Nitrous Oxide Reduction at Agropolychim Fertilizer Plant

DEPA File M124/000-0043t

Joint Implementation

Project Design Document

H&O Project No. 0236



DANCEE Danish Cooperation for Environment in Eastern Europe Ministry of Environment and Energy

Abbreviations

As recommended by ISO 31/0 the comma (,) is used as decimal marker throughout this documentation.

	Prefixes			
k	: kilo		10 ³	
M	: Mega		10 ⁶	
G	· Giga	nultiplies by	10 ⁹	
т	· Tera		10 ¹²	
•	Units of thermodynamic	nronerties	10	
Bar	· bar (unit of pressure over	nressure or diff	orantial prace	suro)
Bara	: bar absolute (absolute pres	scura)	crentiar pres.	Surc
۵C	: degrees Celsius (unit of ter	mperature)		
C	Units of operay and pow			
1	: loule (unit of work)		1 1	– 1 Nm
	· Caloria (unit of work)			- 1 1060 1
	. Calorie (unit of work)			-4,1000 J -11/c
vv kool/b	. Walt (unit of power)	of power)		- 1 162 W
KCdI/II	Tradicas to units of one	bi power)		= 1,105 W
	Electrical		1 MW alactr	ical nowor
e	. Liectrical		1 MW electi	
t	Dimensione and weight	I GJ _t .	I GJ UIEITIA	arenergy
	Dimensions and weight			
m ²	: meter (unit of length)	`		
[[] m ³	: square meter (unit of area)		
	: Cubic meter (unit of volume	e)		
g	: gram (unit of mass)	4 T	1 M -	
1	ton (unit of mass)	11 =	I Mg	
<u> </u>	Chemical substances			
0	: carbon monoxide			
	: carbon dioxide			
N ₂ O	: nitrous oxide			
NO _x	: common designation for ni	trogen oxides		
SO ₂	: sulphur dioxide			
	Other			
BAU	: Business As Usual.			
CDE	: Carbon Dioxide Equivalent			
CDM	: Clean Development Mechai	nism		
CEECs	: Central and East European	Countries		
CER	: Certified Emission Reduction	on		
DEPA	: Danish Environmental Prot	ection Agency		
DERSA	: Danish Emission Reduction	System Admir	istration	
ERU	: Emission Reduction Unit d	lescribes the te	chnical term	tor GHG emis
	sion reduction output of JI	 Project accor 	ding to the K	(yoto Protocol.
EUR	: Euro (currency European U	Jnion)		
IPCC	: Inter governmental Panel of	on Climate Cha	nge	
IL	: Joint implementation Proje	ct according to	Article 6 - Ky	yoto Protocol.
MP	: Monitoring Plan			
PDD	: Project Design Document			

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1 DESCRIPTION OF THE EXISTING PLANT

1.1 Introduction

Agropolychim JSC is located in Devnia, near the city of Varna, in Northeast Bulgaria. It has access to the Varna-West port accomodating ships up to 30.000 T. Additionally Agropolychim is connected to the national railroad network and is situated next to the Varna-Sofia highway. An efficient transportation system has been established which allows Agropolychim to export through the Danube river to the very heart of Europe or through sea shipping to all continents at very competitive rates.

Agropolychim was founded in 1974 and was privatized in November 1999. Acid & Fertilizers, USA acquired 63% of the company from the Bulgaria Privatization Agency.

Acid & Fertilizers LLC, USA is a joint venture between DAVENPORT INDUSTRIES – 99% and UM-ICORE – 1%.

A major restructuring program was implemented. Currently Acid & Fertilizers controls 97% of Agropolychim JSC. Board members are Vassil Alexandrov (CEO), Hristo Petrov (CEO), Philippe Rombaut (CEO).



Map 1 Location of Agropolychim

1.2 Nitric acid production in general

The crucial step in the nitric acid production, the catalytic combustion of ammonia, was developed by Ostwald around the beginning of this century. The first production facility employing the Ostwald process came on stream in 1906 at Gerthe, Germany.

All plants for the production of weak nitric acid (concentrations ranging from 30 to 70 percent nitric acid) are based on the Ostwald process and use the same basic chemical operations:

- a) oxidation of ammonia (NH_3) with air into nitric oxide (NO)
- b) oxidation of nitric oxide (NO) into nitrogen dioxide (NO₂)
- c) absorption of nitrogen dioxide (NO₂) in water to produce nitric acid (HNO₃)



Figure 1 The Ostwald process

1.2.1 Raw material preparation

The liquid ammonia (NH_3) is evaporated and filtered. Air is purified by using two or three stage filtration and is pressurised. Both the ammonia filter and the air filter should remove all particles as good as possible. The air is split in two streams: one stream is led to the catalytic reactor, while the other stream is led to (the bleaching section of) the absorption column.

1.2.2 Oxidation of ammonia

The evaporated ammonia (NH_3) is mixed with the purified air in a ratio of approx. 1:10 and (optionally) filtered. This ammonia/air mixture is led across a catalyst. The mixture reacts according to the following equation:

 $4 \text{ NH}_3 + 5 \text{ O}_2 \leftrightarrow 4 \text{ NO} + 6 \text{ H}_2\text{O}$

Simultaneously nitrous oxide (N_2O), nitrogen (N_2) and water (H_2O) are formed as well, in accordance with the following equations:

 $4 \text{ NH}_3 + 3 \text{ O2} \leftrightarrow 4 \text{ N}_2 + 6 \text{ H}_2\text{O}$

4 NH₃ + 4 O₂ \leftrightarrow 2 N₂O + 6 H₂O <u>Note:</u> forming of laughing gas

Both reactions are undesirable, because they influence the yield of nitric oxide disadvantageously and they have great impact on the environment. The yield (percentage of ammonia that is converted to NO) depends on pressure and temperature as indicated in the following figure:



Figure 2 Possible conversion of NH_3 to NO on Platinum gauze as a function of temperature /4/

The most universally preferred catalyst consists of platinum wire that is knitted into mesh gauze. Five to ten percent rhodium normally is added to the platinum to increase its strength and to reduce platinum costs, and up to 5% palladium is used to reduce cost. Catalyst poisoning (by air pollution or contamination from the ammonia) and unfavourable conditions (like poor ammonia/air mixing and poor gas distribution across the catalyst) may reduce the NO-yield.

During the reaction process, some of the platinum and rhodium from the catalyst vaporises. In most cases a platinum recovery system is installed below the catalyst, known as a "getter" or catchment. This system consists of a palladium alloy. A "getter" allows a 60 to 80% recovery of the total catalyst loss.

Due to loss of the platinum the efficiency of the catalyst drops over time. This leads to an increasing generation of N_2O over the campaign (time between change of platinum gauze). In general the generation of N_2O is approx. 20% below the average at the beginning of a campaign, while the generation is approx. 20% above the average at the end of a campaign.

The generation of N_2O is shown in the following figure:



N₂O generation during a campaign

Figure 3 Typical N_2O generation as a function of time /7/

The oxidation of ammonia (NH₃) is a strongly exothermic process. Transferring heat to a steam system cools down the gases from the catalytic reactor. Further cooling is obtained by transferring heat to the tail gas that leaves the absorbing column. The rest of the process heat is transferred to the cooling water circuit.

1.2.3 Oxidation of nitric oxide

After the catalytic formation of nitric oxide, the gases are cooled down in a cooler condenser and in some cases also compressed. This enhances the oxidation of nitric oxide to nitrogen dioxide. Due to the condensation of water, weak acid solution is formed. This solution is separated and led to the absorption tower. The nitrous gas from the cooler condenser is mixed with NOxbearing secondary air from the bleaching section, which is sometimes housed within the absorption column.

In the absorption section of the absorption column, the remaining nitric oxide (NO) reacts non-catalytically with oxygen (O₂) to form nitrogen dioxide (NO₂):

 $2 \text{ NO} + \text{O}_2 \leftrightarrow 2 \text{ NO}_2$

1.2.4 Absorption of nitrogen dioxide

Demineralised water or steam condensate is added at the top of the absorption column. The weak acid solution (approx. 43%) produced in the cooler condenser is also added to the absorption column. The nitrogen dioxide (NO_2) in the absorption column is led in counter-current flow with the water (H_2O), reacting to nitric acid (HNO_3) and nitric oxide (NO):

 $3 \text{ NO}_2 + \text{H}_2\text{O} \leftrightarrow 2 \text{ HNO}_3 + \text{NO}$

Both the reactions are favoured by a higher pressure and lower temperature. Besides that, both reactions are exothermic so continuous cooling is necessary. The nitric acid produced is rich in dissolved nitrogen oxides and is passed to a bleaching tower (or bleaching section within the absorption tower) where it is contacted with a counter current flow of air. The air and the nitro-

gen oxides that have been stripped out, are used as secondary air, mixed with the gases leaving the cooler condenser and recycled to the absorption section.

An aqueous solution of nitric acid is withdrawn from the bottom of the absorption tower. The acid concentration can vary depending on the temperature, pressure, number of absorption stages and the concentration of nitrogen oxides entering the absorber. The gases that were not absorbed in the nitric acid solution leave the absorption column at the top, at a temperature of approx. 20-30 °C.

This gas mixture is commonly referred to as tail gas and is heated in the heat recovery section. The hot tail gas is in certain cases led through a NO_x abatement system and through a tail gas expander for energy recovery. The resulting expanded tail gas is vented through the stack.

1.3 Plant types in general

In general, two types of nitric acid plants can be distinguished: mono pressure and dual pressure plants. In mono pressure (single pressure) processes, ammonia oxidation and NO_2 absorption take place at the same pressure. In the past, nitric acid plants worked at atmospheric pressure or low pressure (mono pressure below 1,7 bar).

Nowadays, mono pressure/low pressure plants hardly exist anymore. Mono pressure/medium pressure plants (pressure between 1,7 bar and 6,5 bar) and mono pressure/high pressure plants (pressure between 6,5 bar and 13 bar) are commonly present. Most plants operate with dual pressure due to a higher yield and less environmental impact.

Older plants operate with low pressure/medium pressure, while more modern plants operate with medium pressure/high pressure. To make a higher pressure in the absorption section possible, a compressor is installed between the cooler condenser and the absorption column. The heat of compression is removed by heat exchange with the tail gas and/or by heat recovery in a steam boiler. A second cooler condenser reduces the temperature to 50 $^{\circ}$ C by cooling with water

The next figure gives a simplified scheme of a typical dual pressure plant.



Figure 4 Dual pressure nitric acid plant

1.4 Emissions

The main atmospheric emissions of environmental significance are NO_x and N_2O . During stable operation, the gas composition at the absorber outlet normally varies within the following ranges:

Tailgas composition	Range
NO _x	100-2.000 ppm _{vol}
N ₂ O	300-1.700 ppm _{vol}
0 ₂	10.000-40.000 ppm _{vol}
H ₂ O	3.000-7.000 ppm _{vol}
N ₂	Balance
Flow rate	3.130-3.330 Nm³/T 100% HNO ₃

Table 1 Composition of tailgas /2/

Plant start-up and shut-down increases the $NO_{\rm x}$ emissions. In addition, small amounts af gaseous ammonia are occasionally released by the concentration of water in the ammonia vaporizer and periodic blow-downs. Maintenance operations may also generate small amounts of ammonia and nitric acid.

There are normally no unrecovered solid wastes in nitric acid manufacture. Catalysts have to be periodically replaced, but these are regenerated.

1.5 Reduction of N₂O

The formation of N₂O is unavoidable, since the NO yield is limited. From an environmental point of view, emissions of N₂O need to be prevented; N₂O has a global Warming Potential (GWP) of 310 times greater than $CO_{2.}$ NO_x and N₂O can be minimized by various means, as shown in the following figure:



Figure 5 Abatement Technologies

Extended absorption in water in a high pressure system can achieve a NO_x content of about 100 ppm. The technology does not have any effect on the N_2O emissions.

Homogeneous decomposition has been developed and patented by Norsk Hydro. This technology consists of an 'empty' reaction chamber of approx. 3,5 m extra length between the platinum and the first heat-exchanger. Due to longer residence time of 1-3 seconds, a N₂O reduction of 70-85 % is obtained, since N₂O is unstable at higher temperatures and decomposes into nitrogen and oxygen.

Non-selective catalytic reduction (NSCR): hydrogen or a hydrocarbon is burned in the tail gas over a platinium, rhodium or palladium catalyst, reducing NO₂ to NO, with an excess of fuel reducing NO_x to nitrogen. Tail gases may need to be pre-heated, and the use of hydrocarbon fuel incurs the release of CO and hydrocarbons to the atmosphere. Conversely, the use of hydrogen is not possible if the ammonia plant is shut down and there is no synthesis gas. A possible advantage is the system's ability to decompose both N₂O and NO_x.

NSCR units were widely installed in nitric acid plants built between 1971 and 1977. Today, however NSCR units are generally not preferred because of high energy costs and associated high gas temperatures. NSCR uses a fuel and a catalyst to consume free oxygen in the tail gas and convert NO_x to elemental nitrogen. NSCR is an expensive abatement technology, both in terms of investments and operation costs.

Selective catalytic reduction (SCR): NH_3 is used to reduce NO_x to nitrogen over a catalyst. The latter can be vanadium pentoxide, platinium, iron/chromium oxides or zeolites, among others. Whether or not the tail gas needs to be pre-heated depends on the process. In all cases it needs to be at the right temperature. There is some ammonia leakage, depending on catalyst efficiency, and the tail gas must be kept above 100° C after expansion. On the other hand, NH_3 is always available, there is no oxygen consumption and no added pollution with a high efficiency catalyst, and NO_x can be reduced to about 100 ppm.

High temperature catalytic decomposition for reducing N_2O emissions is a new technology that has been developed by e.g. BASF in Germany and Grande Paroisse in France.

The new technology can be applied by introducing a new catalyst bed which is installed in a new basket, directly under the Platinum Gauze in the NH_3 burner. This new catalyst does not have any effects on the present production (no yield loss).

The technology has been installed in a few plants and operated without problems. The technology has proven to be reliable.

Catalytic decomposition for reducing N₂O emissions is also a new technology available, that has been developed by e.g. Krupp Uhde in Germany. The technology requires rather high temperatures (above 400° C) and is therefore not suited for most existing plants, with low tail gas temperatures up stream the gas expander.

A new alternative is developed by Johnson Matthey in England. The catalyst is called AMOXIS / Gauze Hybrids Catalyst. This product has been installed and operated without problems and great success in three plants after successful testing in pilot plants.

AMOXIS destroys N2O. The catalyst converts the Nitrous Oxide to Nitrogen (N2) and Oxygen (O2).

This catalyst can be used in low, medium and high pressure plants and there is no temperature limit as experienced with simple cobalt oxide.

1.6 Summary of abatement technologies

Abatement Technology	Costs per ton CO ₂ - equivalent (€)	Comments
High temperature decomposition (850-950° C)	0,3-0,5	Full scale, commercial
Catalytic decomposition (tail gas 400-500° C)	0,5-1,0	Pilot scale.
Selective Catalytic Reduction with hydro-carbons (tail gas <400° C)	1,5-3,0	Lab scale.

The following table shows cost for the technologies:

Table 2 Cost effectiveness for abatement technologies in existing plants /8/

<u>Note</u>: Catalytic decomposition with Amoxis Catalyst has approx. the same cost as high temperature decomposition.

Consequently, the most cost effective solution regarding reduction of N_2O is catalytic decomposition, which *can* be combined with either Selective Catalytic Reduction or Extended Absorption to lower emissions of NO_x .

1.7 Agropolychim's nitric acid plant

The nitric acid plant at Agropolychim is a French made dual pressure plant commissioned in 1974. Basic key information of the plants are summarised in the following table:

Subject	Grand Paroisse plant
Production in 2003	223.815 tons of nitric acid 100 v%
Production in 2002	250.312 tons of nitric acid 100 v%
Production in 2001	325.728 tons of nitric acid 100 v%
Capacity	1.100 tons of nitric acid per day 100 v%
Oxidation	4 burners
	Pressure for catalytic oxidation is 3,5 bara
	Oxidation temperature is 853 °C
	Gauzes are knitted
	Burner diameter is 4,254 m
	Basket diameter is less than 4,254 m
Absorption	Pressure in absorption column is 12,8 bara
	Absorption temperature is 20-40 °C
Abatement Technologies	None
Tail gas	NOx concentration is around 170-200 ppm _{vol}
	N_2O concentration is 895 ppm (indicative - to be confirmed by online monitoring)
	The temperature is 20 °C
	The flow is 148.500 Nm³/h

Table 3Key information for the plant (Grande Paroisse)

The oxidation process at the plant is in the lower end of medium pressure nitric acid plants.



Figure 6 Foto of one of the four reactors (NH₃ burners)

1.7.1 N₂O Emissions

 N_2O emissions vary significantly from one nitric acid plant to another. The emissions depend very much on site-specific factors such as plant design, process conditions and abatement technologies employed.

The following specification of N_2O emission from the plant is based on actual indicative measured emissions and expected productions of 100 % nitric acid.

	Year	Production of Nitric Acid (tons/year)	Emission of N ₂ O (tons/year)	GWP fac- tor	Annual emission of CO _{2- equivalent} (tons/year)
JI – Project	2005	325.000	1.800	310	558.000

Table 4 Specifications of present N₂O emissions

The plants operate around the clock with planned shut down normally from July to September.

The N_2O generation at Agropolychim is 5,54 kg N_2O per ton 100% nitric acid, based on indicative measurements.

The following figures show the N_2O generation from European nitric acid plants /9/:

European designed dual pressure plants:	2-10 kg N_2O / ton 100% HNO_3
Older plants pre 1975 without NSCR:	10-19 kg N ₂ O / ton 100% HNO ₃

2 DESCRIPTION OF THE JI PROJECT

The project will be implemented either by technology from BASF or Johnson Matthey as described in the following paragraph.

2.1 Project details

The objective for the project is to reduce the N_2O emission by utilizing new developed technology that converts the Nitrous Oxide into Oxygen and Nitrogen, which have zero Global Warming Potentials.

BASF technology

The new technology can be applied by introducing a new catalyst bed which is installed in a new basket, directly under the Platinum Gauze in the reactors. This new catalyst does not have any effects on the present production (no yield loss).

The catalyst installation is fairly easy being poured from drums and raked level into the burner basket located directly under the Platinum gauze. The installation only takes a month and can be done under a planned shut-down.

The new catalysts are composed by weight of 20% CuO, 16% ZnO and AL_2O_3 plus promoters. Ring tablets can be utilized at this specific plant and the thickness of the layer in the basket will be around 100 mm.



Figure 7 BASF Technology

The technology is owned and patented by BASF (German patent BASF Catalysts 03-80, 03-85 and 03-86). The technology has been installed in a few plants and operated without problems. The performance of the catalyst technology is guaranteed by BASF. The technology has proven to be reliable having been installed in two plants since 1997 without requiring replacement while still achieving target conversions.

The pressure drop over the catalyst is not significant and is normally about 15 mbar. The lifetime of the catalyst is about 3 years.

Johnson Matthey technology

The alternative catalyst is supplied by Johnson Matthey. The catalyst is called AMOXIS / Gauze Hybrids Catalyst. This product has been installed and operated without problems and great success in three plants after successful testing in pilot plants.

AMOXIS destroys N_2O . The catalyst converts the Nitrous Oxide to Nitrogen (N_2) and Oxygen (O_2).

Results also show that the there is no base metal loss from AMOXIS catalyst and hence no contamination of the end product.

Basic characteristics of the AMOXIS Catalyst:

- A pelleted La / Ce /Co Perovskite ammonia oxidation catalyst;
- La 0.8 Ce 0.2 CoO3 ;
- The cobalt is locked into a refractory matrix;

This catalyst can be used in low, medium and high pressure plants and there is no temperature limit as experienced with simple cobalt oxide.

The catalyst is installed in a basket between the Pt gauzes and the catchment ones. This catalyst can also be installed within few months.

Investment

The project does not have any significant effect on the operating costs. The estimated investments for the project are as follows:

New baskets in reactors	200.000 EUR
Monitoring equipment	50.000 EUR
Initial investment	250.000 EUR

The license fee and cost of catalyst have to be negotiated. Investment and operation cost are similar for both technology from BASF and Johnson Matthey.

2.2 **Project characteristics**

The project characteristics for the nitric acid plant are presented below. The characteristics are given for the plant during normal operation conditions.

Subject	Grand Paroisse plant
Production of HNO ₃	47,083 tons of nitric acid 100 v% per hour
Air intake to NH_3 burner	152.800 Nm³/h
Ammonia intake	17.350 Nm ³ /h
O_2 in tail gas	2,8 v%
N_2O in tail gas	895 ppm (average, based on indicative measurements)
Tail gas flow	148.500 Nm ³ /h

 Table 5
 Project characteristics for the plant (Grande Paroisse)

2.3 Project sustainability

The plant is functional and running presently. The sustainability of the project is related to future maintenace of the plant and the situation of the fertilizer market.

There are no significant risks related to the project in technical terms, but it is essential that the plant keeps on producing nitric acid in the future. The risks are more related to the prediction of the market situation for fertilisers in the future and the company's investment plans for rehabilitation of the plant.

2.3.1 Sustainability of resources

The catalyst can be provided by BASF or Johnson Matthey for at least 10 years, so the sustainability of resources is very good.

2.3.2 Environmental sustainability

The technology has been tested by both BASF and Johnson Matthey at multiple plants, and the results show no significant reductions for the catalyst over a 3 year period.



The following figure shows the performance of BASF technology:

Figure 8 Long-term N₂O conversion, BASF Works, Ludwigshafen

Similar to the above the technology of Johnson Matthey provides reduction as shown on the figure below.



AMOXIS Hybrid Trial 2 - Daily Average Nitrous Oxide Concentration (Exit De-NOX Unit)

Figure 9 Long-term N₂O conversion, Johnson Matthey

The environmental sustainability in terms of benefits comprises reduction of GHG in form of N_2O for both technologies. The environmental impact of the project is high.

2.3.3 Economic sustainability and financial analysis

2.3.3.1 Project Investment costs

Estimated project investment costs are shown in the table below.

Project Investment costs

Component	Investment costs
4 new baskets in reactors	200.000
Monitoring equipment	50.000
Initial installation costs	250.000

To the specified costs should be added buying and renewal of a catalyst. Likewise, a license fee will have to be negotiated with BASF or Johnson Matthey.

2.3.3.2 Project income

Since the investment is expected to have no effect on production, no direct income will be generated from the project investment. Income will be based entirely on carbon credit sales.

2.3.3.3 Project financing

The project will be financed by Agropolychim. Income will be generated through carbon credit sales to Denmark (through an agreement with the Danish Ministry of the Environment).

2.3.3.4 Economic Sustainability

Since income will be directly related to carbon credit sales, the economic sustainability of the project investment will depend strictly on the emission reduction obtained as a consequence of this project. *Emission reduction potential is again directly related to future production levels.*

Agropolychim has developed a Business Plan (2003 - 2008) for the company, as well as a prioritized investment plan related to environmental improvements up to 2012.

Agropolychim was privatized in 1999 and in year 2000 new owners took over. During, the period from 2000 – 2002 the company went through a process of restructuring and stabilisation. The number of employees in the company has went down from 2.500 employees in year 2000 to currently 1.100 employees.

Through the company Business Plan for the period 2003 – 2008, the company has turned into a process of strategic development. This includes a more diversified production line in the future as well as increased production levels. According to Agropolychim's own expectations, production of Nitric Acid will increase from 223.815 t/y in year 2003 up to 325.000 t/y in 2005, due to expected increase in demand, mainly within the national Bulgarian market. From 2005 and onwards Agropolychim expects to maintain the 2005-level of production.

Agropolychim has recently demonstrated a consolidated development of production and economic performance.

2.3.4 Market analysis

The national market for fertilizers in Bulgaria is strongly dominated by the two big Bulgarian fertilizer production companies, Agropolychim and Neochim.

Currently, Agropolychim's production sale is divided more or less 50/50 between the national market and for export (main countries for export are USA, Brazil, Mexico, France, Italy and Spain). However, according to information provided by Agropolychim, the company expects to increase the share of products to be sold nationally and, consequently, decrease the export share. Agropolychim expects that by 2010 – 2012 around 70% of their products will be produced for the Bulgarian market while around 30% will be exported. Agropolychim has a preferential for the national market, which is more profitable compared to exportation (due to freight costs etc.).

Agropolychim's own expectations to future market development in Bulgaria are positive. The positive expectations are based on increases in demand for fertilizers in Bulgaria, between 10 – 20% p.a. during the period 2000 – 2003.

It must be expected, however, that future development on the fertilizer market in Bulgaria will face opportunities as well as challenges for Agropolychim.

First, market competition from foreign companies will increase, although this has already occurred gradually over the last decade due to Bulgaria's increasing involvement and participation in bilateral and international (trade) agreements.

In 1993, Bulgaria signed an association agreement with the European Union. This agreement included a gradually lowering of tariffs on import/export items between Bulgaria and the EU. Bulgaria is the fifth most important exporter of fertilizers to the EU; Russia, Poland, Norway and Lithuania are in the first places. With Bulgarian EU membership, it must be expected that Agropolychim could improve their relative EU market position to Russian and Norwegian companies.

Likewise, Bulgaria has been member of the World Trade Organization (WTO) since 1996 and part of the Central European Free Trade Agreement (CEFTA) since 1999 (other member countries: Poland, Czech Republic, Slovakia, Hungary, Slovenia and Romania). Furthermore, a free-trade agreement between Bulgaria and Turkey was implemented from January 1999.

Second, part of the increased demand for fertilizers in Bulgaria during the last few years can be related to agricultural subsidies and EU agricultural support programmes (SAPARD). The SA-PARD programme, however, will be faded out when/if Bulgaria enters the EU.

Third, it is to be expected that foreign investments will increase within the Bulgarian agricultural sector with Bulgarian EU membership. This could have a positive influence on development of production and fertilizer demand within the Bulgarian agricultural sector in the future.

In conclusion, at this stage it is difficult to predict market development for Agropolychim after 2008. The production projections presented by Agropolychim in their business planning must therefore be considered with the above mentioned opportunities and risks for future market development in mind.

2.3.5 Project outcome

The outcome of the project will be the instalment of a new catalyst bed at the nitric acid plant, which facilitates a decrease in N_2O -emissions through nitrous oxide reduction.

It is considered an environmental safe technology and does not affect the plant operation, neither in form of constraints nor capacity increase.

Expected lifetime of the catalyst bed is minimum 3 years.

2.4 Time schedule

The design process is expected to take a few months. The installation itself could probably be carried out within a month.

It is expected that design and installation could be ready from late summer 2004 (September). The reductions of CO_2e emissions could be generated immediately the technology is installed, that means from September 2004.

2.5 Project stakeholders

The following key stakeholders are identified for the project:

- Agropolychim (Devnya Plant)
- Regional Environmental Inspectorate, Varna
- Government of Bulgaria (Ministry of Environment and Water, Ministry of Finance)
- Government of Denmark (Ministry of the Environment)

3 APPROVAL OF THE PARTIES INVOLVED

A JI project has to be approved by the parties involved, but the JI guidelines do not provide specific guidance concerning the form or content of the approval from the parties involved. Parties have to appoint a JI Focal Point to approve the project which should be listed at the www.unfccc.int. According to information Denmark has not yet listed a JI Focal Point at the UNFCCC, but the process in ongoing.

Due to no specific guidelines for obtaining an approval from parties involved the following procedures have been selected to secure approval by the parties,

- Letter of approval signed by the Bulgarian government and the Danish government
- Consultation of stakeholders in Bulgaria and Denmark will be performed by announcements in newspapers, websites or direct contact to relevant organisation like NGOs.
- Purchasing agreement signed by the Bulgarian government and the Danish government will be developed.

Consultation of stakeholder will respect the requirements in the Marrakech Accords Decision 16/CP.7.

3.1 Host country party to Kyoto Protocol

Bulgaria has signed the Framework Convention on Climate Change (ratified in 1995) and the Kyoto Protocol with 1988 as base year.

3.2 Memorandum of understanding

A memorandum of understanding (MoU) between the Government of Denmark and the Government of Bulgaria was signed on 24 July 2003.

3.3 Letter of intend

A letter of intend will have to be signed for this project, between the parties involved.

3.4 Crediting period

The crediting period will be 2008 - 2012 or 2004 (September) - 2012 (if early crediting will be included in the agreement).

3.5 Criteria host country PDD, BS and MP

Bulgaria has no particular requirements to PDD, BS and MP further to those presented in the documentation related to the Kyoto Protocol.

3.6 Public Hearings

Public hearings will be performed in Bulgaria and in Denmark through publication of the PDD in the web site of the Bulgarian Ministry of Environment and the Danish Ministry of the Environment.

Upon completion of the public hearing, a summary will be prepared and included in the final version of the PDD.

3.7 Impact assessment

Since project implementation will not affect production and near surroundings, no particular social or environmental impacts are expected from the project.

4 ADDITIONALITY ASSESSMENT

4.1 Emission additionality

The GHG emission reduction generated by the project will not occur without this specific JI-project. There is no national or international legislation regarding N_2O emissions, and the project does not enhance the productivity of the plant.

4.2 Program additionality

No existing law in Bulgaria requires or encourages implementation of this kind of projects.

4.3 Financing additionality

Considering the fact that the instalment of the catalyst bed does not improve yield or process efficiencies and thus has no direct benefits to the plant, there would be no incentive to implement the investment without the prospect of carbon credit sales.

Furthermore, the project will not receive funding from any international assistance funds in order to support greenhouse reductions.

The income from carbon credit sales is therefore to be considered as a financing additionality for this particular project.

4.4 Accession to the European Union

Bulgaria has now transposed most of the EU environmental regulation and requirements. In the case of Agropolychim, this means that the company faces serious environmental investments for the future.

Within the next 7 years, Agropolychim will need to invest around 20 million EURO in environmental improvements at the factory in order to comply with EU standards by 2012. The main environmental issues that Agropolychim will have to confront up to 2012 are related to solid waste and waste water.

Construction of a waste water treatment plant is part of the investments to be carried out by Agropolychim. Estimated investment costs for a waste water treatment plant are around 6 - 8 million EURO. Establishment of a waste water treatment plant will allow for re-use of the water for production. Expected pay back time of the investment is 10 years.

5 BASELINE STUDY

5.1 Project category

The industrial project at Agropolychim is an environmental project entirely based on reduction of laughing gas emissions from the factory's nitric acid plant.

5.2 Project boundaries

The proposed project boundaries are assumed to be valid for the entire crediting period.

The direct on-site emission reduction generated by the project is only N_2O emissions from the nitric acid plant.

5.3 Assessment of leakages

There are no significant leakage generated by the project because the project does not have any impact related to: energy consumption or generation, waste, raw material consumption and emissions other than N_2O .

It can be argued that the pressure drop over the new catalyst will increase the energy consumption. However, the pressure drop of 15 mbar does not have any significant effect on the energy export from the plant.

5.4 Baseline

Today JI-guidelines do not provide specific guidelines for selecting a baseline methodology. In this respect CDM guidelines have been used in this document developing baseline. The only guideline is that establishment of baselines (emission baselines) shall be transparent when selecting the choice of approaches, assumptions, methodologies, parameters, emission factors etc.

According to CDM guidance the baseline approach forms the basis for the baseline methodology.

5.4.1 Baseline approach

The Marrakech Accords define three different baseline approaches for CDM projects that can be applied for JI - projects. For development of baseline an approach of actual or historical data has been used.

Historical data and actual emissions have been selected to develop the baseline. The historical data are available based upon production data collected continuously during several years and the reliability is considered to be good.

Actual emissions from the nitric acid plant have been measured in March 2004, but for more preciseness online measurement will commence in June 2004 in order to establish the preproject emissions parameters and elaborate the most correct baseline.

5.4.2 Baseline methodology

The assumptions made concerning production of nitric acid can vary both up and down in future years, primarily depending on the market situation for fertilizers. To reflect this the Baseline does not fix the annual production, and variations will be recorded in the Monitoring Plan and finally determine the actual number of ERUs to be generated.

Historical data for production of nitric acid has been obtained for year 2001, 2002 and 2003. Actual measured emissions (and production) have been carried out. N_2O concentration was not known prior to the project.

The emissions reductions, represented as N_2O is calculated to CO_2 equivalent.

The baseline calculates the present generation of N_2O per ton HNO_3 produced. In the future, when the technology has been implemented, the actual emission reduction can be calculated by substraction the actual generation from the baseline generation.

Online easurements of the N_2O concentration will be performed in June 2004, in order to verify the actual emission level. The measurements in March 2004 are indicative spot measurements.





5.4.3 Baseline conditions for emission baseline

The prediction of the emission baseline for Agropolychim's nitric acid plant is based on the methodologies described in this paragraph.

The annual production of 100% nitric acid is assumed to be 325.000 tons. The production time represents an annual time of approx. 7.000 hours for this production. The production is assumed to be constant in the future.

	Environmental project	Emission Baseline Development
B.I.A	Starting point for emission baseline is September 1 st 2004	The crediting period for the baseline is September 1 st 2004 to December 31 st 2007
B.I.B	Starting point for emission baseline is January 1 st 2008	The crediting period for the baseline is January 1^{st} 2008 to December 31^{st} 2012
B.I.C	Starting point for emission baseline is September 1 st 2004	The crediting period for the baseline is Sep- tember 1 st 2004 to December 31 st 2012

Table 6 Emission baseline

5.5 Calculation of emission baseline

The calculation of the net emission baseline of the project is described in this paragraph and Annex I (Data and calculations for emission baseline).

The baseline has been developed in accordance with the French standard BP X 30-331 "Protocol for quantification for nitrous oxide emissions in manufacture of nitric acid".

Today, the 4 reactors in the nitric acid plant do not have abatement technology to minimize the N_2O emissions.

When the new catalyst has been installed in baskets under the NH_3 burners, the project begins to generate N_2O reductions immediately.

The procedure for calculation the emission baseline is:

- Measurement of actual N2O concentration in tail gas. ISO or other organisations do not have standard procedures for measurement of N2O. Annex II describes the analysis methodology.
- Calculation of average N2O concentration, based on the measurement.
- Actual flow rate for the tail gas.
- Actual production of nitric acid 100 %
- Calculation of N2O emission generation (factor for ratio between N2O and the production of HNO3).
- The baseline emission is calculated by multiplying the average N2O generation factor with the assumed production.

5.5.1 Emission factors

The GWP used for N_2O is 310 according to IPCC default values,

The following conversion factors from ppm to mg/Nm³ (Nm³: 1 m³ air at 273 K, 101.3 kPa, dry) for various emissions to air:

Emission	Conversion factor
NO _x	2,05
N ₂ O	1,96
$\rm NH_3$	0,76

Table 7 Conversion factors /3/

5.5.2 Actual calculations and measurements

In March 2004 measurements were conducted at the nitric acid plant, with the following results:

Tail gas and production	Result
Production of 100% HNO_3	47,1 T /h
Flow rate of tail gas	148.500 Nm³/h
N_2O concentration in tail gas	860 ppm
Temperature of tail gas	20° C
Age of Pt gauze	5 months

Table 8 Measurements in March 2004

The measurement results and calculations are presented in Annex I.

Calculation results (Annex I):

Average N_2O emission:	261 kg/h
Emission factor:	5,54 kg N ₂ O/t HNO ₃
Annual emission of N_2O :	1.800.000 kg N₂O
Annual emission of CO ₂ equivalent:	558.000 T CO _{2 eq.}

5.5.3 Calculation of emission reductions (Annex III)

The starting point for the methodology for prediction of emission baseline is based on the assumed production of nitric acid in the future, of 325.000 t HNO₃ 100%.

Assumptions used predicting the $CO_{2 eq.}$ emission reduction generated by the project:

• The only GHG emission reduction generated is N₂O

- The plant operates the entire year with an annual production of 325,000 tons of 100% nitric acid (HNO_3)
- The production of nitric acid is multiplied with the generation factor of N_2O before and after implementing the project, see Annex III.

5.5.4 Net GHG emission reduction

The net GHG emission reduction generated by the project has been calculated using the results from Annex I and III.

A new calculation will be made after actual performance of longer term (min. 10 days) online monitoring.

2004	2005	2006	2007	2008	2009	2010	2011	2012	Total
160	403	403	403	403	403	403	403	403	3.384

Table 9 Net emission reduction in 1.000 tons CO_{2 eq.}

The total GHG emission reductions are:

September 1 st 2004 to December 31 st 2007:	1.369.000 tons $CO_{2 eq.}$
January 1 st 2008 to December 31 st 2012:	2.015.000 tons $CO_{2 eq.}$
September 1 st 2004 to December 31 st 2012:	3.384.000 tons CO _{2 eq.}

<u>NOTE</u>: The above figures are considered to be restrictive as far as it is expected to be somewhat higher based on the online monitoring to be performed in June 2004.

5.6 Conclusion

The baseline developed for the project is considered to be the must likely baseline, which fulfils the criteria for a JI-project according to the Kyoto Protocol and Marrakech Accordings.

Emission baseline

The baseline is based on the assumptions of an annual production of 325.000 tons of 100% HNO_3 and an average concentration of N₂O of 250 ppm in the tail gas, after implemmentation.

Risks

The net emission reduction generated by the baseline is strongly connected to the assumption of an annual production of 325.000 tons 100% HNO₃.

6 MONITORING PLAN

6.1 **Objective of the Monitoring Plan**

The objective of the Monitor Plan (MP) is to provide a practical framework for collection and management of performance data, in order to monitor and varify the GHG emission reduction generated by the JI-project. The project comprises reduction of nitrous oxide by means of a new catalyst introduced to the reactors of the nitric acid plant.

The MP has been developed in accordance with the French standard BP X 30-331 "Protocol for quantification for nitrous oxide emissions in the manufacture of nitric acid".

This MP provides monitoring methodologies for monitoring and estimation of GHG emission reduction referring to the emission baseline in the baseline study, included in this PDD.

The monitoring results shall be filled in the forms in Annex IV (Monitoring Plan) for the entire monitoring period.

Further more is it essential to store data in a safe manner, to prevent loss of data.

The proposed monitoring methodology, data collection, data management and guidelines can only be changed after agreement with the Bulgarian Government, the Danish Government and the Verifier.

6.2 **Requirements for the Monitoring Activities**

- 1. Monitoring of the GHG emission reduction generated by the project shall be performed by data collection at Agropolychim's nitric acid plant.
- 2. Monitoring reports include the actual GHG emission reduction and GHG emission generated by the project and should be issued annually during the entire crediting period.
- 4. Based on monitoring results the GHG emission reductions and GHG emissions shall be calculated and submitted for verification as approved ERUs.
- 5. Persons trained in the monitoring procedure shall conduct the monitoring.
- 6. QA system shall be implemented to secure accurate and transparent monitoring.
- 7. The governing language is English in monitoring reports.
- 8. The outcome of the MP shall enable a legacy entity to accrediting the ERUs generated by the project according to requirements of the Executive Board/JI Supervisory Committee, the Bulgarian government and the Danish government.
- 9. The monitoring procedures shall follow the guidelines in the Marrakech Accords.
- 10. Draft versions of the annual monitoring reports shall be submitted to the Bulgarian government and the Danish Government or their representatives before issuing the final version. The annual monitoring reports shall be issued to:

Receiver of annual reports	Draft version monitoring report	Final version monitoring report
Bulgarian Government	2 copies	2 copies
Danish Government	2 copies	2 copies
Verifier	none	2 copies

Table 10 Monitoring reports

6.3 Frequency of Monitoring and Verification Procedures

The overall time period for the monitoring procedures is defined in the PDD after agreement between the Bulgarian government and the Danish government.

Time period	Monitoring	Verification
From September 1 st 2004	online	End of year

Table 11 Time period for monitoring and verification procedures

6.4 Monitoring equipment

The nitric acid plant needs to be fitted with the following monitoring equipment:

- On-line measurement of tail gas flow with an ultra-sonic flow meter.
- On-line measurement of N₂O concentration
- On-line measurement of temperature of tail gas
- On-line measurement of absolute pressure of tail gas
- On-line measurement of HNO₃ production by an ultra-sonic flow meter.

The data from the on-line measurements are linked to a computer with a database to store actual measurements. The calculations can be performed on the computer (e.g. a spreadsheet) and the following has to be taken into account:

- The flow rate of the tail gas has to compensate for temperature and pressure.
- The flow rate of HNO₃ has to compensate for the solution flow (approx. 58% HNO₃).

Since some of the listed equipment is already on place, and some new one will be installed (like N_2O online analyser), the above mentioned measuring equipment has to be approved by the validator before installation.

6.5 Verification and Basic Assumptions

The MP provides a practical approach and describes the methodology in order to quantify the project performance in terms of the GHG emission reduction as mentioned before. The precondition is that baseline described in the BS is accepted as the model for this project. Monitoring of the GHG emission reductions and GHG emissions shall be based on transparent data management and calculation methods.

6.6 CO₂ Emission Reduction

6.6.1 Basic Assumptions

The MP is based on on-line measurement of the tail gas and the production flow. Emission factors are calculated in the baseline and measured on-line continuously.

The emission reduction is calculated as the difference between the emission factor (kg N_2O per ton 100 % HNO₃) and the actual emission factor multiplied by the actual production.

6.6.2 Methodology

The actual emission reduction (over a period of time) is obtained by the following equations:

The *emission factors* are calculated as follows (both before and after the project):

$$F_{N2O} = \frac{1}{t} x \sum_{0}^{t} \frac{C_{N2O} x Q_{S} x 44}{P_{N2O} x V_{M}} x 10^{-6} \Delta t$$

Where

F _{N2O}	kg/T	N ₂ O emission in kg per ton of 100% HNO ₃ produced
t	hours	Period of time
C _{N2O}	ppm	N_2O concentration in tail gas
Qs	Nm³/h	Output air flow (tail gas)
V _M	22,4 l/mol	Molar volume N_2O (normal conditions)
P _{N2O}	T/h	Production of 100% HNO ₃

The actual emission reduction is calculated as follows:

$$ERU = \frac{GWP}{1.000} x \sum_{0}^{t} \left(F_{N2O \text{ baseline}} - F_{N2O \text{ actual}} \right) x P_{N2O} \Delta t$$

Where

ERU	CO _{2 eq.}	Emission Reduction Units
GWP	310	Global Warming Potential for N ₂ O
F _{N2O baseline}	kg/T	N ₂ O emission in kg per ton of 100% HNO ₃ produced (baseline)
F _{N2O actual}	kg/T	N_2O emission in kg per ton of 100% HNO ₃ produced (actual)
t	hours	Period of time
P _{N2O}	T/h	Production of 100% HNO_3 (actual)

6.7 Environmental Impacts

6.7.1 Basic Assumptions

The MP and the corresponding Baseline Study is based on the assumption that the project will reduce emission of GHG, which is emitted from the nitric acid plant. As mentioned earlier the reduced environmental impacts shall be recorded in order to monitor that the expected environmental benefits are achieved. Local stakeholders can at any time submit comments to the project's environmental impact. Important comments and its solution will be included in the annual monitoring report.

6.7.2 Methodology

The environmental impacts caused by the project will be recorded by the company, which is described in Inspection reports, and Forms following the guidelines in this MP.

6.7.3 Operation- and Monitoring Obligation

This paragraph describes requirements for storing data of the key performance parameters necessary to achieve verifiable emission reduction data. This will call for certain operational obligations and data collection obligations to be fulfilled by the company.

The on-line data has to stored on a PC and back-up of the data has to stored in a secure manner (e.g. on a CD-ROM or a server situated elsewhere)

Paper prints of the data has to stored in two paper copies (one copy at the plant and one copy elsewhere – in case of fire)

In the event of significant improvements or changes to the process, several assessments shall be carried out to define a new emission factor.

6.8 Management of the Monitoring Plan

Management of the MP shall ensure registration of performance data for verification of the GHG emission, which shall be executed by an independent entity.

6.8.1 Responsibilities

The management and operation of the plant shall ensure environmental credibility through systematic and accurate performance of monitoring procedures for the entire lifetime of the MP.

6.8.2 Management

The company is responsible for implementation of the management system according to the guidelines in this MP. The management system shall be based on the guidelines mentioned in paragraph 6.9 to 6.11 and the form included in the Annexes

6.8.3 Data handling

Data handling shall be conducted in a transparent way to secure high quality data recording and data filing. The forms included in the MP shall be used as a protocol for data handling, which as a minimum comprise recording of monitoring data.

Uncertainty related to data handling shall be recorded by the company and the verifier shall be noticed about this, and if necessary monitoring procedures shall be modified according to agreement with the verifier.

Data recorded in the first month (1) of the monitoring period (first monitoring year) shall be forwarded to the verifier immediately after expiry of this month, for identification of possible mistakes or irregularities.

6.9 Quality Assurance System

The quality assurance system shall secure that monitoring procedures and requirements are followed. The QA system will not be according to any ISO 9000 or similar standards. The QA system comprises inspection of the monitoring procedure by an independent third party. The management of Agropolychim is responsible for QA system.

The QA system can be changed according to request from the verifier.

QA –	Procedure	Time for Inspection	Inspection
1.0	Calibration of meters and transmitters All flow meters and transmitters have to cali-	Every 6 months	Independent third party
	during planned shut down.		
	Calibration reports must be obtained, including name, official company registration number, ad-dress, phone and fax number.		
2.0	Control of meters and transmitters	Weekly	Operational staff
3.0	Control of monitoring data	Daily	Operational staff
	The data and the calculations have to be con- trolled every day, to secure minimum errors		
4.0	Observations, comments, control of calibration reports and measurements of N_2O concentration.	Every 6 months	Independent third party

5.0 Training of staff members

Before commissioning of project and hereafter annually Management

Table 12 Quality Assurance System

6.10 Training and instruction of operational staff

Training of operational staff members shall be conducted before commissioning of project. Training shall be replicated, when needed, in order to secure full understanding of the monitoring procedures and to secure the highest possible reliability of the monitoring results.

The management is responsible for training and instruction of operational staff.

6.11 Instruction of independent third party

As part of the QA – system the independent third party will frequently visit the plant and conduct inspection of the monitoring procedures described in this MP.

The independent third party will conduct inspection twice every year during the entire crediting period and in this way secure that the monitoring procedures will be based on the forms presented in Annexes.

Inspection reports which is elaborated in both Bulgarian and English, is described below.

Inspection Report (headlines)

Issues	
1.0	Basic Information
	Name Inspection report Name of independent third party elaborating the inspection report Name of plant and factory Name, address, phone plant Time for inspection Name, address, phone inspector
2.0	Control of calibration reports
3.0	Control of data handling
4.0	Environmental and social impacts
5.0	Observations and comments

Table 13 Inspection Report

6.12 Monitoring Report

The management shall every year during the entire crediting period elaborate the monitoring reports with the content following the guidelines presented below. The number of monitoring reports per year can be changed according to request of the verifier, the Bulgarian government or the Danish government.

Contents of annual monitoring reports (guidelines)

Issues	
1.0	Basic Information
	Name Monitoring report Name of plant and factory Name, address, phone plant Time period for monitoring Name, address, phone verifier
2.0	Description of plant performance
	Production Key figures Results Environmental impact
3.0	Monitoring procedures
	<u>Description of:</u> Monitoring methods Adjustments of monitoring methods Errors
4.0	Printouts of measurements and forms
5.0	Changes in monitoring procedures
	<u>Description of:</u> Changes in production Changes conducted according to agreement with verifier

Table 14 Annual monitoring report

6.13 Verification

Verification of the management procedures and monitoring procedures for carrying out a satisfactory MP must be approved before the project can begin generating ERUs.

6.14 Summary - Management of the monitoring plan

The summary aims to highlight the key elements and responsibilities of the management of the MP.

Obligations	Utility	Independent third party	Verifier
Monitoring Plan	Review of the MP and comments. Review management of monitoring plan Preparation of monitoring proce- dures Training of staff members perform- ing monitoring procedures Updating of MP if necessary Preparation for data collection, data handling and data storing	Elaboration of inspec- tion reports every 6 months	Review of MP and com- ments Review of management system
Data collection	Review of methods and system for data collection system including updating of these if necessary		Review of methods and system for data collection including comments
Data handling	Appointment of person(s) responsi- ble for data handling		Review of data handling systems
Data storing	Establishment of data storing sys- tem for written and digital data Establishment of back-up system for data storing		Review of data storing system including backup systems
Monitoring	Timetable for monitoring activities		Review and assist elabo- rationg timetables, monitoring sheets etc.
Reporting	Establish framework for reporting which fulfil requirements in MP		Review of framework for reporting
Instruction	Instruction of staff members		Assist during perform- ance of the training

Table 15 Management of Monitoring Plan

7 **REFERENCES**

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- /2/ Integrated Pollution Prevention and Control, Draft May 2003. Reference document on Best Available Techniques in the large volume inorganic chemicals, ammonia, acids and fertilisers industries.
- /3/ IFA Technical Report no. 26.
- /4/ Dutch notes on BAT for the production of nitric acid, December 1999.
- /5/ Market analysis DeN₂O by Jacobs Ebgineering, May 2001.
- /6/ IRMA and Grande Paroisse note on a new catalytic process for combined treatment of nitrous oxide and nitrogen oxides for nitric acid workshops, July 2002.
- /7/ French Standardization, BP X 30-331, Protocol for quantification for nitrous oxide emissions in the manufacture of nitric acid.
- /8/ Reduction of nitrous oxide (N₂O) in the nitric acid Industry by the Netherlands Agency for Energy and the Environment, October 2001.
- /9/ Good practice guide and uncertaincy Management in National Greenhouse Inventories by the Intergovernmental Panel on Climate Change (IPCC), 2000.

Annex I Data and calculations for emission baseline

The emission baseline is based on actual production, and calculations are done in accordance with the French standard BP X 30-331 "Protocol for quantification for nitrous oxide emissions in the manufacture of nitric acid".

Key data from the nitric acid plant

On March the 23^{rd} measurement of N₂O concentration were conducted, and information about the production were provided, with the following results:

Production of 100% $HNO_3 (P_{HNO3})^{-1}$:	47,1 t/h
Flow rate of tail gas $(Q_S)^{1}$:	148.500 Nm³/h
O_2 concentration in tail gas $(C_{O2})^{1}$:	2,8%
N_2O concentration in the tail gas (C_{N2O}) $^2\colon$	860 ppm
Temperature of the tail gas $(T_{gas})^{1}$:	20° C
Pressure of tail gas ¹	1,08 mbar abs.
Age of Pt gauze ¹	5 months

¹ Informed by Agropolychim

² Indicative measurement, see Annex II

The production was normal at the time and representative.

Calculation of average N₂O concentration:

The Platinum gauze is expected to have a lifetime of approx. 11 months. The actual concentration measured is therefore slightly lower than the average during a campaign. The age of the Platinum gauze was approx. 40% of the campaign, and the measured concentration has to be multiplied with a factor of 1,04 (see figure 3), in order to find the correct average generation.

The average concentration of N_2O , during the campaign is

 $C_{N2O} = 860 \cdot 1,04 \approx$

895 ppm

Note: N₂O concentration will be verified during online monitoring in June 2004.

Calculation of emissions:

The N_2O emission is obtained by the following equation:

$$Q_{N20} = \frac{C_{N20} x Q_S x \ 44}{V_M} x 10^{-6}$$

Where

 $Q_{N2O} =$

Q _{N2O}	kg/h	N_2O emission
C _{N2O}	ppm	N_2O concentration in tail gas
Qs	Nm³/h	Output air flow (tail gas)
V _M	22,4 l/mol	Molar volume N_2O (normal conditions)

$$\frac{895 \ x \ 148.500 \ x \ 44}{22.4} \ x10^{-6} \approx$$
 261 kg/h

The actual N_2O generation factor is obtained by the following equation:

$$F_{N2O} = \frac{Q_{N2O}}{P_{N2O}}$$

Where

F _{N2O}	kg/T	N_2O emission in kg per ton of 100% HNO ₃ produced
Q_{N2O}	kg/h	N ₂ O emission
P _{N2O}	T/h	Production of 100% HNO ₃

$$F_{N20} = \frac{261}{47,1} \approx 5,54 \text{ kg } N_2 O/T \text{ HNO}_3$$

Annual emission of N₂O:

$$5,54 \text{ kg } N_2 O / T HNO_3 \text{ x } 325.000 \text{ } T / \text{ year} \approx$$
 1.800.000 kg N₂O

Annual emission of CO₂ equivalent:

$$1.800T N_2O/year \times 310 \approx$$
 558.000 T CO_{2 eq.}

Annex II Analysis of gas samples (indicative measurement)

Gas samples from the tail gas have transported to Denmark and have been analysed by the Danish company Analytech ApS, with the following results:



Bogi osmindevej 21 - 9400 Nørresundby Tif, 98 19 39 00 - Fax 98 19 39 70 lab@analytech.dk - www.analytech.dk

Report 247 C

Report of analysis - Emission

Results of analysis

	_		-
N ₂ O ppm	670	1200	< 100

The analysis have been performed at a temperature at 25 ° C.

Methods

Parameter	Principle	Limit of detection	Uncertainty of analysis
N ₂ 0	; IR	100 ppm	10 %
Receipt of sample:	26 th march 2004.		. 1
Type of sample:	2 x 3 airsamples in PVF-bags.		
Period of analysis:	29 th march 2004.		

AnalyTech Miljølaboratorium ApS Bøglidsmindevej 21 DK-9400 Nørresundby

my linderen

Jacob Bang-Andersen department manager



Bøgildsmindevej 21 - 9400 Nørresundby Tif, 98 19 39 00 - Fax 98 19 39 70 lab@analytech.dk - www.analytech.dk

Report of analysis - Emission

Report 247 D

Results of analysis

Parameter	Unit	Agro B	Neo before A	Neo after A
02	vol%	6,8	5,7	5.0
N ₂	vol%	93	94	95

The analysis have been performed at a temperature at 25 ° C.

Methods

Parameter	Principle	Limit of detection	Uncertainty of analysis
02	GC	0,1 vol%	10 %
N ₂	GC	0.1 vol%	10 %

Receipt of sample: Type of sample: Period of analysis: 26th march 2004. 2 x 3 airsamples in PVF-bags. 29th march 2004.

AnalyTech Miljølaboratorium ApS Bøglidsmindevej 21 DK-9400 Nørresundby

Menneg- Murdenson

Jacob Bang-Andersen department manager

Calculation of actual N2O concentration in tail gas

The actual concentration of N_2O has been calculated for the gas samples from the tail gas.

The tail gas has an O_2 concentration of 2,8% while the gas sample has an O_2 concentration of 6,8%. This means that some atmospheric air has infiltrated the sample (which is normal).

The actual N_2O concentration in the tail gas is obtained by the following equation:

$$C_{N20 tail gasl} = C_{N20 measured} x \left(1 + \frac{C_{O2 measured} - C_{O2 tail gas}}{C_{O2 atm} - C_{O2 measured}} \right)$$

Where

$C_{N2O \ tail \ gas}$	ppm	N ₂ O concentration in tail gas
C _{N2O measured}	670 ppm	N_2O concentration in sample
C _{O2 measured}	6,8%	O ₂ concentration in sample
C _{O2 tail gas}	2,8%	O ₂ concentration in tail gas
C _{O2 atm}	20,9%	O ₂ concentration in atmosphere

Calculation of actual N₂O concentration:

$$C_{N2Otail\,gasl} = 670 \, ppm \, x \left(1 + \frac{0,068 - 0,028}{0,209 - 0,028} \right) \approx$$
 860 ppm

<u>Note</u>: The actual N_2O concentration is indicative, and will be verified by online measurements in June 2004.

Annex III Net emission reduction

The emission reduction is based on actual production, and calculations are done in accordance with the French standard BP X 30-331 "Protocol for quantification for nitrous oxide emissions in the manufacture of nitric acid".

Key data from the nitric acid plant

The plant is expected to produce nitric acid without changes in capacity, method etc. The expected annual production of 100% HNO_3 is 325.000 tons per year. The only change, in the future, is the concentration of N_2O . The average concentration of N_2O is assumed to be 250 ppm vol, which will be monitored by actual measurements.

The production is expected to have the following key figures:

Production of 100% $HNO_3 (P_{HNO3})^{1}$:	47,1 T/h
Flow rate of tail gas $(Q_S)^{1}$:	148.500 Nm³/h
O_2 concentration in tail gas $(C_{O2})^{1}$:	2,8%
N_2O concentration in the tail gas ($C_{N2O})\ ^2$:	250 ppm
Temperature of the tail gas $(T_{gas})^{1}$:	20° C
Pressure of tail gas ¹	1,08 mbar abs.

- ¹ Informed by Agropolychim
- ² Expected average concentration during campaign

Calculation of emissions:

The N_2O emission is obtained by the following equation:

$$Q_{N20} = \frac{C_{N20} x Q_S x \ 44}{V_M} x 10^{-6}$$

Where

Q _{N2O}	kg/h	N ₂ O emission
C _{N2O}	ppm	N ₂ O concentration in tail gas
Qs	Nm³/h	Output air flow (tail gas)
V _M	22,4 l/mol	Molar volume N ₂ O (normal conditions)

$$Q_{N20} = \frac{250 \ x \ 148.500 \ x \ 44}{22.4} \ x \ 10^{-6} \approx$$
 73 kg/h

The average N_2O generation factor is obtained by the following equation:

$$F_{N2O} = \frac{Q_{N2O}}{P_{N2O}}$$

Where

F _{N2O}	kg/T	N_2O emission in kg per ton of 100% HNO ₃ produced
Q_{N2O}	kg/h	N ₂ O emission
P _{N2O}	T/h	Production of 100% HNO ₃

$$F_{N20} = \frac{73}{47,1} \approx 1,5 \text{ kg } N_2 O/T \text{ HNO}_3$$

Annual emission of N₂O:

 $1.5 kg N_2 O/T HNO_3 x 325.000 T/year \approx$ 490.000 kg N₂O

Annual emission of CO₂ equivalent:

$$490T N_2O/year \ x \ 310 \approx 155.000 \ T \ CO_{2 \ eq.}$$

Annual emission reduction:	<u>403.000 T CO_{2 eq}</u>
JI situation	<u>155.000 T CO₂ eq.</u>
Present situation	558.000 T CO _{2 eq.}
Annual reduction of emission of CO_2 equivalent:	

Annex IV Monitoring Plan – Emissions of N₂O

Agropolychim

Nitric acid plant, Grande Paroisse

Week	Production of 100% HNO ₃	N_2O emission	Emission factor	Emission factor	Emission reduction N ₂ O	Emission reduction CO ₂
	ton	Ka	actual	baseline	Ka	Ton
		Kġ	Kg/ton	Kg/ton	Ny	1011
1	7.900	11.850	1,50	5,54	31.916	9.894
2						
3						
4						
5						
6						
49						
50						
51						
52						
Total	7.900	11.850	1,50	5,54	31.916	9.894

Table 16 Key results from Monitoring Plan (example)