1/campaign
Rate Measurement Components					
Temperature	Daily	1/year	1/year	NA	1/campaign
Diff. Pressure	Daily	1/year	1/year	NA	
Static Pressure	Daily	1/year	1/year	NA	
Flow Element	1/yr.	NA		NA	1/campaign
Data Acquisition Components					
Recorder	Daily	See Note b	See Note b		
PLC/DCS	Daily	See Note b	See Note b		

^a Frequency is subject to requirements in Section 5.2.

^b The inputs to a PLC/SCADA or DCS must be checked as part of the trouble shooting procedures, only if the analyzer or flow system is found to be out-of-control.

(f) Data Receiver Subsystem Verification

The inputs to the digital data acquisition system (e.g., PLC, DCS, Scada) or chart recorder must be verified at the frequency specified in Table 6 using an appropriate calibrator as identified in the QAP.

5.2 Relative Accuracy Test Audits and Cylinder Gas Audits

5.2.1 General Requirements (applicability)

The approval holder shall conduct Relative Accuracy Tests and Cylinder Gas Audits on each CEMS. A minimum of one Relative Accuracy Tests and a minimum of one CGAs must be conducted on each CEMS.

5.2.2 Relative Accuracy Test Procedures

The procedure for carrying out the relative accuracy and bias tests is given in Subsections 4.5.9 of this Code.

5.2.3 Cylinder Gas Audits

The Cylinder Gas Audit procedure and acceptance criteria are the same as the Linearity Procedure of 4.5.4.

5.2.4 Test Procedure Requirements

The associated QA/QC test procedures applicable to each CEMS and a description of the actual test procedures shall be contained in the facility QAP and adhered to by the facility operator.

During periods of scheduled CEMS quality control procedures, such as Relative Accuracy Test, the facility should be operated at a rate of at least 90 % of "normal" production. Normal production is defined as the average production or throughput for the facility over the previous month.

At least one month must elapse between conducting either a CGA or a RATA.

6.0 REPORTING REQUIREMENTS

6.1 General

All reporting will be as required in Section 2.3.6 of the Specified Gas Emitters Regulation Offset Credit Project Guidance Document (February 2008).

APPENDIX D.1 - DEFINITIONS

Refer to the 1998 Alberta CEMS Code Appendix A

APPENDIX D.2 - RELATIVE ACCURACY SAMPLE CALCULATIONS

Refer to the 1998 Alberta CEMS Code Appendix B

APPENDIX D.3 - BIBLIOGRAPHY

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