EPA
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AVAILABLE AND EMERGING TECHNOLOGIES FOR REDUCING GREENHOUSE GAS EMISSIONS FROM THE NITRIC ACID PRODUCTION INDUSTRY

Available and Emerging Technologies for Reducing Greenhouse Gas Emissions from the Nitric Acid Production Industry

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Table of Contents

Abbreviations and Acronyms

atm	Pressure in atmospheres
BACT	Best Available Control Technologies
Btu	British Thermal Unit
Btu/lb	Btu per lb of 100% nitric acid
CAR	Climate Action Reserve
CDM	Clean Development Mechanism
CHP	Combined Heat and Power
CO_2	Carbon dioxide
CO_2e	Carbon dioxide equivalent
EU	European Union
GHG	Greenhouse Gases
H_2	Hydrogen
IPCC	Intergovernmental Panel on Climate Change
IPPC	Industrial Pollution Prevention and Control
JI	Joint Implementation
kg N_2O/tonne	kilograms of N_2O per tonne of 100% nitric acid
kg CO_2e/tonne	kilograms of CO_2e per tonne of 100% nitric acid
lb N_2O/ton	pounds of N_2O per ton of 100% nitric acid
N_2	Nitrogen
NH_3	Ammonia
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_x	Nitrogen oxides
NSCR	Nonselective Catalytic Reduction
N_2O_4	Nitrogen tetraoxide
N_2O	Nitrous oxide
O_2	Oxygen
PSD	Prevention of Significant Deterioration
SCR	Selective Catalytic Reduction
TPD	Tons per day

I. Introduction

This document is one of several white papers that summarize readily available information on control techniques and measures to mitigate greenhouse gas (GHG) emissions from specific industrial sectors. These white papers are solely intended to provide basic information on GHG control technologies and reduction measures in order to assist States and local air pollution control agencies, tribal authorities, and regulated entities in implementing technologies or measures to reduce GHGs under the Clean Air Act, particularly in permitting under the prevention of significant deterioration (PSD) program and the assessment of best available control technology (BACT). These white papers do not set policy, standards or otherwise establish any binding requirements; such requirements are contained in the applicable EPA regulations and approved state implementation plans.

Purpose of this Document

This document provides information on control techniques and measures that are available to mitigate greenhouse gas (GHG) emissions from the nitric acid production industry at this time. Because the primary GHG emitted by the nitric acid production industry is nitrous oxide (N_2O), the control technologies and measures presented in this document focus on this pollutant. While a large number of available technologies are discussed here, this paper does not necessarily represent all potentially available technologies or measures that that may be considered for any given source for the purposes of reducing its GHG emissions. N_2O has a global warming potential that is 310 times that of CO_2 due to its long atmospheric lifetime relative to carbon dioxide.

The information presented in this document does not represent U.S. EPA endorsement of any particular control strategy. As such, it should not be construed as EPA approval of a particular control technology or measure, or of the emissions reductions that could be achieved by a particular unit or source under review.

As of the date of this document, the only known BACT determination for GHG emissions in the nitric acid industry was made by the State of Idaho on November 30, 2009. The agency issued a Permit To Construct for the Southeast Idaho Energy, LLC plant Advanced Energy Center in American Falls, Idaho. More details on this determination are contained in Appendix A.

II. Description of the Nitric Acid Production Process (U.S. EPA, AP-42 Background Report)
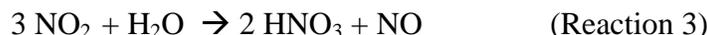
There are two different nitric acid production methods: weak nitric acid and high-strength nitric acid. The first method utilizes oxidation, condensation, and absorption to produce nitric acid at concentrations between 30 and 70 percent nitric acid. High-strength acid (90 percent or greater nitric acid) can be produced from dehydrating, bleaching, condensing, and absorption of the weak nitric acid. The basic process technology for producing nitric acid has not changed significantly over time. Most US plants were built between 1960 and 2000. There are presently 40 active weak nitric acid production plants and one high-strength nitric acid production plant. These plants are listed in Appendix B. Also, additional information is contained in, "Technical Support Document for the Nitric Acid Production Sector: Proposed Rule for Mandatory Reporting of Greenhouse Gases, January 22, 2009."

A. Weak Nitric Acid Production

Weak nitric acid is produced by a three-step high-temperature catalytic ammonia oxidation process. An overall process flow diagram is shown in Figure 1. Each step of the process relates to a specific chemical reaction. A mixture of ammonia and heated air is reacted in a catalytic converter to produce nitric oxide (NO) and water, as shown in Reaction 1. The most common catalyst consists of a 90 % platinum and 10 % rhodium gauze constructed from squares of fine wire. Up to 5 % palladium is also used. This exothermic reaction results in a 93 to 98 percent yield of NO. Higher temperatures and lower pressures result in a higher yield of NO while lower temperatures and higher pressures result in the production of more nitrogen (N_2) and N_2O. Oxidation temperatures typically range from 750 – 900 C (1,380 – 1,650 F). The heat byproduct is usually recovered and utilized for steam generation in a waste heat boiler. This steam is then used for liquid ammonia evaporation in addition to non-process plant requirements.

The NO produced from ammonia oxidation is then oxidized, as shown in Reaction 2. Residual oxygen and the NO process stream react in a cooler/condenser to form nitrogen dioxide (NO_2) and nitrogen tetroxide (N_2O_4), a liquid dimer. This process step is temperature and pressure dependant. Low temperatures and high pressures result in better oxidation.

The final step for the production of weak nitric acid is absorption, as shown in Reaction 3. The NO_2 and liquid dimer mixture are pumped into the bottom of an absorption tower, with additional liquid dimer introduced at a higher point in the tower. Deionized process water is added at the top of the absorption tower. The water flows countercurrently through the NO_2/dimer mixture and absorption occurs on bubble cap or sieve trays. Any residual NO_2 is removed by a secondary air stream.

$$4\,NH_3 + 5\,O_2 \rightarrow 4\,NO + 6\,H_2O \qquad \text{(Reaction 1)}$$

$$2\,NO + O_2 \rightarrow 2\,NO_2 \qquad \text{(Reaction 2)}$$

$$3\,NO_2 + H_2O \rightarrow 2\,HNO_3 + NO \qquad \text{(Reaction 3)}$$

Weak nitric acid production utilizes either a single- or dual-stage pressure system. The most common employed method is single pressure. In a single pressure plant, air fed into the plant is compressed to the process pressure, and this single pressure is used in both the ammonia oxidation and nitrogen oxides absorption phases. Medium pressure plants operate at (4 -8 atm). High pressure plants operate at (8 – 14 atm). In 1991, the majority of new smaller capacity plants (< 300 TPD) used high pressure (US EPA, Dec.1991).

The NO conversion is favored under lower pressures while NO_2 and nitric acid formation are favored at higher pressures during the final reaction. A dual pressure system combines low pressure ammonia oxidation with high pressure absorption. Ammonia oxidation is usually carried out at slightly negative pressure to about 4 atm. The reaction heat is recovered by a waste heat boiler, which supplies steam for the turbine driven compressor. After passing through the cooler/condenser, the gases are compressed to the absorber pressure between 8 and 14 atm. In this system, the nitric acid produced during absorption is sent to an external bleacher where dissolved NO is removed. These gases are compressed and passed through the absorber. The resulting tail gas is sent through one or more gas-to-gas heat exchangers, where it is heated and sent to an energy-recovery turbine. The resulting energy that is recovered is used to drive the compressor. Dual pressure plants have the advantage of superior ammonia conversion efficiency *i.e.* less ammonia raw material is necessary to produce nitric acid. Further, dual pressure plants have a longer catalyst life, and require less frequent catalyst replacement. The disadvantage of dual pressure plants is their substantially higher capital cost for construction and installation versus single pressure plants.

EMISSION POINT

(SCC 3-01-013-02)

AIR

TAIL GAS

EFFLUENT STACK

AMMONIA VAPOR

AMMONIA OXIDIZER

COMPRESSOR EXPANDER

NO$_x$ EMISSIONS CONTROL
CATALYTIC REDUCTION UNITS

2   1

FUEL

TAIL GAS

AIR PREHEATER

NITRIC OXIDE GAS

ENTRAINED MIST SEPARATOR

WATER

WASTE HEAT BOILER

STEAM

AIR

PLATINUM FILTER

NITROGEN DIOXIDE

ABSORPTION TOWER

COOLING WATER

SECONDARY AIR

COOLER CONDENSER
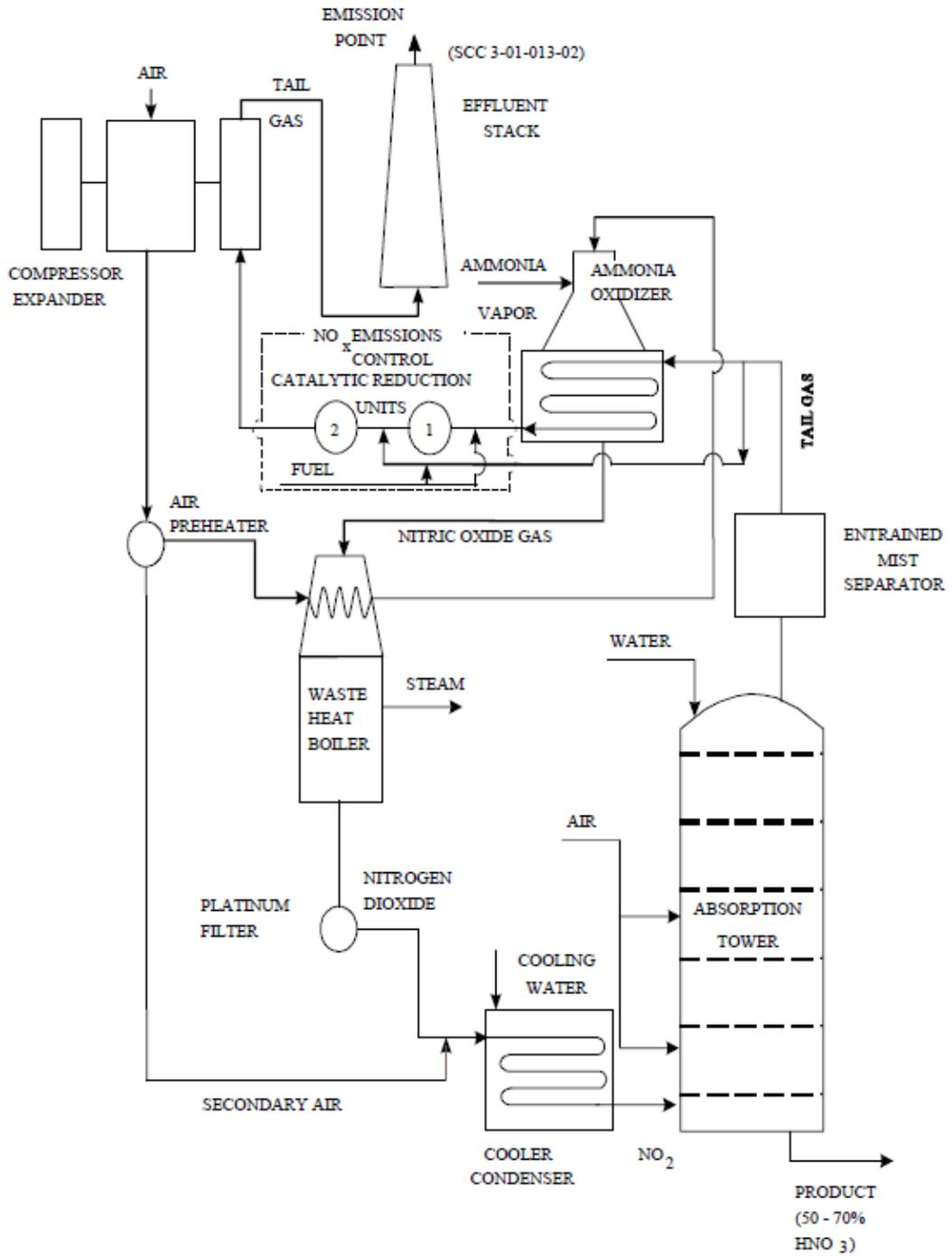
NO$_2$

PRODUCT
(50 - 70% HNO$_3$)

Figure 1 - Process Flow Diagram for Weak Nitric Acid Production – Single Pressure – Source: U.S.EPA,   January 1996.

B. High-Strength Nitric Acid Production Process

The only known strong acid plant in the US (El Dorado, AR) uses the direct strong process(DSN). This process does result in N_2O emissions and produces concentrated nitric acid directly from ammonia.   While several DSN processes exist, the Uhde process has been commercial applied in the United States. The Uhde process is shown in Figure 2.
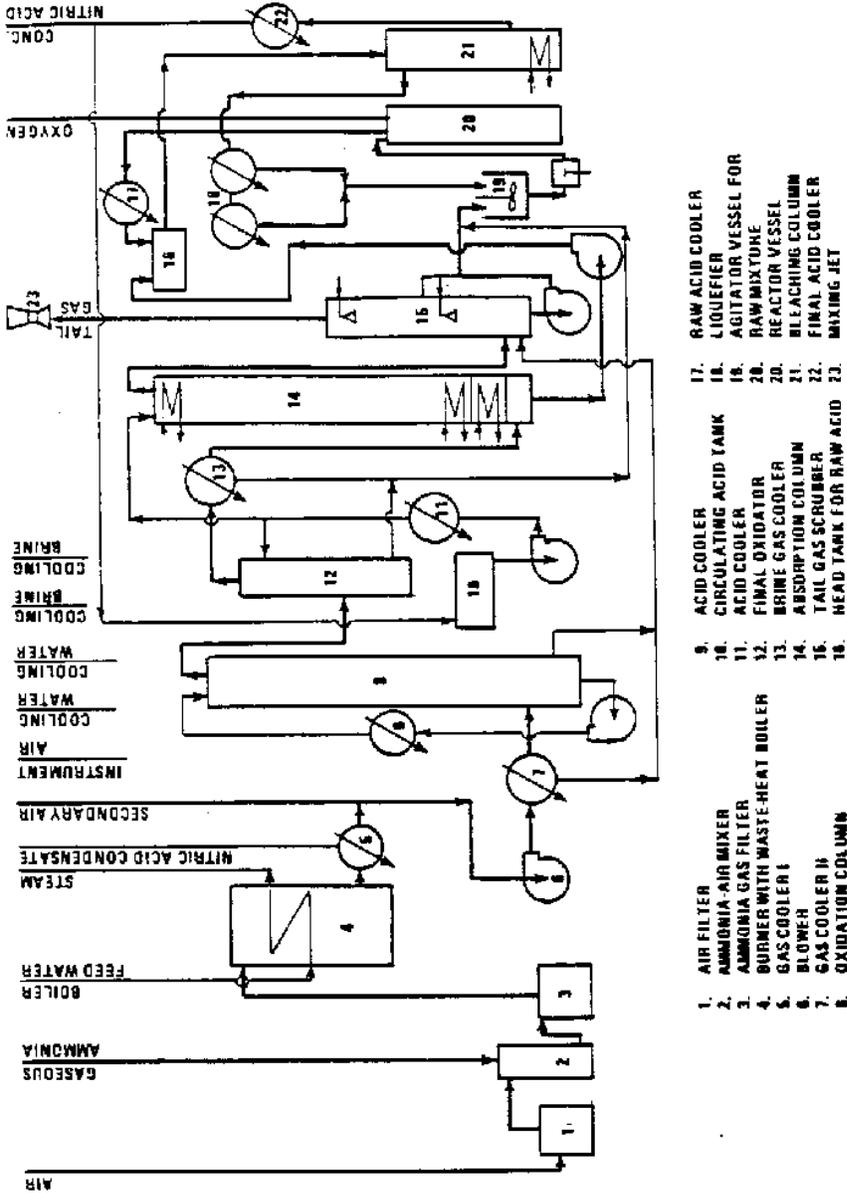
Figure 2 Nitric acid concentration using the direct strong nitric process (Uhde process). (US EPA; December 19910

Air and gaseous ammonia are mixed and reacted. The heat of reaction produces steam in the burner/waste-heat boiler. Upon

cooling, the reaction products condense to form weak nitric acid. After separating the liquid nitric acid, the remaining NO is oxidized to NO_2 by passing through two oxidizing columns. The vapors are then compressed and cooled to form liquid dinitrogen tetroxide. At a pressure of 5 MPa (50 atm), the liquid N_2O_4 reacts with O_2 to form strong nitric acid of 95 to 99 percent concentration. Because NO_x from the absorber is a valuable raw material, tail gas emissions are scrubbed with water and condensed N_2O_4. The scrubber effluent is then mixed with the concentrated acid from the absorber column. The combined product is oxidized in the reactor vessel, cooled, and bleached, producing concentrated nitric acid.

High-strength nitric acid can also be produced from dehydrating, bleaching, condensing, and absorption of weak nitric acid. However, there are no known US plants that utilize this method. Figure 3 presents a process flow diagram of this high-strength nitric acid production process. The secondary production of high strength acid from weak acid is not known to result in additional N_2O emissions. Sulfuric acid is fed with weak nitric acid into a packed dehydrating column. The resulting acid vapor is condensed to form 98 to 99 percent nitric acid.
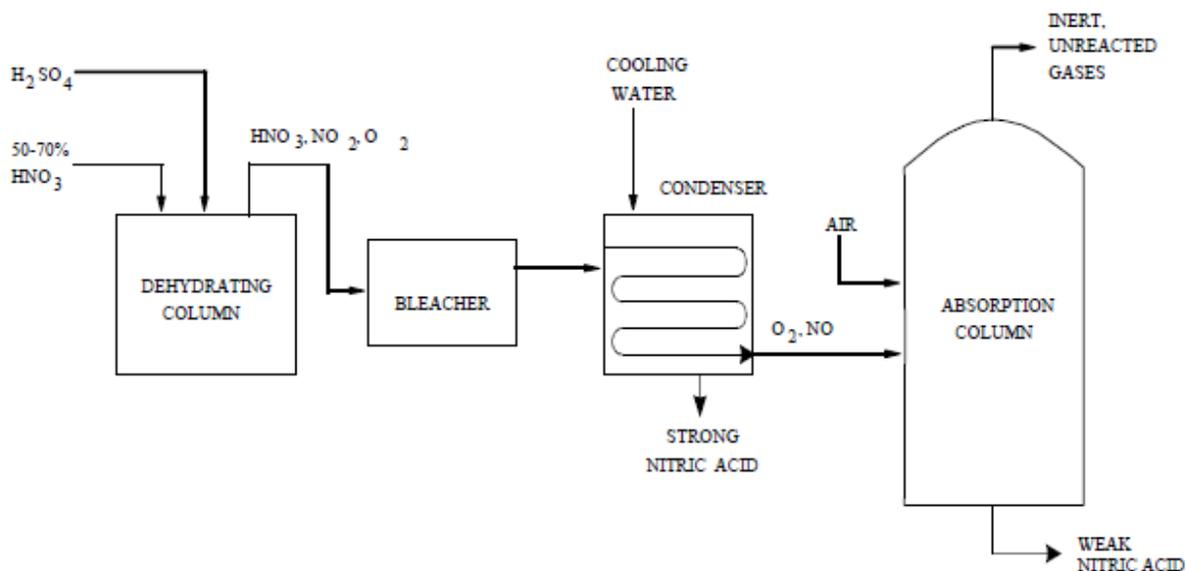

Figure 3 - Process Flow Diagram for High-Strength Nitric Acid Production from Weak Nitric Acid

Source: U.S.EPA, January 1996.

III. N_2O Emissions and Nitric Acid Production Process

N_2O emissions from nitric acid are a byproduct of the process stream and therefore characterized as "industrial process" emissions. Ammonia oxidation is the source of N_2O emissions from nitric acid production. The amount of N_2O formed depends on combustion conditions in the oxidizing unit, catalyst compositions, catalyst age, and burner design. Reactions 4 through 6 show the formation of N_2O at nitric acid plants.(EPA, 2009). More details on N_2O formation are contained in Perez-Ramirez, J. et al, 2003.

$$2\ NH_3 + 2\ O_2 \rightarrow N_2O + 3\ H_2O \qquad \text{(Reaction 4)}$$

$$2\ NH_3 + 8\ NO \rightarrow 5\ N_2O + 3\ H_2O \qquad \text{(Reaction 5)}$$

$$4\ NH_3 + 4\ NO + 3\ O_2 \rightarrow 4\ N_2O + 6\ H_2O\ \text{(Reaction 6)}$$

The default values that were used in the Technical Support Document (TSD) for the proposed GHG Reporting Rule are shown in Table 1. These values are from the IPCC Guidelines for National Greenhouse Gas Inventories (2006). In determining uncontrolled N_2O emissions from nitric acid plants for the GHG inventory, EPA used 9 kg N_2O/metric ton HNO_3. (US EPA April, 2010) The low and high values represent the uncertainty bounds of the default factors provided by IPCC.

Table 1. Default N_2O Emission Factors

Production Process	Approximate Pressure (atm)	N_2O Emissions (kg N_2O/ metric ton Nitric Acid)		
		Low	**Average**	**High**
Plants with NSCR		1.9	2.0	2.1
Plants with process-integrated or tailgas N_2O destruction		2.25	2.5	2.75
Atmospheric pressure(low pressure)	1	4.5	5.0	5.5
Medium pressure plants	4-8	5.6	7	8.4
High Pressure plants	8 -14	5.4	9	12.6

Source: IPCC 2006 Guidelines for National GHG Inventories

Also, uncontrolled N_2O emission factors are available from Clean Development Mechanism(CDM) projects. A summary of the emission tests at these projects is contained in Appendix C. A summary of the uncontrolled N_2O emission tests from these projects is contained in Table 2. The uncontrolled default N_2O emissions factor used for nitric acid plants from the IPCC guidelines for the U.S GHG inventory (9 kg N_2O/metric ton HNO_3) is very close to the average uncontrolled N_2O emission rate of 8.9 kg N_2O/metric ton of HNO_3 from the CDM projects.

Table 2. Uncontrolled N_2O Emissions – CDM Projects

Type of Control	Number of Test Reports	Range (kg N_2O /metric ton HNO_3; lb N_2O /T)	Average (kg N_2O /metric ton HNO_3; lb N_2O /T)
Secondary	38	4.0 - 19;8.1 – 38	8.5; 17.1
Tertiary	11	6.2 – 15.7; 12.4 – 31.4;	10; 20.0
	49	4.0 – 19; 8.1 - 38	8.9; 17.8

Source: CDM Projects

In the US, N_2O emissions contributed approximately 4.6% of total GHG emissions in 2008 in terms of CO_2 equivalents. The nitric acid production process is the third largest source

of N_2O emissions in the US, comprising 6% of total N_2O emissions or 19 million metric tons (tonnes) of CO_2 equivalents (EPA 2010 Inventory).

IV.   Summary of Control Measures

Table 3 summarizes the GHG control measures presented in this document. Where available, the table includes the emission reduction potential, energy savings, costs, and feasibility of each measure.

Table 3. Summary of GHG Control Measures in the Nitric Acid Production Industry

Pollutant	Control Technology	Emission Reduction (%)	Energy Savings	Capital Costs ($/ton CO_2e)	Operating Costs ($/ton CO_2e)	Demonstrated in Practice?
N_2O	Primary	30 - 85	None	Unknown	Unknown	Yes
N_2O	Secondary	70 -90	None	Unknown	0.12 – 0.97	Yes
N_2O	NSCR	> 80	None	6.27	0.14 – 0.22	Yes
N_2O	Other Tertiary Controls	>80	None	2.18 – 3.55	0.14 – 1.91	Yes

Sources: EPA 2006; European Commission August 2007

Three types of controls exist for N_2O at nitric acid plants based on the location of the control within the nitric acid production process: (Durilla, 2009)

- Primary – reduces the amount of N_2O formed in the ammonia oxidation step. This can be done by modifying the catalyst used in the oxidation process and/or modifying the operating conditions of this process.
- Secondary – reduces N_2O immediately after it is formed in the ammonia oxidation step.
- Tertiary – reduces N_2O by installing a catalytic reactor either upstream or downstream of the tailgas expansion unit following ammonia oxidation.

The most commonly applied controls are secondary and tertiary controls. These control technologies employ abatement or decomposition control techniques.   These technologies are capable of and typically achieve greater than 80 percent reduction of N_2O emissions.   A 2006 EPA economic report constructed marginal abatement curves to be used for modeling the cost of emissions reductions of non-CO_2 greenhouse gases globally in the 2010 to 2020 timeframe (US EPA, June 2006). In the nitric acid sector, the report utilized engineering reports to characterize catalytic reduction methods developed by several companies. The capital costs for control technology ranged from $2 to $6 per ton of carbon equivalent removed. Operating costs ranged from $0.14 to $1.91 per ton carbon equivalent removed (US EPA; June 2006).

One tertiary technology, nonselective catalytic reduction (NSCR) has been installed in numerous nitric acid plants in the U.S. and throughout the world to reduce NO_x emissions. As discussed further in this report, NSCR achieves substantial N_2O reduction. Most of the other technologies discussed here were first developed in Europe to support national commitments or GHG emission reduction targets established under the Kyoto Protocol. Under the recently updated European Union Industrial Pollution Prevention and Control (IPPC) Directive, EU member countries are required to set permit limits for N_2O emissions based on the best available technologies. Controls were also evaluated in the context of offsets programs such as Climate Action Reserve (CAR), Clean Development Mechanism (CDM), and Joint Implementation (JI) under the Kyoto Protocol. Information on N_2O controls and related projects is available on CAR's website at http://www.climateactionreserve.org/how/protocols/adopted/nap/current-nitric-acid-production-project-protocol/. Detailed descriptions on the monitoring of emissions with application of these controls at plants located world-wide are found at the United Nations Framework Convention on Climate Change website: http://unfccc.int. (8/13/09 email Carolyn Slaughter to Bill Neuffer).

A count of the projects listed in the CDM shows 66 nitric acid lines using N_2O controls at nitric acid plants outside the US. Fifty three lines use secondary controls and 13 use tertiary controls (http://cdm.unfccc.int/Projects/projsearch.html). These numbers do not include the use of nonselective catalytic reduction (NSCR) which is used in 14 process trains in the US. Also, there are at least another 10 European lines using secondary controls and 4 additional European lines using tertiary controls. (European Commission, August 2007).

At an adhoc European Climate Change Programme (ECCP) stakeholder's meeting, benchmark values of GHG emissions from various industries were discussed. These values represent the average performance (arithmetic mean) of the 10% most efficient installations. The value for nitric acid was 342 kg CO_2e/tonne or 1.1 kg N_2O/tonne or 2.2 lb N_2O/ton. Units using NSCR were excluded in this calculation as units are not required to monitor other GHGs (methane, CO_2) that are emitted from NSCR units. (Product Benchmark, 2010).

A. Primary Controls– Suppression of N_2O formation

One primary control is the extension of the NH_3 oxidation reactor. Yara has developed and patented a technology that consists of an "empty" reaction chamber of approximately 10 ft in length between the platinum catalyst and the first heat exchanger. This allows an additional residence time of 1 to 3 seconds. Reductions are estimated to be 70% to 85% (4 to 6 lb N_2O/ton 100% acid or about 400 ppm). This technique is applicable to new plants with low additional investments. For existing plants, costs are much higher as a new reactor may be required along with other plant modifications. (European Commission, August 2007).

Another primary control is modifying the ammonia oxidation gauzes. These catalysts can be improved platinum catalysts. A few plants have shown a 30 -40 % N_2O reduction. Alternative oxidation catalysts (not platinum based) can achieve 80 – 90% reduction but lower NO is produced. (European Commission, August 2007).

Data from 14 European units with improved oxidation catalyst showed a range of 3.6 –9.7 kg N_2O/tonne (7.2 – 19.4 lb N_2O/ton). The average was 6.2 kg N_2O/tonne (12.4 lb N_2O/ton). (European Commission, February 2008).

B. Secondary Control - Catalytic N_2O Decomposition in the Oxidation Reactor

For this control, a catalyst is located immediately downstream of the NH_3 oxidation step. Using this catalyst, N_2O is decomposed to N_2 and O_2 almost instantly as shown in Equation 1. Four companies (Yara, BASF, Johnson Matthey, and Hereaus) have developed selective catalysts for the removal of N_2O. The catalyst is contained in the ammonia burner and is termed "selective" as it promotes the decomposition of N_2O to N_2 and O_2, as shown in Reaction 7. No major modification of the ammonia oxidation reactor is typically required and the installation of this catalyst has shown no effect on ammonia conversion. The placement of the catalyst in the ammonia burner allows for reduction of N_2O emissions by increasing the residence time of the gas in the burner. The average lifetime for the pellet catalyst is 4 years (ICAC, 2009). Up to 90% reduction is possible (ICAC, 2009) and rates of 130 to 400 ppm of N_2O are achievable. Yara's system (Figure 4) was first installed in 2002 and is presently operating in 17 plants. The plants applying the secondary controls range in size from 200 to 2,650 million tonne per day.
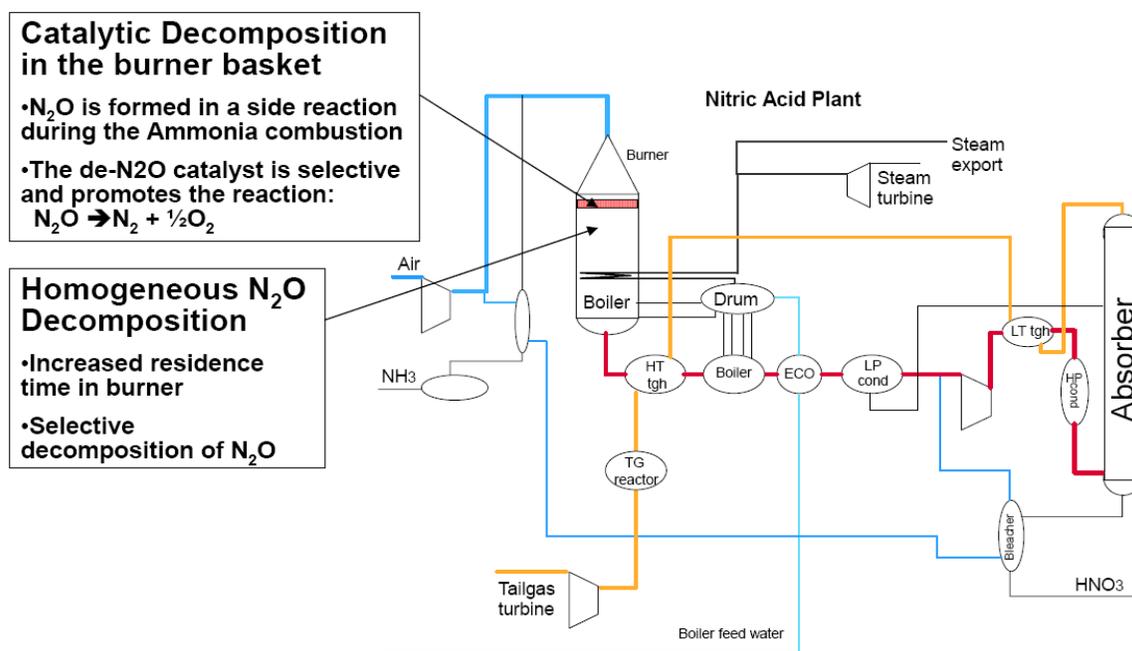
$$2 N_2O \rightarrow 2N_2 + O_2 \qquad \text{(Reaction 7)}$$

Catalytic Decomposition in the burner basket

•N_2O is formed in a side reaction during the Ammonia combustion

•The de-N2O catalyst is selective and promotes the reaction:
  $N_2O \rightarrow N_2 + \frac{1}{2}O_2$

Homogeneous N_2O Decomposition

•Increased residence time in burner

•Selective decomposition of N_2O

Figure 4 – Yara Secondary N_2O Control from Nitric Acid Production
Source: ICAC, 2009.

One reference states this control has the lowest capital cost as minimal modifications are required to the reactor for the ammonia oxidation catalyst. There are no additional operating costs. A total of 53 process lines at nitric acid plants worldwide have implemented this technology.   Three facilities have installed this technology in the United States.   A recent article discussed a secondary catalyst being installed at El Dorado's Nitrogen LP's Baytown, Texas plant (Industrial GHG, 6/17/10). The project began operating around July 2010. The facility has applied to obtain GHG emission credits under the Climate Action Reserve program. Also, Terra

Industries has installed secondary catalysts in Yazoo City, Mississippi and Claremore, Oklahoma under this program.

Emission test results from use of secondary controls were available from 2 sources – European Commission (February 2008) and emissions monitoring reports from CDM projects (Appendix C). These results are summarized in Table 4. For the CDM projects, 30 of the 37 test results had efficiencies greater or equal to 70%. Twenty three of 37 test results had efficiencies greater or equal to 80%. The CDM projects include 2 units with percent reductions (9, 39%) much lower than the other 30 units tested.   Figure 5 shows the data on secondary controls from these CDM projects. As shown here, many secondary catalysts achieve less than 3 lb of N_2O/ton of 100% nitric acid. These projects are also presented in Appendix C.

Table 4. N_2O Emission Test Results- Secondary Controls

Source	Units tested	Range (lb N_2O/ton)	Average (lb N_2O/ton)	% Reduction Range	% Reduction Average
EC	8	1.8 – 5.0	3.2	Unknown	Unknown
EC*	4*	3.0 – 3.8*	3.4*	Unknown	Unknown
CDM Projects	30 (37 test periods)	0.15 – 11.6	4.1	9 – 98	76

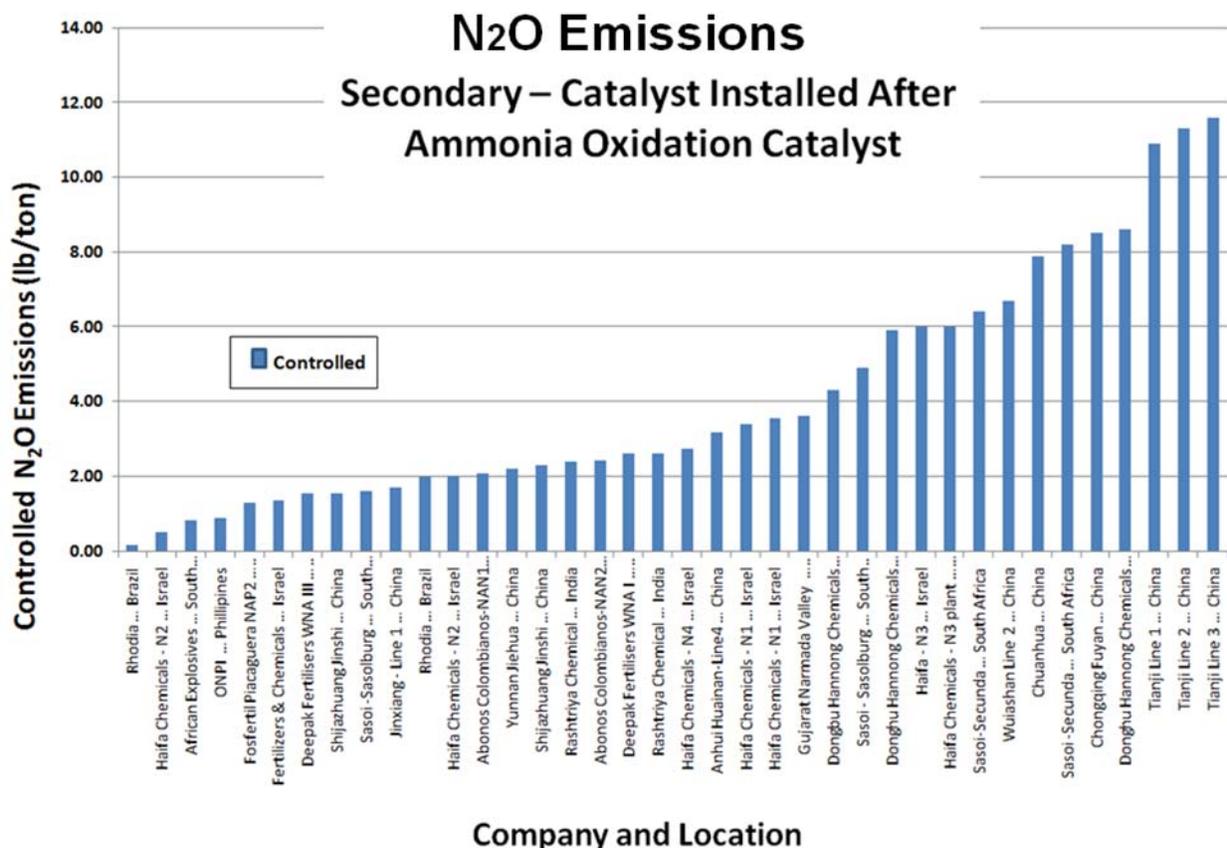 * With Improved oxidation catalyst

Figure 5 - N_2O Emissions from Secondary Controls – CDM Projects

C. Tertiary Controls –Catalytic Reduction

Nonselective Catalytic Reduction (NSCR) is a common control technology utilized at nitric acid production facilities to reduce NO_x emissions where a reagent fuel, such as natural gas, propane, butane, or ammonia plant purge gas (mainly H_2) is used as a reagent to reduce NO_x, and N_2O over a catalyst to produce N_2 and water. Similar to a three-way catalytic converter, reductions of NO_x and N_2O occur while other emissions are oxidized. Catalysts for NSCR are usually based on platinum, vanadium pentoxide, iron oxide or titanium. Catalyst supports are typically made of alumina pellets or a ceramic honeycomb substrate. NSCR has a N_2O reduction efficiency of 80-95 percent (European Commission, August 2007). As far as selection of a NO_x control, NSCR is typically used at plants that have the capability to preheat tailgas to 200 - 450º C and requires a greater reagent input than SCR (RTI, 2009). As stated earlier, 14 process trains in the US use NSCR. These facilities have installed NSCR to control NO_x emissions and as an additional benefit NSCR reduces N_2O emissions. The one US plant with NSCR with emission test data was at 0.43 lb N_2O/ton. In numerous nitric acid plants outside of the US, NSCR/catalytic reduction is used in conjunction with SCR.

One NSCR manufacturer, Süd-Chemie, has a unit (EnviCat® HNO_3) that works best when the tailgas temperature is greater than 400°C. This unit is a direct disintegration process with the catalyst positioned close to the reactor. Hydrocarbons are required in the tailgas stream to provide efficient control. Both N_2O and NO_x react with the hydrocarbons to break down the compounds to nitrogen and oxygen. (Süd-Chemie, n.d.).

Süd-Chemie along with Uhde have developed a process referred to as EnviNO$_x$® process More details are shown in Figures 6 and 7. There are two variants of the EnviNO$_x$® process depending on the tail gas temperature. Variant 1 is discussed under the next section – catalytic decomposition. Variant 2 is suitable for lower tail gas temperatures ranging from 300 to 520 C.

The low temperature variant (Variant 2) utilizes hydrocarbons, such as natural gas, to drive catalytic reduction. The reaction vessel is positioned upstream of the tailgas expander (turbine). Ammonia is mixed with the tailgas that contains both N_2O and NO_x. The mixture passes through a single catalyst bed where parallel reduction of the pollutants takes place. A vanadium-free catalyst is used to convert N_2O and NO_x to nitrogen, oxygen, and water. This particular catalyst also removes the ammonia that was added to drive the reaction between the catalyst and N_2O, thus preventing ammonia leakage. Conversion rates greater than 98 percent have been achieved with the EnviCat® N_2O system right below the platinum gauze (Süd-Chemie, n.d.). The addition of hydrocarbons to drive this reaction is not thought to produce significant CO_2 emissions when compared to the reduction of N_2O in the unit (Uhde, 2005). This process utilizes a tailgas reactor positioned directly upstream of the tailgas expander (turbine).

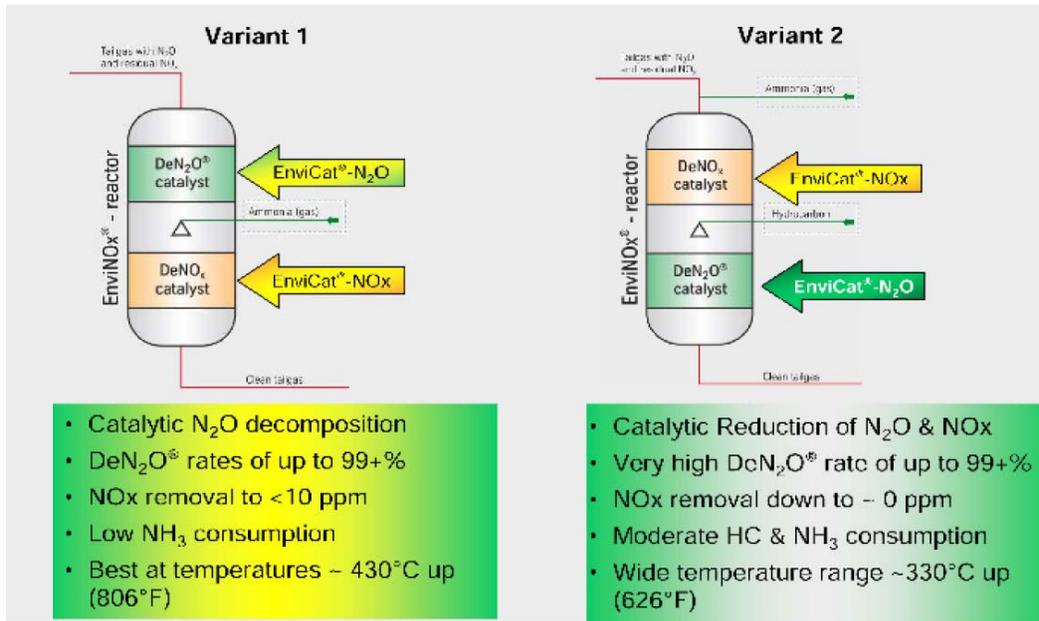**Figure 6– Uhde Combination N₂O and NOₓ Control for Nitric Acid Production Plants** Source: ICAC, 2009.

Figure 7 – Uhde EnviNOₓ® Reactor in Linz, Austria Source: ICAC, 2009.

C. Tertiary Controls – Catalytic Decomposition

Decomposition technology, which can be high temperature or low temperature, does not require any additional reducing agents or additives, and no undesirable byproducts are formed

from the reaction. The basis of decomposition technology is to simply decompose N_2O to form nitrogen and oxygen (ICAC, 2009).   A catalyst is used to drive the decomposition. This catalyst is stable in the presence of NO_x and ammonia, allowing placement either upstream or downstream of the SCR used to reduce NO_x (ICAC, 2009). Decomposition can remove up to 99 percent of the N_2O in the process stream.

As mentioned above, Uhde along with Süd-Chemie have developed a process referred to as EnviNO$_x$®.   More details are shown in Figures 4 and 5. There are two variants of the EnviNO$_x$® process depending on the tail gas temperature. Variant 1 is discussed under this section – catalytic decomposition.   Variant 1 is good for higher tail gas temperatures ranging from 425 to 520 C.   For these temperatures, EnviNO$_x$® is a two stage process. In the first stage, N_2O is decomposed to oxygen and nitrogen in a catalyst bed. The resulting tailgas is then mixed with ammonia and enters a second catalyst bed where NO_x is reduced to water vapor and nitrogen. The N_2O is further removed in this catalyst bed. (Uhde, 2005 and ThyssenKrupp, 2005).

Another decomposition technology is the Shell N_2O Abatement Technology (C-NAT). A pellet catalyst (manufactured by CRI, a wholly own affiliate of Shell), is contained within a lateral flow reactor. The tailgas is forced laterally through the packed-bed design to achieve more efficient utilization of the catalyst surface area than traditional catalyst design. This technology works best at temperatures between $450°C$ and $650°C$ but can operate as low as 300^0C. The Shell C-NAT system can achieve greater than 98 percent reduction of N_2O (CRI, 2009;ICAC, 2009).

Another decomposition technology is the BASF NO_x CAT ^{TM} ZN_20 Catalyst. This technology removes both NO_x and N_2O at temperatures from $300\text{-}600^0C$.   In this process ammonia is injected into a catalyst bed that consists of an SCR catalyst (e.g,. Vandium/Titanium) and the NO_xCAT^{TM} Z N_2O reduction catalyst. (ICAC, 2009)

Emission test results for tertiary controls were obtained from 2 sources – European Commission (February 2008) and monitoring reports from CDM projects (Appendix B). These results are summarized in Table 6.   Also, the results from the CDM projects and 1 US plant using NSCR are shown in Figure 8. Most controls achieve less than 1.0 lb of N_2O per ton of 100% acid. The CDM projects are also presented in Appendix C.

Table 6. N_2O Emission Test Results- Tertiary Controls

Source	Units tested	Range (lb N_2O/ton)	Average (lb N_2O/ton)	% Reduction Range	% Reduction Average
EC	7	0.02 – 0.48	0.18	Unknown	Unknown
CDM Projects	11	0.41 – 2.2	1.2	88 - 98	94

N$_2$O Emissions –
Tertiary - NSCR or Other Catalytic Controls
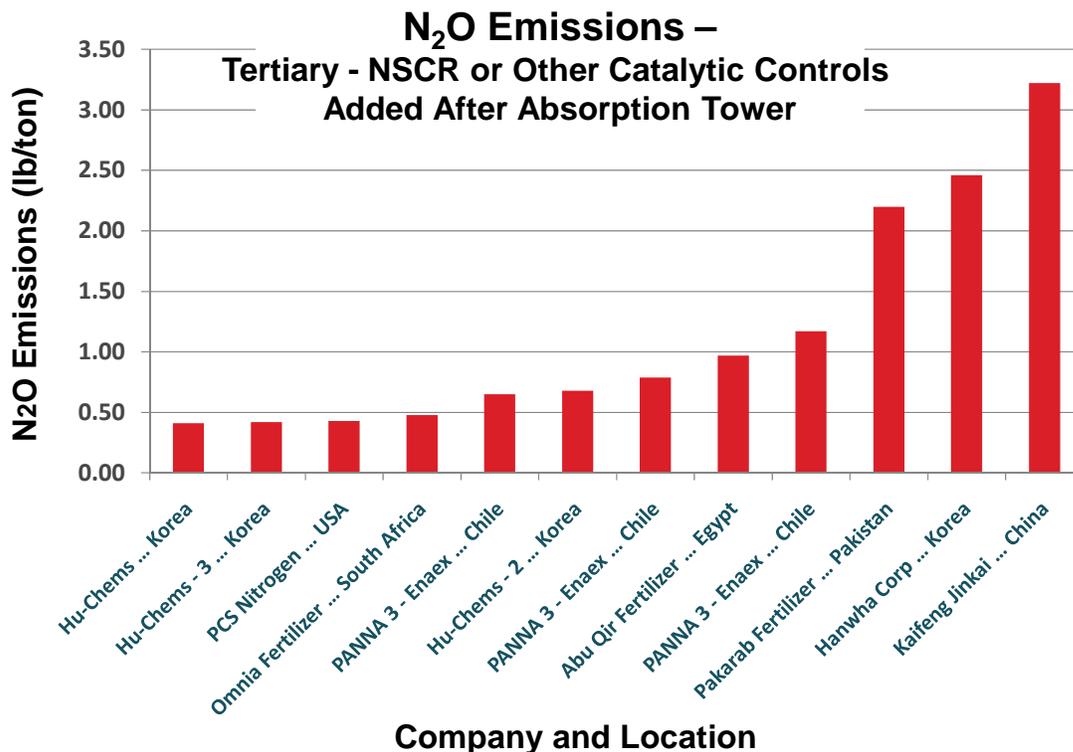**Added After Absorption Tower**

Figure 8. N$_2$O emissions from Tertiary Controls

D. Selective Catalytic Reduction (SCR)

SCR is not an effective control technology for N$_2$O emissions (Perez-Ramirez et al 2003). The CAR's Nitric Acid Production Project Protocol elaborates that SCRs can have at least a slight unintentional impact on N$_2$O emissions (+/- <5%) of total emissions (Climate Action Reserve, 2009).

V.   Other Greenhouse Gas Emissions

Nitric acid plants may also indirectly generate emissions of carbon dioxide (CO$_2$), N$_2$O and methane (CH$_4$) by consuming steam or electricity produced through the combustion of fossil fuels during startup. This is common for plants with steam powered compressors that require the use of natural gas at startup.   Once the plant begins operating normally, the plant will generate enough steam to power the compressor. Also, the plant will also be able to export additional steam to the rest of the facility which offsets steam production that could be produced by burning fossil fuels. During this limited time period, carbon dioxide is produced.

Also, CO$_2$ and methane (in small amounts) can be emitted by nitric acid plants controlled by nonselective catalytic reduction (NSCR) and other catalytic reduction technologies. Methane is often the fuel used in NSCR. Combustion of methane or other organic fuels produces carbon

dioxide. As far as CO_2 (equivalent) is concerned, the CO_2 emissions result in a less than a 2% increase in GHG compared to the 80+% reduction in GHG obtained from controlling N_2O emissions using NSCR. This less than 2% increase is also lowered when considering that much of the heat produced in NSCR is recovered in the expander which is then used to power the compressor which in turn powers the nitric acid plant. This reduces the amount of power needed from either a steam turbine or electric motor.

In contrast to the above, a European report (Fraunhofer, 2009) estimates that methane slip form an NSCR has a significant impact on the overall GHG emissions from a nitric acid plant controlled with an NSCR. This report estimates that the average emissions from NSCR are 2.0 lb N_2O/ton which includes an additional 1.54 lb N_2O(equiv)/ton attributable to methane slip and CO_2 emitted from operation of the NSCR. Average emissions from NSCR, according to this report, are shown in Table 7. It should be noted that the methane slip rate of 4500 ppm presumed in this study is higher than slip rates discussed in other literature.

Table 7. Emissions from NSCR

Pollutant	Concentration (ppm)	Emissions [lb N_2O(equiv)/ton]
N_2O	50	0.66
Methane	4,500	1.5
CO_2	1,000	0.04
NO_x	150	
NH_3	100	

VI.   Energy Efficiency Improvements to Reduce other GHG Emissions (RTI, 2009)

Energy Recovery

Nitric acid production is a net exporter of energy. Therefore, energy recovery is a valuable resource for these facilities. External sources of fuel can be minimized through recovery of energy from the production process.

There are two exothermic reactions, oxidation and absorption, that produce more energy than the total production process consumes. Single and dual-pressure plants are used within the US. For new plants, dual-pressure is the most predominant design. However, there is not a substantial difference in the total energy required or recovered from the two designs.

The energy requirements of controls should also be considered. As far as NOx controls, SCR units require less energy than NSCR units because they operate at lower temperatures. As shown earlier NSCR has the additional benefit of controlling N_2O. The overall energy recovery is dependent on the design of the facility. Approximately 1,660 Btu/lb of 100% nitric acid (Btu/lb) is produced from the catalytic reactor. The absorption tower produces approximately 370 Btu/lb. All of this energy is potentially available for recovery. Additionally, the expansion unit has the potential to recover 80 percent of the mechanical energy used, or approximately 325 Btu/lb. This provides for an overall amount of energy available for recovery of approximately 1,955 Btu/lb. The potential CO_2 equivalent emissions that are avoided by this level of steam energy recovery are 0.26 tonnes CO_2e per ton of 100% nitric acid. An additional 0.77 tonnes CO_2e per ton 100% nitric acid is avoided through electric energy production. However, the

actual levels of energy recovery, due to economic and practical considerations, are around 50-65 percent of the theoretical values. Therefore, between 969 and 1,217 Btu/lb is available for recovery. This equates to an offset of 0.12 to 0.5 tonnes CO_2e/ton HNO_3.

Steam production is the most common form of energy recovery for process lines in nitric acid production. Heat from the process is typically recovered and used to generate a large portion of the steam needed elsewhere in the plant. During startup, natural gas is used to augment this steam when nitric acid production is at levels below those needed to recover enough steam for the rest of the facility. Although not widely practiced currently at nitric acid production facilities, bottoming cycle combined heat and power (CHP) could also be used for energy recovery at nitric acid plants. With this type of CHP system, steam would be generated from heat recovery at a higher pressure than is needed in the other processes and run through a steam turbine generator before being sent to the processes at the required pressure. The power generated could be used within the plant, offsetting power purchases from the grid. This would not result in direct CO_2 reductions at the facility from the power produced, but indirect reductions from displacing grid power. The level of reduction is a function of the CO_2 intensity of the displaced external power production.

Energy Efficiency

There are energy efficiency measures that can be implemented at nitric acid plants. These areas include building lighting and HVAC, motors, compressed air and pumps. Energy Star has not prepared an Energy Guide specific to nitric acid plants. A general guide "Managing Your Energy," is available.

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APPENDIX   A

SOUTHEAST IDAHO ENERGY, LLC
POWER COUNTY ADVANCED ENERGY CENTER
MERICAN FALLS, IDAHO

http://www.deq.idaho.gov/Applications/NewsApp/showNews.cfm?news_id=2848&CFID=217875&CFTOKEN=16675422

The following is a summary from the press release (link) provided above, the Statement of Basis and the Permit to Construct (PTC). The facility will produce fertilizer products through the gasification of coal and petcoke. A pure H_2 stream is used to manufacture ammonia which is used to produce nitrogen-based fertilizers. The nitric acid produced will be approximately 57% concentration at a rate of 575 TPD of 100% acid.

A final PTC was issued on 11/30/09 for this plant. As far as the nitric acid facility at this plant is concerned, the installation of an extended absorption tower and SCR is required for NO_x control. Catalytic decomposition is required for N_2O control. There are NO_x, NH_3 and N_2O and emission limits for the plant. These limits are:

- For NO_x, reduce NO_x emissions by 4.2 tpy from the Nitric Acid Plant. The NO_x emission limits are 50 ppmv, 0.60 lb/T, 14.4 lb/hr, and 63.0 TPY. There is an ammonia slip limit of 10 ppmv (dry) converted to 15 % oxygen.

- For N_2O, reduce the N_2O emissions by 90% by volume from 3000 ppmv to 300 ppmv.

- The N_2O emission limit was based on a performance guarantee by the technology provider.

APPENDIX B – US Nitric Acid Plants

Company	Parent Co	City	State
Cherokee Nitrogen	LSB Industries	Cherokee	AL
El Dorado Nitrogen	LSB Industries	El Dorado	AR
Apache Nitrogen		Benson	AZ
Agrium		West Sacramento	CA
J R Simplot		Helm	CA
Ascend Performance Materials		Pensacola	FL
Trademark Nitrogen		Tampa	FL
PCS Nitrogen Fertilizer	Potash Corp	Augusta	GA
Rentech		East Dubuque	IL
Terra Nitrogen	CF Industries	Sergeant Bluff	IA
Koch Nitrogen		Fort Dodge	IA
Coffeyville Resource		Coffeyville	KS
Koch Nitrogen		Dodge	KS
Angus Chemical	Dow Chemical	Sterlington	LA
CF Industries		Donaldsonville	LA
Lyondell Chemical		Lake Charles	LA
PCS Nitrogen Fertilizer	Potash Corp	Geismar	LA
Rubicon		Geismar	LA
First Chemical	DuPont	Pascagoula	MS
Terra Nitrogen	CF Industries	Yazoo City	MS
Dyno Nobel		Louisiana	MO
Koch Chemical		Beatrice	NE
Dyno Nobel		Battle Mountain	NV
Agrium		Cincinnati	OH
PCS Nitrogen Fertilizer	Potash Corp	Lima	OH
Koch Nitrogen		Enid	OK
Pryor Chemical Co.	LSB Industries	Pryor	OK
Terra Nitrogen	CF Industries	Vendigris	OK
Terra Nitrogen	CF Industries	Woodward	OK
Dyno Nobel		St Helens	OR
Dyno Nobel		Donora	PA
Air Products		Pasadena	TX
Dupont		Beaumont	TX
El Dorado Nitrogen	LSB Industries	Baytown	TX
Invista		Victoria	TX
Invista		Orange	TX
Geneva Nitrogen	Orica USA	Geneva	UT
US Army – Ammunition Plant		Radford	VA
Agrium		Kennewick	WA
Dyno Nobel		Cheyenne	WY

APPENDIX C - Summary of CDM Monitoring Reports – from
`http://cdm.unfccc.int/Issuance/index.html`

Plant	Location	Control	Test Dates	Uncontrolled (lb/ton)	Controlled (lb/ton)	Efficiency
Rhodia	Brazil	2	9/15/08 - 5/11/09	9.90	0.15	98%
Haifa Chemicals – N2	Israel	2	5/20/08 - 3/24/09	23.30	0.52	98%
African Explosives	South Africa	2	2/8/08 – 5/23/09	8.10	0.81	90%
ONPI	Philippines	2	3/1/10 – 7/11/10	8.90	0.89	90%
Fosfertil Piacaguera NAP2	Brazil	2	3/21/09 - 7/28/09	9.60	1.30	86%
Fertilizers & Chemicals	Israel	2	11/29/07 – 5/10/09	13.46	1.35	90%
Deepak Fertilisers WNA III	India	2	02/08 -- 03/16/10	10.22	1.53	85%
Shijazhuang Jinshi	China	2	6/27/08- 3/13/09	12.20	1.54	87%
Sasoi -Sasolburg	South Africa	2	12/11/08- 8/3/09	19.30	1.60	92%
Jinxiang – Line 1	China	2	3/2/08 - 5/15/08	14.60	1.70	88%
Rhodia	Brazil	2	5/12/09 -1/3/10	11.80	1.98	83%
Haifa Chemicals – N2	Israel	2	3/25/09 – 11/23/09	13.34	2.00	85%
Abonos Colombianos-NAN1	Colombia	2	10/01/07- 4/15/08	13.74	2.06	85%
Yunnan Jiehua	China	2	11/1/07- 5/15/08	10.80	2.20	80%
Shijazhuang Jinshi	China	2	3/14/09 -9/8/09	13.10	2.30	82%
Rashtriya Chemical	India	2	11/20/09 - 2/12/10	23.80	2.40	90%
Abonos Colombianos-NAN2	Colombia	2	10/01/07 – 4/15/08	16.12	2.42	85%
Deepak Fertilisers WNA I	India	2	11/09 -- 3/10	17.20	2.60	85%

Plant	Location	Control	Test Dates	Uncontrolled (lb/ton)	Controlled (lb/ton)	Efficiency
Rashtriya Chemical	India	2	3/14/08-7/21/09	25.00	2.60	90%
Haifa Chemicals – N4	Israel	2	11/5/08 – 2/28/10	18.20	2.73	85%
Anhui Huainan-Line 4	China	2	4/1/09 -- 10/3/09	15.04	3.16	79%
Haifa Chemicals – N1	Israel	2	5/20/08 - 3/24/09	23.30	3.40	85%
Haifa Chemicals – N1	Israel	2	11/13/08-3/19/08	23.72	3.56	85%
Gujarat Narmada Valley	India	2	10/29/09 - 1/15/10	12.50	3.60	71%
Dongbu Hannong Chemicals	Korea	2	01/27/07 -- 03/30/10	21.56	4.31	80%
Sasol - Sasolburg	South Africa	2	8/10/08 - 12/7/08	19.30	4.90	75%
Donghu Hannong Chemicals	Korea	2	1/8/09 - 10/15/09	21.40	5.90	72%
Haifa Chemicals – N3 plant	Israel	2	5/25/08 - 2/4/09	15.70	6.00	62%
Sasol-Secunda	South Africa	2	5/2/09-1/31/10	9.10	6.40	30%
Wuiashan Line 2	China	2	6/27/08 - 12/29/09	13.40	6.70	50%
Chuanhua	China	2	10/24/08-11/15/09	38.00	7.90	79%
Sasol-Secunda	South Africa	2	8/31/08-4/26/09	9.00	8.20	9%
Chongqing Fuyan	China	2	10/20/08-4/1810	28.20	8.50	70%
Donghu Hannong Chemicals	Korea	2	1/4/08 - 5/15/08	21.40	8.60	60%
Tianji Line 1	China	2	12/18/08 - 7/27/08	22.20	10.90	51%
Tianji Line 2	China	2	9/21/08 -5/3/09	29.00	11.30	61%
Tianji Line 3	China	2	12/31/08 - 8/17/09	20.30	11.60	43%

Plant	Location	Control	Test Dates	Uncontrolled (lb/ton)	Controlled (lb/ton)	Efficiency
			AVERAGE	17.14	4.10	76%
Hu-Chems - 4	Korea	3	3/1/09 -6/30/09	13.70	0.41	97%
Hu-Chems - 3	Korea	3	3/1/09 - 6/30/09	24.60	0.42	98%
Omnia Fertilizer	South Africa	3	2/1/09 - 5/31/09	12.40	0.48	96%
PANNA 3 – Enaex	Chile	3	7/1/09 - 9/30/09	16.60	0.65	96%
Hu-Chems - 2	Korea	3	3/1/09 - 6/30/09	26.00	0.68	97%
PANNA 3 – Enaex	Chile	3	4/1/09 - 6/30/09	18.40	0.79	96%
Abu Qir Fertilizer	Egypt	3	3/10/09 - 6/30/09	14.10	0.97	93%
PANNA 3 – Enaex	Chile	3	9/1/07 --	18.57	1.17	94%
Pakarab Fertilizer	Pakistan	3	6/1/09 - 8/31/09	22.80	2.20	90%
Hanwha Corp	Korea	3	1/7/07 -	21.17	2.46	88%
Kaifeng Jinkai	China	3	1/7/2007 -	31.43	3.22	90%
			AVERAGE	19.98	1.22	94%