

Technical Support Document for the Nitric Acid Production Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases

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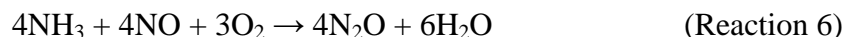
1. Industry Description

Nitric acid is an inorganic chemical that is used in the manufacture of nitrogen-based fertilizers, adipic acid, and explosives. Nitric acid is also used for metal etching and processing of ferrous metals. Production levels for 2006 have been estimated at 6.6 million metric tons of nitric acid and indicate an estimated 17.7 million metric tons of nitrous oxide (N₂O) emissions [in units of metric tons of carbon dioxide (mtCO₂) equivalent emissions].

The production process begins with the stepwise catalytic oxidation of ammonia (NH₃) through nitric oxide (NO) to nitrogen dioxide (NO₂) at high temperatures. Then the nitrogen dioxide is absorbed in and reacted with water (H₂O) to form nitric acid (HNO₃). The steps in the process are shown below.



The main greenhouse gas (GHG) emitted during this process is N₂O, which has a global warming potential of 310 metric tons of CO₂ equivalent emissions (mtCO₂e) per metric ton of N₂O. Nitric acid production is the main source of N₂O emissions in the chemical industry (IPCC, 2006). Nitrous oxide is formed through side reactions during the oxidation of ammonia, as shown in Reactions 4, 5, and 6. The amount formed depends on pressure, temperature, catalyst composition, catalyst age, and burner design (EFMA, 2000). EPA estimates that approximately 15.6 million metric tons CO₂ equivalent emissions (MMTCO₂e), accounting for about 5 percent of all GHG emissions from stationary industrial sources (excluding utilities) and less than 1 percent of the total U.S. GHG inventory, originate from nitric acid production (USGHG, 2008). The N₂O is formed in the converter where the ammonia and air are reacted in the presence of a platinum catalyst and the gas stream is then cooled as it passes through the waste heat boiler.

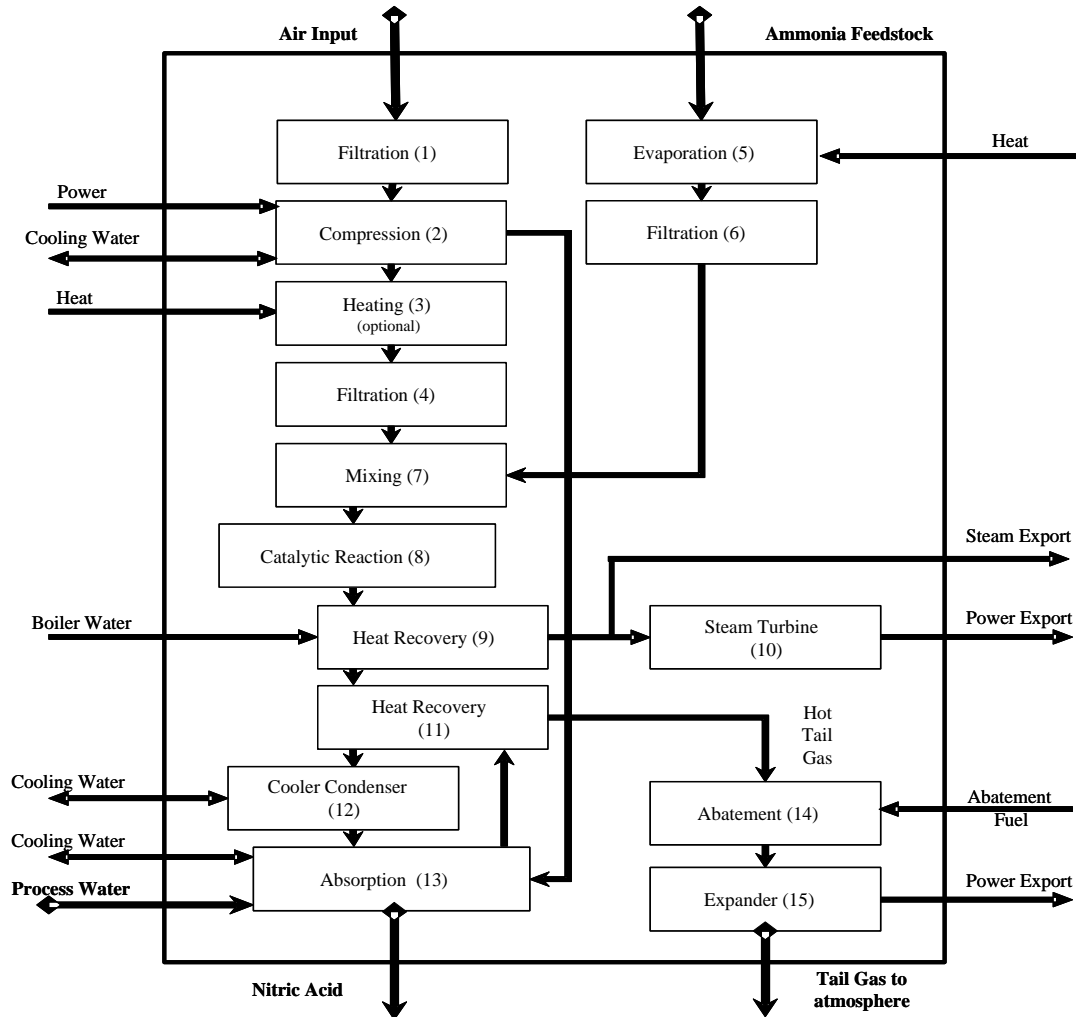


In the United States, nitric acid is produced in two different types of plants due to differences in the three reactions. Reaction 1 is more efficient at lower pressures and higher temperatures while Reactions 2 and 3 are more efficient at higher pressures and lower temperatures. In single pressure plants, the oxidation and absorption take place at essentially the same pressure, and in dual pressure plants absorption takes place at a higher pressure than oxidation. Figure 1 contains a simplified block diagram for single pressure plants (BCS, 2008).

There are a few technologies that control N₂O and NO_x (i.e., nitrogen oxides, NO and NO₂) emissions. These abatement technologies include extended absorption, and catalytic reduction.

Extended absorption reduces NO_x emissions by increasing the efficiency of the absorption tower or incorporating an additional absorption tower.

Figure 1 – Simplified Single Pressure Block Diagram



In catalytic reduction, the tail gases from the absorption tower are mixed with fuel, heated to ignition temperature, and passed over a catalyst bed. Nonselective catalytic reduction (NSCR) transforms NO_x and also N₂O emissions into water, carbon dioxide, and nitrogen in a low oxygen environment. Selective catalytic reduction (SCR) uses ammonia to reduce NO_x emissions into nitrogen and water, but is not known to reduce N₂O emissions. Seventeen percent of the processes use SCR and five percent of the processes use NSCR as abatement technologies. Fifty eight percent of the processes use continuous emission monitoring systems (CEMS) to measure NO_x emissions; use of CEMS to monitor NO_x emissions is required by the New Source Performance Standard (NSPS) for the nitric acid source category (40 CFR Part 60 Subpart G).

Co-location issues arise when a single manufacturing location is covered by multiple GHG source categories. Nitric acid production facilities can be co-located with ammonia production and adipic acid production facilities and possibly other chemical source categories. The three types of facilities are related because ammonia is used to produce nitric acid and nitric acid is used to produce adipic acid. Co-location can influence the GHG emissions from the overall facility but should not influence the assessment of emissions from the production of nitric acid. Each co-located facility should be assessed individually for N₂O emissions from nitric acid production and reported as indicated by the other appropriate process-specific source categories.

2. Total Emissions

Production levels for 2006 have been estimated at 6.6 million metric tons of nitric acid and indicate an estimated 17.7 MMTCO₂e from nitric acid production processes. According to the facility-level (bottom-up) inventory, there are 45 nitric acid production plants operating in 25 states with a total of 65 process units. There are 9 small businesses which own a total of 18 nitric acid facilities. Table 1 contains a list of all nitric acid facilities. As shown in Table 1, 17 percent of the processes use SCR, 5 percent of the processes use NSCR, and 58 percent of the processes use continuous emission monitoring systems (CEMS) to measure NO_x emissions. Table 2 shows the estimated amount of N₂O emissions from the nitric acid facilities.

Nitric Acid process emissions were estimated by the *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006* at 15.4 MMTCO₂e in 2006 or 0.2 percent of total U.S. greenhouse gas emissions. The main reason for the difference in estimates is that the methodology of the Greenhouse Gas Inventory assumed 20 percent of the nitric acid facilities were using nonselective catalytic reduction (NSCR) as an N₂O abatement technology. The facility-level analysis showed that only five percent of the nitric acid facilities are using NSCR.

The estimate above includes only process-related GHG emissions. Combustion emissions (CO₂, CH₄, and N₂O) from nitric acid production plants result from the combustion of natural gas and fuel oil. Combustion sources include turbine steam generators and boilers. Although other fuels may be combusted for energy, MECS data for NAICS code 325311, “Nitrogenous Fertilizers” which includes nitric acid production, indicates 98 percent of the total fuel energy consumption (i.e., excluding purchased electricity) is natural gas. For more information on reporting options for stationary combustion refer to EPA-HQ-OAR-2008-0508-004.

Table 1. U.S. Producers of Nitric Acid (metric tons per year)

Facility Name	City	State	Number of nitric acid processes	Abatement Technology	Co-location	Monitoring	2006 Nameplate Capacity (metric tons HNO ₃ per year) [100% Acid Basis]	Estimated 2006 HNO ₃ Production (metric tons HNO ₃)
Agrium US	Beatrice	NE	1	SCR		NO _x CEMS	145,000	101,248
Agrium US	Kennewick	WA	1				285,000	199,005
Agrium US	North Bend	OH	1				85,000	59,352
Agrium US	West Sacramento	CA	1				70,000	48,878
Air Products	Pasadena	TX	2	SCR			110,000	76,809
Angus Chemical	Sterlington	LA	1				65,000	45,387
Apache Nitrogen Products	Benson	AZ	2			NO _x CEMS	140,000	132,489
CF Industries	Donaldsonville	LA	3	extended absorption and SCR	ammonia production		680,000	474,820
Dyno Nobel	Battle Mountain	NV	1				250,000	174,566
Dyno Nobel	Cheyenne	WY	3		ammonia production	NO _x CEMS	100,000	69,826
Dyno Nobel	St. Helens	OR	1	NSCR	ammonia production		20,000	13,023
Coffeyville Resources	Coffeyville	KS	1	SCR	ammonia production		170,000	118,705
DuPont	Orange	TX	1		adipic acid production		170,000	118,705
DuPont	Victoria	TX	1		adipic acid production		300,000	209,479
Dyno Nobel	Donora	PA	1				115,000	80,300

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Facility Name	City	State	Number of nitric acid processes	Abatement Technology	Co-location	Monitoring	2006 Nameplate Capacity (metric tons HNO ₃ per year) [100% Acid Basis]	2006 HNO ₃ Production (metric tons HNO ₃)
Dyno Nobel	Louisiana	MO	1				270,000	188,531
El Dorado Nitrogen	Baytown	TX	1	SCR		NO _x CEMS	445,000	310,728
El Dorado Nitrogen	Cherokee	AL	1		ammonia production		270,000	188,531
El Dorado Nitrogen	El Dorado	AR	5	SCR		NO _x CEMS	425,000	296,762
First Chemical	Pascagoula	MS	1			NO _x CEMS	75,000	52,370
Geneva Nitrogen	Orem	UT	2	SCR			80,000	74,230
Hercules	Parlin	NJ	1				80,000	55,861
JR Simplot	Helm	CA	1			NO _x CEMS	80,000	50,973
JR Simplot	Pocatello	ID	1				20,000	13,965
Koch Nitrogen	Beatrice	NE	1	NSCR	ammonia production	NO _x CEMS	55,000	38,405
Koch Nitrogen	Dodge City	KS	1	NSCR	ammonia production		70,000	48,878
Koch Nitrogen	Enid	OK	1	NSCR	ammonia production	NO _x CEMS	40,000	27,931
Koch Nitrogen	Fort Dodge	IA	1	SCR	ammonia production	NO _x CEMS	165,000	115,214
LSB Industries	Crystal City	MO	1				180,000	125,688
Lyondell Chemical	Lake Charles	LA	1				170,000	118,705
Bayer Corporation	Baytown	TX	1				45,000	31,422

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Facility Name	City	State	Number of nitric acid processes	Abatement Technology	Co-location	Monitoring	2006 Nameplate Capacity (metric tons HNO ₃ per year) [100% Acid Basis]	2006 HNO ₃ Production (metric tons HNO ₃)
Bayer Corporation	New Martinsville	WV	1				90,000	62,844
Nitrochem	Newell	PA	1				75,000	52,370
Orica	Joplin	MO	1				160,000	111,722
Orica	Morris	IL	1			NO _x CEMS	160,000	111,722
PCS Nitrogen	Augusta	GA	2	SCR	ammonia production	NO _x CEMS	475,000	331,675
PCS Nitrogen	Geismar	LA	4	SCR	ammonia production	NO _x CEMS	825,000	576,068
PCS Nitrogen	Lima	OH	1		ammonia production		105,000	73,318
Rentech Energy Midwest Corporation	East Dubuque	IL	2	extended absorption and SCR	ammonia production	NO _x CEMS	110,000	76,809
Solutia	Pensacola	FL	1	SCR		NO _x CEMS	365,000	254,866
Terra International	Port Neal	IA	2	SCR	ammonia production	NO _x CEMS	255,000	178,057
Terra International	Verdigris	OK	1		ammonia production	NO _x CEMS	630,000	439,906
Terra International	Woodward	OK	1		ammonia production	NO _x CEMS	90,000	62,844
Terra International	Yazoo City	MS	4	extended absorption and SCR	ammonia production	NO _x CEMS	955,000	614,822
TradeMark Nitrogen	Tampa	FL	1	extended absorption		NO _x CEMS	35,000	24,439
TOTALS	45		65		17	20	9,505,000	6,632,249

Table 2. U.S. Estimated Emissions from Producers of Nitric Acid (mtCO₂e per year)

Facility Name	Total N₂O Emissions from HNO₃ production (mtCO₂e)
Facility 1	282,483
Facility 2	165,593
Facility 3	107,149
Facility 4	496,780
Facility 5	68,185
Facility 6	925,374
Facility 7	555,225
Facility 8	311,705
Facility 9	204,556
Facility 10	331,187
Facility 11	175,334
Facility 12	146,112
Facility 13	350,241
Facility 14	1,095,751
Facility 15	487,039
Facility 16	194,816
Facility 17	8,074
Facility 18	331,187
Facility 19	331,187

Facility Name	Total N₂O Emissions from HNO₃ production (mtCO₂e)
Facility 20	584,447
Facility 21	224,038
Facility 22	526,002
Facility 23	866,930
Facility 24	526,002
Facility 25	827,967
Facility 26	146,112
Facility 27	153,232
Facility 28	155,853
Facility 29	142,215
Facility 30	38,963
Facility 31	136,371
Facility 32	17,317
Facility 33	321,446
Facility 34	350,668
Facility 35	175,334
Facility 36	311,705

Facility Name	Total N₂O Emissions from HNO₃ production (mt CO₂e)
Facility 37	1,607,229
Facility 38	214,297
Facility 39	1,227,339
Facility 40	1,334,163
Facility 41	214,297
Facility 42	711,077
Facility 43	87,667
Facility 44	136,371
Facility 45	126,630
TOTALS	17,731,650

3. Review of Existing Programs and Methodologies

In evaluating monitoring options for nitric acid production, multiple GHG emissions reporting guidance documents were consulted. These include documents developed by the U.S. Environmental Protection Agency (EPA, 2008), the Intergovernmental Panel on Climate Change (IPCC, 2006), The Climate Registry (CR, 2007), the European Union (EU, 2007), the United Kingdom (DEFRA, 2003), Australia (NGER, 2007), Japan (Japan, 2006), the World Resources Institute/World Business Council for Sustainable Development (WRI/WBCSD, 2001), the U.S. Department of Energy (U.S.DOE, 2007), and Environment Canada (EC, 2006). The main monitoring methods from each of these reporting programs are reviewed below.

3.1 2006 IPCC Guidelines for National Greenhouse Gas Inventories

The Tier 1 methodology estimates emissions using the total production of nitric acid and the appropriate default emission factor from Table 3. The Tier 1 method should be applied assuming no abatement of N₂O emissions and the use of the highest default emission factor based on technology type. The Tier 2 methodology estimates emissions using facility-specific information, including the production rate of nitric acid, the appropriate emission factor from Table 3, the destruction factor for abatement technology, and the utilization factor of the abatement system (if applicable). The equation is shown below. The Tier 3 methodology estimates emissions using plant level production data and plant level emission factors that are obtained from direct measurement of emissions. These may be derived from irregular sampling of N₂O or monitoring of N₂O over a period that reflects the usual pattern of operation of the plant.

$$E_{N_2O} = \sum (EF_i * NAP_i * (1 - DF_j * ASUF_j))$$

where:

E_{N_2O}	=	emissions of N ₂ O, kg
EF_i	=	N ₂ O emission factor for technology type i, kg N ₂ O/metric ton nitric acid produced
NAP_i	=	nitric acid production from technology type i, metric ton
DF_j	=	destruction factor for abatement technology type j, fraction
$ASUF_j$	=	abatement system utilization factor for abatement technology type j, fraction.

Table 3. Default N₂O Emission Factors from Nitric Acid Production

Production Process	Approximate Pressure (atm)	N ₂ O Emission Factor (kg N ₂ O/metric ton nitric acid)			N ₂ O Emission Factor (metric ton N ₂ O/metric ton nitric acid)		
		Low	Average	High	Low	Average	High
Plants with NSCR		1.9	2	2.1	0.0019	0.002	0.0021
Plants with process-integrated or tailgas N ₂ O destruction		2.25	2.5	2.75	0.00225	0.0025	0.00275
Atmospheric pressure plants (low pressure)	1	4.5	5	5.5	0.0045	0.005	0.0055
Medium pressure plants	4-8	5.6	7	8.4	0.0056	0.007	0.0084
High pressure plants	8-14	5.4	9	12.6	0.0054	0.009	0.0126

3.2 WRI/WBCSD *The Greenhouse Gas Protocol - A corporate reporting and accounting standard*

Approach 1 involved precise direct monitoring of N₂O emissions, with measurements at both the exit stream and the uncontrolled stream. Data quality is satisfactory when measurement data are only available for the exit stream. Approach 2 involves site-specific N₂O emission factors. This approach is based on the IPCC Tier 2 methodology. Approach 3 involves the use of default emission factors for N₂O emissions. This approach is based on the IPCC Tier 1 methodology.

3.3 United States Department of Energy’s *Technical Guidelines Voluntary Reporting of Greenhouse Gases (1605(b)) Program*

The “A” rated approach involves continuous emission monitoring (CEM) from confined and uncontrolled streams. If pollutant information is not available for uncontrolled streams, monitoring of confined streams only is acceptable. If CEM is not possible, emissions can be estimated using an emission factor based on direct, periodic measurements of plant emissions during a stack test. Emission factors must account for emission rates and abatement system efficacy and frequency of use of abatement technologies. The “B” rated approach involves the use of default IPCC emission factors and production if plant-level emission information is not available. The “C” rated approach involves the use of estimates based on “other published default values.”

3.4 *The Climate Registry*

The Tier A1 methodology is specified as direct measurement. The Tier A2 methodology is a mass balance approach based on plant-specific factors for destruction and utilization factors for an abatement technology and N₂O emission factor based on direct measurements. The Tier B methodology is a mass balance approach based on default N₂O emission factors by technology type. This methodology is consistent with Tier 2 methodology from IPCC.

3.5 *Inventory of U.S. Greenhouse Gas Emissions and Sinks: 1990-2006 (EPA 2008)*

The Tier 1 methodology includes the use of an emission factor for estimating N₂O emissions from total national production of nitric acid. The emission factor was determined as a weighted average of 2 kilograms (kg) N₂O per metric ton HNO₃ for 28 plants using NSCR systems and 9 kg N₂O per metric ton HNO₃ for plants not equipped with NSCR (IPCC, 2006). In the process of destroying NO_x, NSCR systems destroy 80 to 90 percent of the N₂O, which is accounted for in the emission factor of 2 kg N₂O per metric ton HNO₃. An estimated 20 percent of HNO₃ plants in the United States are equipped with NSCR (Choe et al. 1993). Hence, the emission factor is equal to $(9 \times 0.80) + (2 \times 0.20) = 7.6$ kg N₂O per metric ton HNO₃ (USGHG, 2008). Emissions are calculated by multiplying this emission factor by national production of nitric acid.

3.6 *European Union's Commission Decision of 18 July 2007 establishing guidelines for the monitoring and reporting of greenhouse gas emissions pursuant to Directive 2003/87/EC of the European Parliament and of the Council*

This report has no specific guidance for nitric acid production and generally follows IPCC guidelines.

3.7 *United Kingdom's Guidelines for the Measurement and Reporting of Emissions by Direct Participants in the UK Emissions Trading Scheme*

The method outlined for nitric acid production is specific to one company and is not recommended for all nitric acid production facilities. Other companies are required to submit their own protocols for approval by DEFRA.

3.8 *Australia's Technical Guidelines for the Estimation of Greenhouse Emissions and Energy at Facility Level: Energy, Industrial Process and Waste Sectors in Australia*

The default method follows the Tier 2 methodology of the IPCC.

3.9 *Greenhouse Gas Inventory Report of Japan*

Emissions data in Japan are considered confidential, so nitric acid production volume and emission factors were set for Japan's total production. The method is based on IPCC Tier 1 and Tier 2 methodologies.

3.10 *Environment Canada's Technical Guidance on Reporting Greenhouse Gas Emissions*

The guidance for mandatory reporting in Canada primarily references the IPCC guidelines. There is no specific guidance on nitric acid production.

4. Options for Reporting Threshold

4.1 Emissions Thresholds

For the reporting of process CO₂ emissions from nitric acid production, EPA considered emissions-based thresholds of 1,000, 10,000, 25,000, and 100,000 mtCO₂e for process-related emissions only. Data were not available to incorporate combustion-related emissions. The results of the threshold analysis incorporating these four threshold options are summarized in Table 4. The IPCC Tier 2 method was used to determine process CO₂ emissions from the facilities presented in Table 1. The types of abatement equipment used for N₂O control were available from permits and in many cases, facility-level production data were also available. When facility-level production data were not known, capacity data were used along with a utilization factor of 70 percent. The utilization factor is based on total 2006 nitric acid production (USCB 2007) and capacity estimates (ICIS 2005) (Innovation Group 2002).

The IPCC Tier 3 method could not be used because facility-specific emission factors have not been determined.

Table 4. Threshold Analysis for Nitric Acid

Threshold Level (mtCO ₂ e)	Process N ₂ O Emissions (mtCO ₂ e/yr)	Process N ₂ O Emissions Covered		Facilities Covered	
		mtCO ₂ e	%	Number	%
100,000	17,731,650	17,511,444	98.8	40	88.9
25,000	17,731,650	17,706,259	99.9	43	95.6
10,000	17,731,650	17,723,576	99.95	44	97.8
1,000	17,731,650	17,731,650	100	45	100

A threshold of 1,000 mtCO₂e captures all facilities in the inventory. A threshold of 10,000 mtCO₂e captures 99.95 percent of emissions and 97.8 percent of the facilities. A threshold of 25,000 mtCO₂e captures 99.9 percent of emissions and 95.6 percent of the facilities. A threshold of 100,000 mtCO₂e captures 98.8 percent of emissions and 88.9 percent of the facilities.

4.2 Capacity Thresholds

For the capacity thresholds analysis for nitric acid production, EPA considered six different capacities of nitric acid production. Capacity is the largest amount of nitric acid that a facility can produce on an annual basis. The thresholds considered were 500,000, 250,000, 150,000, 100,000, 50,000, and 20,000 metric tons of nitric acid produced per year. The results of the capacity threshold analysis are shown in Table 5. A threshold of 20,000 metric tons captures all facilities in the inventory. A threshold of 50,000 metric tons captures 98.8 percent of emissions, and 91.1 percent of the facilities. A threshold of 100,000 metric tons captures 87.9 percent of

emissions and 62.2 percent of the facilities. A threshold of 150,000 metric tons captures 78.5 percent of emissions and 46.7 percent of the facilities. A threshold of 200,000 metric tons captures 65.7 percent of emissions and 31.1 percent of the facilities. A threshold of 500,000 metric tons captures 29.4 percent of emissions and 8.9 percent of the facilities.

Table 5. Capacity Threshold Analysis for Nitric Acid Production

Capacity Threshold (metric tons nitric acid produced per year)	Process N ₂ O Emissions (mtCO ₂ e/yr)	Process N ₂ O Emissions Covered		Facilities Covered	
		mtCO ₂ e	%	Number	%
500,000	17,731,650	5,212,385	29.4	4	8.9
200,000	17,731,650	11,654,838	65.7	14	31.1
150,000	17,731,650	13,921,270	78.5	21	46.7
100,000	17,731,650	15,592,792	87.9	28	62.2
50,000	17,731,650	17,526,379	98.8	41	91.1
20,000	17,731,650	17,731,650	100	45	100

4.3 No Emissions Threshold

The no emissions threshold includes all nitric acid production facilities regardless of their emissions or capacity.

5. Options for Monitoring Methods

5.1 Option 1: Simplified Emissions Calculation

A simplified emissions calculation option would use the default emission factors established by the Intergovernmental Panel on Climate Change (IPCC, 2006). Two different approaches could be used.

Approach 1. Use the default emission factors using total national production of nitric acid using the Tier 1 approach established by the IPCC. The emissions are calculated using the total production of nitric acid, assumes no abatement of N₂O emissions, and uses the highest default emission factor based on technology type.

This is consistent with the Tier 1 methodology from the U.S. Greenhouse Gas Inventory, the Tier 1 methodology from IPCC, the first approach from Japan’s guidance document, Approach 3 from the World Business Council for Sustainable Development (WBCSD), and the “B” rated approach from the United States Department of Energy (USDOE).

Approach 2. Use the default emission factors on a site-specific basis using the Tier 2 approach established by the IPCC. These emission factors are dependent on the type of nitric acid process used, the type of abatement technology used, and the production activity. The amount of N₂O

emissions are determined by multiplying the emission factor by the production level of nitric acid (on a 100 percent acid basis).

This is consistent with the Tier 2 methodology from IPCC, the Tier B methodology from The Climate Registry, the default method from Australia’s guidance document, the second approach from Japan’s guidance document, Approach 2 from WBCSD, and the “B” rated approach from USDOE.

The default emission factor values for nitric acid production are uncertain. First, N₂O may be generated in the gauze reactor section of nitric acid production as an unintended by-product reaction. Second, the exhaust gas may or may not be treated for NO_x control, and the NO_x abatement system may or may not reduce (or may even increase) the N₂O concentration of the treated gas. A properly maintained and calibrated monitoring system can determine emissions to within ±5% at the 95% confidence level (IPCC 2006).

5.2 Option 2: Hybrid (Facility Specific Emission Factor Using Stack Test)

Follow the Tier 3 approach established by IPCC using non-continuous monitoring. Directly monitor N₂O emissions and determine the relationship between nitric acid production and the amount of N₂O emissions; i.e., develop a site-specific emissions factor. The site-specific emissions factor and production rate (activity level) is used to calculate the emissions. Annual testing of N₂O emissions would also be required to verify the emission factor over time. Testing should be conducted without using any NO_x or N₂O abatement technologies. Testing would also be required whenever significant process changes are made. This approach is consistent with the Tier 3 methodology from IPCC, the Tier A1 methodology from the Climate Registry, and Approach 1 from WBCSD.

This option uses non-continuous direct monitoring of N₂O emissions to determine the relationship between nitric acid production and the amount of N₂O emissions. As the production rate changes, a new N₂O emission rate could be calculated. Annual testing of N₂O emissions would also be required to verify the emission factor over time. Testing would also be required whenever significant process changes are made.

Emissions would be calculated according to the following equations.

The average site-specific emission factor for the process would be calculated according to the following equation:

$$EF_{N_2O} = \frac{\sum_1^n \frac{C_{N_2O} * 1.14 \times 10^{-7} * Q}{P}}{n}$$

Where:

EF_{N₂O} = Average site-specific N₂O emissions factor (lb N₂O/ton nitric acid produced, 100 percent acid basis)

C_{N₂O} = N₂O concentration during performance test (ppm N₂O)

- 1.14×10^{-7} = Conversion factor (lb/dscf-ppm N₂O)
Q = Volumetric flow rate of effluent gas (dscf/hr)
P = Production rate during performance test (tons nitric acid produced per hour (100 percent acid basis))
n = Number of test runs

The N₂O emissions for the process are then calculated by multiplying the emission factor by the total production, according to following equation:

$$E_{N_2O} = \frac{EF_{N_2O} * P_a * (1 - DF_N) * AF_N}{2205}$$

Where:

- E_{N_2O} = N₂O mass emissions per year (metric tons of N₂O)
 EF_{N_2O} = Site-specific N₂O emission factor (lb N₂O/ton acid produced, 100 percent acid basis)
 P_a = Total production for the year (ton acid produced, 100 percent acid basis)
 DF_N = Destruction factor of N₂O abatement technology (percent of N₂O removed from air stream)
 AF_N = Abatement factor of N₂O abatement technology (percent of year that abatement technology was used)
2205 = Conversion factor (lb/metric ton).

The amount of N₂O emitted varies based on production rate, equipment condition, and abatement technology used. The emission factor is not expected to vary significantly on a day-to-day basis. Annual testing should be sufficient to account for changes in equipment over time and repeat testing should be sufficient to account for any reduction in emissions due to equipment installation or shutdown. All other variables that could impact N₂O emissions (changes in production rate and abatement technologies) are accounted for in the equation.

5.3 Option 3: Direct Measurement

Process and combustion emissions resulting from nitric acid production can also be determined through direction measurement. Two approaches could be used to comply with Option 3. Under either a CEMS approach or a stack testing approach, the emissions measurement data would be reported annually.

5.3.1. Stack Test Data

Direct measurement could also be carried out through stack testing, whereby sampling equipment would be periodically brought to the site and installed temporarily in the stack to withdraw a sample of the stack gas and measure the flow rate of the stack gas. Similar to CEMS,

for stack testing the emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. The difference between stack testing and continuous monitoring is that the CEMS data provide a continuous measurement of the emissions, while a stack test provides a periodic measurement of the emissions. Two approaches could be used to comply with Option 3.

5.3.2. New Source Performance Standard Approach

Direct measurement is required by the Nitric Acid New Source Performance Standard (NSPS) (40 CFR Part 60, subpart G). Under the NSPS approach, however, owners or operators must use CEMS to directly measure NO_x and use a site-specific emission rate factor to convert the NO_x measurement to N₂O emissions per ton of acid produced. This option would require monitoring NO_x emissions on a continuous basis and measuring N₂O emissions to establish an emission rate factor and periodic monitoring (using a stack test) to verify the emission rate factor over time. Testing should be conducted without using any NO_x or N₂O abatement technologies. Testing would also be required whenever significant process changes are made. According to the facility-level (bottom-up) inventory, 44 percent of facilities are currently using NO_x CEMS. This approach is consistent with the approach used by the Nitric Acid NSPS to determine NO_x emissions in units of the emissions limit, lb NO_x per ton of 100 percent nitric acid produced.

5.3.3. Continuous Emissions Monitoring Systems

Another applicable monitoring method to estimate N₂O emissions from nitric acid production facilities for which the process emissions and/or combustion GHG emissions are contained within a stack or vent is direct measurement using a Continuous Emissions Monitoring System (CEMS). Though available, CEMS for monitoring N₂O emissions are not currently in use in the industry and there is no existing EPA method for certifying N₂O CEMS.

Direct measurements of the GHG (in this case N₂O) concentration in the stack gas and the flow rate of the stack gas can be made using a CEMS. Elements of a CEMS include a platform and sample probe within the stack to withdraw a sample of the stack gas, an analyzer to measure the concentration of the GHG (e.g., CO₂) in the stack gas, and a flow meter within the stack to measure the flow rate of the stack gas. The emissions are calculated from the concentration of GHGs in the stack gas and the flow rate of the stack gas. A CEMS continuously withdraws and analyzes a sample of the stack gas and continuously measures the GHG concentration and flow rate of the stack gas.

Because a CEMS would continuously measure actual N₂O emissions at a given nitric acid production facility when it is in operation, this method is the most accurate monitoring method for determining GHG emissions from a specific source. This method would be consistent with the Tier 3 approach established by IPCC, the Tier A1 methodology from the Climate Registry, Approach 1 from WBCSD, and the “A” rated approach from USDOE.

6. Options for Estimating Missing Data

Options and considerations for missing data will vary depending on the proposed monitoring method. Each option would require a complete record of all measured parameters as well as parameters determined from company records that are used in the GHG emissions calculations (e.g., carbon contents, monthly fuel consumption, etc.).

6.1 Procedures for Option 1: Simplified Emission Calculation Method

If facility-specific production data are missing for one year, an average value using the production data from the year prior and the year after the missing year may be calculated. Default emission factors are readily available through IPCC guidelines (IPCC 2006).

6.2 Procedures for Option 2: Facility Specific Emission Factor Using Stack Test

For process sources that use the hybrid approach, the following data would be needed: nitric acid production rate, nitric acid production capacity, number of operating hours, emission rate factor, and the type of abatement technology used and its utilization factor. In general, the substitute data value could be the arithmetic average of the quality-assured values of that same parameter immediately preceding and immediately following the missing data incident. If no quality-assured data are available prior to the missing data incident, the substitute data value would be the first quality-assured value obtained after the missing data period. For missing oil or gas flow rates the standard missing data procedures in section 2.4.2 of appendix D to part 75 could be required.

6.3 Procedures for Option 3: Direct Measurement

6.3.1 Continuous Emission Monitoring Data

CEMS for monitoring N₂O emissions are not currently in use in the industry and there is no existing EPA method for certifying N₂O CEMS. In general, the missing data procedures for CO₂ CEMS, listed below would be adequate.

For options involving direct measurement of CO₂ emissions using CEMS, Part 75 establishes procedures for the management of missing data. Specifically, the procedures for managing missing CO₂ concentration data are specified in §75.35. In general, missing data from the operation of the CEMS may be replaced with substitute data to determine the CO₂ emissions during the period for which CEMS data are missing. Section 75.35(a) requires the owner or operator of a unit with a CO₂ CEMS to substitute for missing CO₂ pollutant concentration data using the procedures specified in paragraphs (b) and (d) of §75.35; paragraph (b) covers operation of the system during the first 720 quality-assured operation hours for the CEMS, and paragraph (d) covers operation of the system after the first 720 quality-assured operating hours are completed.

During the first 720 quality-assured monitor operating hours following initial certification at a particular unit or stack location, the owner or operator would be required to substitute CO₂ pollutant concentration data according to the procedures in §75.31(b). That is, if prior quality-assured data exist, the owner or operator would be required to substitute for each hour of missing data, the average of the data recorded by a certified monitor for the operating hour immediately preceding and immediately following the hour for which data are missing. If there are no prior quality-assured data, the owner or operator would have to substitute the maximum potential CO₂ concentration for the missing data.

Following the first 720 quality-assured monitor operating hours, the owner or operator would have to follow the same missing data procedures for SO₂ specified in §75.33(b). The specific

methods used to estimate missing data would depend on the monitor data availability and the duration of the missing data period.

6.3.2 Stack Test Data

For options involving direct measurement of flow rates or emissions using stack testing, “missing data” is not generally anticipated. Stack testing conducted for the purposes of compliance determination is subject to quality assurance guidelines and data quality objectives established by the U.S. EPA, including the Clean Air Act National Stack Testing Guidance published in 2005 (USEPA 2005). The 2005 EPA Guidance Document indicates that stack tests should be conducted in accordance with a pre-approved site-specific test plan to ensure that a complete and representative test is conducted. Results of stack tests that do not meet pre-established quality assurance guidelines and data quality objectives would generally not be acceptable for use in emissions reporting, and any such stack test would need to be re-conducted to obtain acceptable data.

7. QA/QC Requirements

Facilities could be required to conduct quality assurance and quality control of the reported data. Specific QA/QC requirements would vary depending on the monitoring methods, but facilities could be required to prepare an in-depth quality assurance and quality control plan which would include checks on production data and calculations performed to estimate GHG emissions.

7.1 Stationary Emissions

For more information on the QA/QC requirements associated with methods for estimating CO₂, CH₄, and N₂O emissions from stationary combustions see the General Stationary Fuel Combustion Technical Support Document at EPA-HQ-OAR-2008-0508-004.

7.2 Process Emissions

Options and considerations for QA/QC will vary depending on the proposed monitoring method. Each option would require unique QA/QC measures appropriate to the particular methodology employed to ensure proper emission monitoring and reporting.

For facilities using CEMS to measure CO₂ emissions, the equipment could be tested for accuracy and calibrated as necessary by a certified third party vendor. These procedures could be required to be consistent in stringency and data reporting and documentation with the QA/QC procedures for CEMS described in Part 75 of the Acid Rain Program.

For facilities using stack test data, U.S. EPA regulations for performance testing under 40 CFR § 63.7(c)(2)(i) could be required. These regulations state that before conducting a required performance test, the owner/operator is required to develop a site-specific test plan and, if required, submit the test plan for approval. The test plan is required to include “a test program summary, the test schedule, data quality objectives, and both an internal and external quality assurance (QA) program” to be applied to the stack test. Data quality objectives are defined under 40 CFR § 63.7(c)(2)(i) as “the pre-test expectations of precision, accuracy, and completeness of data.” Under 40 CFR § 63.7(c)(2)(ii), the internal QA program is required to include, “at a minimum, the activities planned by routine operators and analysts to provide an

assessment of test data precision; an example of internal QA is the sampling and analysis of replicate samples.” Under 40 CFR § 63.7(c)(2)(iii) the external QA program is required to include, “at a minimum, application of plans for a test method performance audit (PA) during the performance test.” In addition, according to the 2005 Guidance Document, a site-specific test plan should generally include chain of custody documentation from sample collection through laboratory analysis including transport, and should recognize special sample transport, handling, and analysis instructions necessary for each set of field samples (USEPA 2005).

7.3 Data Management

Data management procedures could be included in the QA/QC Plan. Elements of the data management procedures plan are as follows:

- Check for temporal consistency in production data and emission estimates. If outliers exist, they could be required to be explained by changes in the facility operations or other factors. A monitoring error is probable if differences between annual data cannot be explained by: changes in activity levels, changes concerning fuels or input material, or changes concerning the emitting process (e.g. energy efficiency improvements) (EU 2007).
- Determine the “reasonableness” of the emission estimate by comparing it to previous year’s estimates and relative to national emission estimate for the industry:
 - Comparison of data on fuel or input material consumed by specific sources with fuel or input material purchasing data and data on stock changes,
 - Comparison of emission factors that have been calculated or obtained from the fuel or input material supplier, to national or international reference emission factors of comparable fuels or input materials,
 - Comparison of emission factors based on fuel analyses to national or international reference emission factors of comparable fuels, or input materials,
 - Comparison of measured and calculated emissions (EU 2007).
- Maintain data documentation, including comprehensive documentation of data received through personal communication.
- Check that changes in data or methodology are documented.

8. Types of Emission Information to be Reported

Nitric acid facilities owner and operators should report both process (N₂O) and combustion related (CO₂, CH₄, and N₂O) greenhouse gas emissions. The data to be reported may vary depending on monitoring options selected. However, all nitric acid production facilities should report the number of nitric acid production lines, annual nitric acid production (on a 100% acid basis), annual nitric acid production capacity (on a 100% acid basis), electricity usage (kilowatt-hours), emission factor(s) used, type of nitric acid production process(es) used, abatement technology used (if applicable), abatement utilization factor (percent of time that abatement system is operating), abatement technology efficiency, and annual operating hours.

Combustion-related emissions would be reported consistent with the stationary fuel combustion methods. The specific data to be reported, and any additional information to be reported to support verification, depends on the calculation methodology implemented. For more

information on reporting options for stationary combustion refer to EPA-HQ-OAR-2008-0508-004.

8.1 Types of Emissions to be Reported

8.1.1 Option 1: Simplified Emission Calculation

For process sources that use a simplified emission calculation, the facility could report its production data, fuel type, fuel consumption, carbon content of fuel, and emission factor calculated.

8.1.2 Option 2: Facility Specific Emission Factor Using Stack Test

For the hybrid method, the facility could report its production data and site-specific emission factor. They could also be required to report testing of N₂O emissions that was conducted to verify the emission factor over time. Information on the type and use of abatement technologies could also be required. If significant process changes are made, and additional testing is carried out, this information could also be reported.

8.1.3 Option 3: Direct Measurement

For options for which the monitoring method is based on direct measurement, either using a CEMS or through stack testing, the GHG emissions are directly measured at the point of emission.

8.1.3.1 CEMS

For direct measurement using CEMS, the facility could be required to report the GHG emissions measured by the CEMS for each monitored emission point and could also report the monitored GHG concentrations in the stack gas and the monitored stack gas flow rate for each monitored emission point. These data would illustrate how the monitoring data were used to estimate the GHG emissions.

The facility could report the following data for direct measurement of emissions using CEMS:

- The unit ID number (if applicable);
- A code representing the type of unit;
- Maximum product production rate and maximum raw material input rate (in units of metric tons per hour [metric tons/hr]);
- Each type of raw material used and each type of product produced in the unit during the report year;
- The calculated CO₂, CH₄, and N₂O emissions for each type of raw material used and product produced, expressed in metric tons of each gas and in metric tons of CO₂e;
- A code representing the method used to calculate the CO₂ emissions for each type of raw material used (e.g., part 75, Tier 1, Tier 2, etc.);
- If applicable, a code indicating which one of the monitoring and reporting methodologies in part 75 of this chapter was used to quantify the CO₂ emissions;
- The calculated CO₂ emissions from sorbent (if any), expressed in metric tons; and

- The total GHG emissions from the unit for the reporting year, i.e., the sum of the CO₂, CH₄, and N₂O emissions across all raw material and product types, expressed in metric tons of CO₂e.

8.1.3.2 Stack Testing

For direct measurement using stack testing, the facility could report the GHG emissions measured during the stack test, the measured GHG concentrations in the stack gas, the monitored stack gas flow rate for each monitored emission point, and the time period during which the stack test was conducted. The facility could also report the process operating conditions (e.g., raw material feed rates) during the time period during which the test was conducted.

8.2 Other Information to be Reported

Facility owners and operators could also submit the following data to understand the emissions data and verify the reasonableness of the reported emissions. The data could include annual nitric acid production capacity, annual nitric acid production, number of operating hours in the calendar year, the emission rate factor used, abatement technology used (if applicable), abatement technology efficiency, and abatement utilization factor.

Capacity, actual production, operating hours will be helpful in determining the potential for growth in the nitric acid industry. A list of abatement technologies would be helpful in assessing the widespread use of abatement in the nitric acid source category, cataloging any new technologies that are being used, and documenting the amount of time that the abatement technologies are being used.

8.3 Additional Data to be Retained Onsite

Facilities could be required to retain data concerning monitoring of GHG emissions onsite for a period of at least five years from the reporting year. For CEMS these data could include CEMS monitoring system data including continuous-monitored GHG concentrations and stack gas flow rates, and calibration and quality assurance records. For stack testing these data could include stack test reports and associated sampling and chemical analytical data for the stack test. Process data including process raw material and product feed rates and carbonate contents should also be retained on site for a period of at least five years from the reporting year. The EPA could use such data to conduct trend analyses and potentially to develop process or activity-specific emission factors for the process.

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