

MAYA STEFANOVA¹, ROZALINA CHUTURKOVA¹

CATALYTIC REDUCTION OF NITROUS OXIDE AT A NITRIC ACID PLANT IN BULGARIA

A nitric acid plant in Devnya, Bulgaria has implemented a project for catalytic decomposition of nitrous oxide which resulted in reducing N₂O emissions from the plant and the overall N₂O emissions from the industrial sector in Bulgaria. After implementing the catalyst in September 2005 till the end of 2011, a total amount of 3133 Mg N₂O emissions has been measured while the supposed value of N₂O emissions without the catalyst being installed would have been 9747 Mg which means a total reduction of 6614 Mg. The results from the research prove the emission reduction potential of the catalyst.

1. INTRODUCTION

Nitrous oxide N₂O is a greenhouse gas under the Kyoto Protocol [1] along with three other gases (carbon dioxide CO₂, methane CH₄, sulphur hexafluoride SF₆) and two groups of gases (hydrofluorocarbons HFCs and perfluorocarbons PFCs). Nitrous oxide has a global warming potential of 310 times that of CO₂ and is considered to be one of the main reasons for the global warming effect.

Nitrous oxide emissions are released from a very large variety of sources with significant technical and economic differences. According to the European Community, *The Greenhouse Gas Inventory 1990–2002* [2], the dominant source is agriculture, in particular emissions from soils. Other important sources are transport and industrial processes. Chemical industry involving technological processes for the production of nitric acid, adipic acid, ammonia, urea and ammonium nitrate based fertilizers is responsible for nitrous oxide emissions into the atmosphere [3]. According to some authors [3, 4] nitrous oxide emissions from fuel combustion may increase significantly thus becoming the biggest anthropogenic source of N₂O emissions into the atmos-

¹Department of Ecology and Environmental Protection, Technical University Varna, Studentska 1, 9010 Varna, Bulgaria, corresponding author M. Stefanova, e-mail: mds78@abv.bg

phere. The production of nitric acid has a high N_2O emission potential that makes it the main industrial source of nitrous oxide emissions [5]. Various types of measures are developed in the nitric acid industry to reduce nitrous oxide emissions [6–10]:

- Primary measures: measures that affect the formation of nitrous oxide during the catalytic oxidisation of ammonia like modifying the geometry of the platinum catalysts which can lead to a higher conversion of ammonia to NO and/or a reduction in the formation of N_2O and the use of a non-platinum catalyst as a second step.

- Secondary measures: measures taken with regard to the process gas stream, produced in the process from the oxidisation catalyst, to the absorption tower (homogeneous decomposition, high temperature catalytic decomposition).

- Tertiary measures: measures that can be taken in the process occurring between the absorption tower and the expansion turbine (low temperature catalytic decomposition, selective catalytic reduction with hydrocarbons, non selective catalytic reduction of NO_x with simultaneous N_2O reduction).

- Sequential (end-of-pipe) techniques: some of the techniques described as tertiary measures can also be placed behind the expansion turbine (selective catalytic reduction, catalytic decomposition).

There are almost 500 nitric acid plants in the world. Attempts have been made to implement the above nitrous oxide reducing techniques at several nitric acid plants around the world.

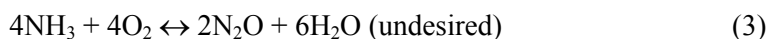
A pilot project for nitrous oxide reduction throughout the use of a non-platinum secondary catalyst was developed and implemented under the *Joint Implementation* mechanism between Denmark and Bulgaria. The project is among the first of its kind in Europe. It was set into operation at a nitric acid plant in Devnya, Bulgaria in September 2005. The N_2O emissions are reduced by introducing a secondary catalyst that converts nitrous oxide into oxygen and nitrogen, which have zero global warming potentials. The project is considered to be an implementation of the obligations of Bulgaria and Europe to the *Kyoto Protocol* and the *United Nations Framework Convention on Climate Change* [11].

The most significant source of N_2O emissions into the atmosphere in Bulgaria for the period 2000–2011 is agriculture (154.55 Gg N_2O), followed by industrial processes (23.25 Gg N_2O) while fuel combustion is on the third position (11.57 Gg N_2O) [12]. Although chemical processes for the production of ammonia, urea and ammonium nitrate based fertilizers have significant nitrous oxide emission indicators [3] the UNFCCC N_2O source sector *2B Industrial processes* includes only technological processes for production of nitric and adipic acids [5, 11]. There is no plant for adipic acid production in Bulgaria but there are two nitric acid plants operating in the country for the period. One of the plants is located in Dimitrovgrad in South Bulgaria and the other one in Devnya, near the city of Varna, in North East Bulgaria. The nitric acid plant in Dimitrovgrad has not been applying any emission abatement measures while the plant in Devnya has implemented a secondary catalyst for high temperature de-

composition of N₂O in the reactor chamber thus becoming a suitable object for studying the effect of the catalyst upon reducing N₂O emissions. The aim of the present research is to explore the effectiveness of the catalyst and its potential emission reduction by comparing N₂O emission levels before and after installing the catalyst.

2. EXPERIMENTAL

The Nitric Acid Plant in Devnya is based on the Ostwald process and uses 3 basic chemical operations [13, 14]. The production of nitric acid involves catalytic combustion of ammonia NH₃ to nitric oxide NO (Eq. (1)). Nitrous oxide N₂O and nitrogen N₂ are formed as undesirable by-products (Eqs. (2) and (3)). The amount of N₂O produced mainly depends on the temperature and residence time in the reactor, since N₂O is unstable at higher temperatures (1123–1223 K). Subsequently, the oxidation of nitric oxide NO into nitrogen dioxide NO₂ takes place (Eq. (4)). Final step of the process is the absorption of nitrogen dioxide NO₂ in water to produce nitric acid HNO₃ (Eq. (5)).



The Nitric Acid Plant is a French made dual pressure plant [15]. Basic key information of the plant is summarized in Table 1.

The choice of the reduction measures depends on the plant characteristics and technical requirements. The catalytic reduction of N₂O in the reactor chamber at high temperature is proven to be very efficient at dual pressure plants; in atmospheric pressure plants the extra pressure drop in the reactor reduces the plant capacity [13]. Another advantage of the method results from the fact that the burners are fitted with a basket filled with Raschig rings giving structural support to the gauzes, and the De-N₂O catalyst can be introduced by partial replacement of the Raschig rings. Hence, no modification of the basket is required and the gauze pack can be installed as usual.

Table 1

Key information for the plant

Parameter	Details	
Capacity	1100 Mg of nitric acid per day 100 vol. % 363 000 Mg of nitric acid per year 100 vol. %	
Oxidation	4 burners pressure for catalytic oxidation – 350 000 Pa oxidation temperature – 1108 K gauzes are knitted burner diameter – 4.254 m basket diameter is 4.254 m	
Absorption	pressure in absorption column – 1 280 000 Pa absorption temperature – 293–313 K	
Tail gas	NO _x concentration – approximately 170–200 ppmv temperature – 293 K flow rate – 148 500 m ³ /h	
	N ₂ O concentration before installing the catalyst 860 ppmv (average)	N ₂ O concentration after installing the catalyst 180 ppmv (average)

The catalytic reduction of N₂O emissions is applied at the nitric acid plant in September 2005 by introducing a new catalyst bed, which is installed directly under the platinum gauze in the reactors as shown in Fig. 1.

The N₂O reduction catalyst is made of precious metal coated ceramic pellets. Each pellet consists of 20% CuO, 16% ZnO and Al₂O₃ plus promoters. The catalyst is installed directly on top of the support grid of the reactors separated on top and bottom by steel screens. All segments are sewn together to avoid gas bypass. The catalyst is installed in the shape of a layer of various steel segments filled with ceramic pellets equally disturbed. The thickness of the catalytic layer in the basket is approximately 28 mm. The pressure drop over the catalyst is not significant and is normally less than 250 Pa [15].

The technology is owned and patented by a leading German company. The catalyst does not have any effects on the present production (no yield loss). The lifetime of the catalyst is expected to be no longer than 3 production work cycles of 320 days each. In case its performance throughout this period is not satisfactory it can be replaced at the next possible shutdown of the plant. In fact the catalyst has been replaced once for the entire monitored period during operational shut down of the plant in 2009. The catalyst's behaviour during the production work cycle of the plant and its dependence on the technological parameters of the process are a subject of further scientific research.

Only N₂O emissions from the Nitric Acid Plant are affected by the catalyst. The catalyst does not have any impact related to the energy consumption or generation, raw material consumption, waste water formation and emissions other than N₂O. The

formation of N_2O is unavoidable, since the NO yield is limited but the catalyst technology has proved positive effect on the environment by reducing N_2O emissions significantly.

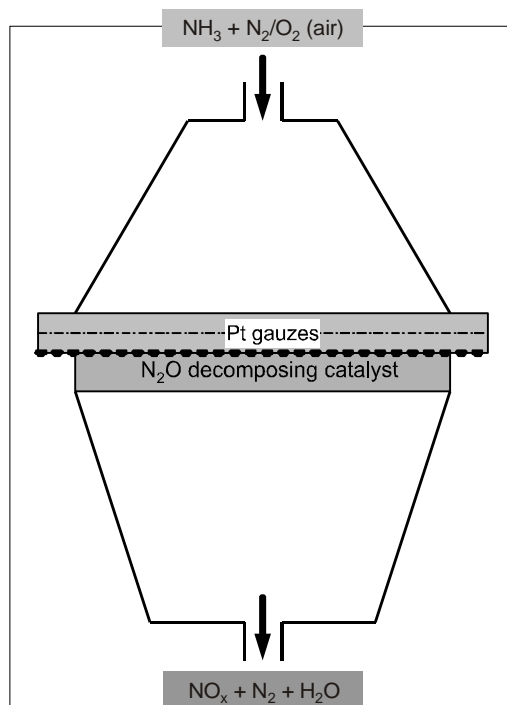


Fig. 1. Catalytic decomposition technology for N_2O emission reduction

Nitrous oxide emissions from the plant have been monitored for a twelve years period from 2000 to 2011. The nitrous oxide emissions from the plant before introducing the catalyst are calculated based on the annual production of nitric acid in Mg multiplied by the experimentally determined baseline emission factor 5.54 kg N_2O per Mg HNO_3 produced [15].

The nitrous oxide emissions from the plant after implementing the catalyst are monitored based on the on-line measurement of the tail gas parameters (N_2O concentration, tail gas flow, temperature, absolute pressure and oxygen concentration of the tail gas) and the production flow parameters. The N_2O concentration in the tail gas is measured directly in ppmv. The monitoring plan 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* [16]. The monitoring method reflects good practice and is in line with the approved monitoring methods for the *Clean Development Mechanism* [11].

Reduction of the N_2O emission is calculated as the difference between the baseline emission factor and the actual emission factor multiplied by the actual nitric acid production [15].

The results of the research are presented as N_2O emissions in Mg. They are also calculated as Mg CO_2 equivalent as the actual N_2O emissions in Mg are multiplied by N_2O global warming potential (310 times that of CO_2) [17].

3. RESULTS AND DISCUSSION

The quantity of N_2O emission from the plant before implementation of the catalyst is presented in Table 2. It was calculated based on the annual production of nitric acid in Mg multiplied by the experimentally determined baseline emission factor (5.54 kg N_2O per Mg HNO_3 produced).

Table 2

Quantity of N_2O emissions for the period January 2000–September 2005 [Mg/year]

Year	Production of nitric acid measured	Emission of N_2O calculated	Annual emission of CO_2 equivalent calculated
2000	338 511	1875	581 359
2001	325 728	1805	559 405
2002	250 312	1387	429 886
2003	223 815	1240	384 380
2004	325 892	1805	559 687
2005	165 220	915	283 749
Total		9027	2 798 466

Data on reduction of actual emission for the period from September 2005 when the catalyst has been installed till the end of 2011 is summarised in Table 3. Calculations about the quantity of actual emissions and emission reduction as CO_2 equivalent for the period September 2005–December 2011 are presented in Table 4.

The monitoring data has been analysed and the results show that from the beginning of 2000 till September 2005 when the catalyst has been installed total N_2O emissions are equal to 9027 Mg. For the period from September 2005 to the end of 2011 total N_2O emissions are 3133 Mg while the supposed N_2O emissions without the catalyst being installed would have been 9747 Mg which makes a total reduction of 6614 Mg N_2O .

A significant reduction of N_2O emissions has been accomplished. Although reduction of the actual emission depends on the annual production of nitric acid the collected data shows that N_2O emissions have been reduced from 1875 Mg in 2000 (annual production of nitric acid 338 511 Mg) to 508 Mg in 2011 (annual production of nitric acid 337 597 Mg) which makes a total N_2O reduction of emission of almost 73%.

Comparison is made based on almost equal quantities of annual production of nitric acid in the years 2000 and 2011 so that the percentage of the actual reduction can be calculated correctly. The lowest levels of N₂O emissions are measured in 2006 – 334 Mg which corresponds to the lowest level of annual nitric acid production – 226 012 Mg.

Table 3

Specifications of N₂O emission and reduction of N₂O emission for the period September 2005–December 2011 [Mg/year]

Year	Production of nitric acid measured	Actual emission of N ₂ O measured	Reduction of N ₂ O emission calculated	Supposed N ₂ O emission with no catalyst installed calculated
2005	100 959	92	468	560
2006	226 012	334	919	1253
2007	342 054	687	1208	1895
2008	266 491	626	850	1476
2009	208 856	547	610	1157
2010	277 366	339	1197	1536
2011	337 597	508	1362	1870
Total		3 133	6 614	9747

Table 4

Specifications of actual emissions and its reduction as CO₂ equivalent for the period September 2005–December 2011 [Mg/year]

Year	Production of nitric acid measured	Actual emission CO ₂ equivalent calculated	Emission reduction CO ₂ equivalent calculated	Supposed CO ₂ equivalent with no catalyst installed calculated
2005	100 959	28 400	144 987	173 387
2006	226 012	103 411	284 742	388 153
2007	342 054	212 835	374 608	587 443
2008	266 491	194 083	263 589	457 672
2009	208 856	169 507	189 183	358 690
2010	277 366	105 205	371 144	476 349
2011	337 597	157 691	422 098	579 789
Total		971 132	2 050 351	3 021 483

In Figure 2, N₂O emission levels have been compared before and after installation of the catalyst as well as the actually measured N₂O emissions after the project took part with the calculated values for supposed N₂O emission levels after September 2005 if the catalyst would have not been installed.

If the catalyst was not installed, the N₂O emission levels would have been significant and even higher than the emission levels before the project took part. The highest

value would have been measured in 2007 – 1895 Mg N₂O (annual production of nitric acid 342 054 Mg) while the actually measured emission is 687 Mg N₂O which makes a total reduction of 1208 Mg N₂O (almost 64% reduction has been achieved).

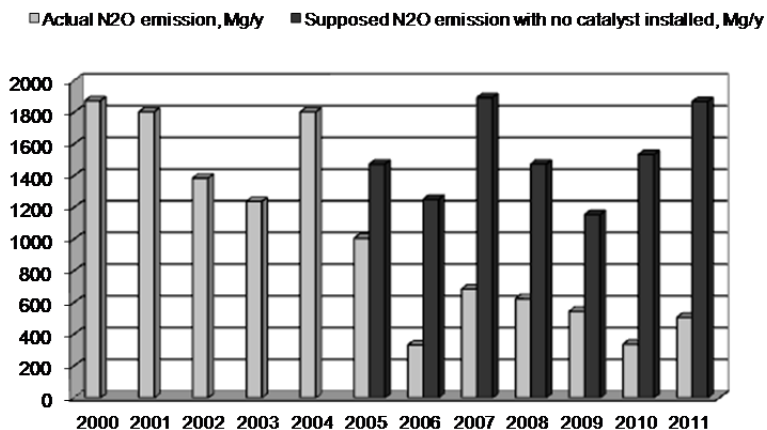


Fig. 2. Annual N₂O emission levels with and without the catalyst being installed

Representing N₂O emissions as CO₂ equivalent shows that for the period January 2000–September 2005 calculated total emissions are 2 798 466 Mg CO₂ equivalent. For the period from September 2005 to the end of 2011 calculated total emissions are 971 132 Mg CO₂ equivalent while the supposed emissions without the catalyst being installed would have been 3 021 483 Mg CO₂ equivalent which makes the total reduction of 2 050 351 Mg CO₂ equivalent.

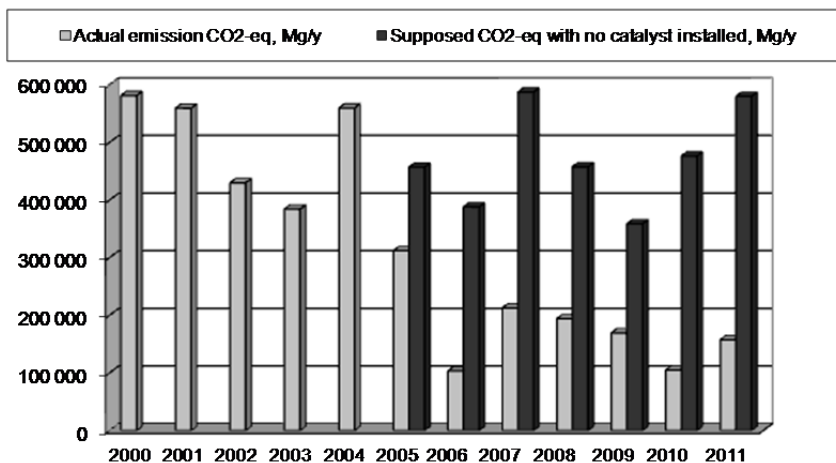


Fig. 3. Annual emission levels as CO₂ equivalent with and without the catalyst being installed

Obviously the project resulted in significant reduction of emission. The highest value for CO₂ equivalent was recorded in 2000 – 581 359 Mg CO₂ equivalent while the lowest level was recorded in 2006 almost immediately after the start of the project – 103 411 Mg CO₂ equivalent.

In Figure 3, emission levels as CO₂ equivalents have been compared: before and after the installation of the catalyst, and the calculated values for supposed CO₂ equivalent emission levels after September 2005 if the catalyst was not installed.

Figure 3 proves significant reduction of emission resulting from the catalytic decomposition. As is seen, if the catalyst was not installed, the emission levels would have been even higher than the emission levels before the project took part. The highest value would have been measured in 2007 – 587 443 Mg CO₂ equivalent while the actually measured emission is 212 835 Mg CO₂ equivalent which is almost 2.8 times lower.

The total amount of N₂O emissions from the Nitric Acid Plant for the period 2000–2005 is 9.119 Gg which is 59% of the whole N₂O emissions released from industrial processes and lower than 9% of the whole N₂O emissions released from all the sources in Bulgaria for that period (agriculture, chemical industry, fuel combustion and transport) [12]. For the period 2006–2011, the total N₂O emissions from the Nitric Acid Plant is 3.041 Gg which is 38.5% of the whole N₂O emissions released from industrial processes and almost 3% of the whole N₂O emissions released from all the sources in the country for that period [12].

4. CONCLUSIONS

A significant reduction of N₂O emissions at the Nitric Acid Plant has been accomplished due to the catalytic decomposition throughout the use of a secondary non-platinum catalyst. Data analysis shows that after implementing the catalyst in September 2005 till the end of 2011 total measured N₂O emissions are 3133 Mg while the supposed N₂O emissions without the catalyst being installed would have been 9747 Mg which makes a total reduction of 6614 Mg N₂O. The implementation of the secondary non-platinum catalyst in the reactor has proved to have a significant effect on reducing the N₂O emissions into the atmosphere from the Nitric Acid Plant and the overall N₂O emissions from the industrial sector in Bulgaria. The reduction of nitrous oxide has a positive effect upon global warming prevention as N₂O is a greenhouse gas under the *Kyoto Protocol*.

As permitted in the *Framework Convention on Climate Change the Nitrous Oxide Reduction Project* is conducted under joint implementation for simultaneous achievement of the obligations for reduction of greenhouse gases emission of both the countries involved – Bulgaria and Denmark. The project results in carbon credit sales

whereas emission reduction units are being transferred to the government buyer according to Memorandum of Understanding.

Bulgaria has signed the *Framework Convention on Climate Change* (ratified in 1995) and the *Kyoto Protocol* with 1988 as a base year. The *Nitrous Oxide Reduction Project at the Nitric Acid Plant* is considered to be an implementation of the obligation of Bulgaria and Europe to the Convention and an activity under Article 6 of the *Kyoto Protocol* for reducing the greenhouse gases emissions. The project is a preparative step for Bulgaria to comply with the eligibility requirements as stated in the Marrakech Accords of the Protocol.

Since the investment has no effect on production, no direct income is generated from the Project. Income is generated through carbon credit sales to Denmark (through an agreement with the Danish Ministry of the Environment). The Republic of Bulgaria as a Supplier and the Kingdom of Denmark as a Government-buyer of emission reduction units have signed *Memorandum of Understanding* for activities under Article 6 of the *Kyoto Protocol*. From the start of the *Nitrous Oxide Reduction Project* in September 2005 till the end of 2011, a total amount of 2050351 emission reduction units has been transferred to Denmark according to the Memorandum. All revenues from carbon credit sale are invested in environmental friendly projects and technologies at the Plant.

Catalytic reduction of N_2O emissions is considered an environmentally safe technology and does not affect the plant operation, neither in form of constraints nor capacity increase. Since the technology does not affect the production, no direct environmental impacts are expected. Indirectly the catalyst's implementation improves the quality of atmospheric air in the area and leads to nitrogen containment decrease in the surrounding soil.

From 1 January 2013 onwards the N_2O emissions from nitric acid production are included in the scope of the *European Union Emission Trading Scheme* [18] thus obliging all the European nitric acid plant operators to apply measures for reducing the overall N_2O emissions. The scientific analysis of the results of the research shows that the catalytic decomposition of N_2O is proved to be an emission abatement technology as its implementation is an action carried out to reduce the emission of greenhouse gases. The results of the project are expected to give a valuable contribution to the setting of new international standards for reduction of N_2O emissions from the production of nitric acid. The project is open to further scientific research in order to determine the most effective technological and constructional options for reducing N_2O emissions.

REFERENCES

- [1] *Kyoto Protocol to the United Nations Framework Convention on Climate Change*, United Nations, 1998.
- [2] BEHREND H., JOL A., BARKMAN A., GUGELE B., HUTTUNEN K., RITTER M., *Annual European Community Greenhouse Gas Inventory 1990–2002 and Inventory Report 2004*, EEA Technical Report, 2, 2004, European Environment Agency, Copenhagen 2004.

- [3] KUROPKA J., *Nitrous oxide emission – potential danger, balance and reduction possibilities*, Environ. Prot. Eng., 2006, 32 (3), 81.
- [4] LECKNER B., KARSSON M., *Influence of additives on selective non-catalytic reduction of NO with NH₃ in circulating fluidized bed boilers*, Ind. Eng. Chem. Res., 1991, 30 (11), 2396.
- [5] WINIWARTER W., AMANN M., *The GAINS Model for Greenhouse Gases. Version 1.0: Nitrous Oxide*, International Institute for Applied Systems Analysis, Interim Report IR-05-55, Laxenburg, Austria, 2005.
- [6] Agency for Energy and the Environment, *Reduction of Nitrous Oxide in the Nitric Acid Industry*, Novem, Utrecht, The Netherlands, 2001.
- [7] *Spatial Planning and the Environment, Directorate for Climate Change and Industry, Reduction of Nitrous Oxide in the Nitric Acid Industry*, Department of Industry, Ministry of Housing, Infomil, The Hague, The Netherlands, 2001.
- [8] PEREZ-RAMIREZ J., KAPTEUN F., SCHOFFEL K., MOULUN J., *Formation and control of N₂O in nitric acid production. Where do we stand today?*, Appl. Catal. B-Environ., 2003, 44, 117.
- [9] SKALSKI A., *Reduction of N₂O Emission from Nitric Acid Plants*. Proceedings of the II International Scientific Conference *Air Protection in Theory and Applications*, TT. Suchecki, J. Kapala, H. Kumazawa. (Eds.), Institute of Environmental Engineering of the Polish Academy of Sciences, Zabrze 1998, 157–158.
- [10] BASIŃSKA A., MACHEJ T., MATACHOWSKI L., SCHROEDER G., DOMKA F., *Catalytic decomposition of N₂O on Ru/Fe₂O₃ catalysts*, Arch. Environ. Prot., 1999, 25 (2), 91.
- [11] *United Nations Framework Convention on Climate Change*, United Nations, 1992.
- [12] *Bulgaria's National Inventory Report for Greenhouse Gas Emissions*, Republic of Bulgaria, Ministry of Environment and Water, Executive Environment Agency, Submission Under UNFCCC and the Kyoto Protocol, May 2013.
- [13] *Integrated Pollution Prevention and Control, Reference Document on BAT for the Manufacture of Large Volume Inorganic Chemicals – Ammonia, Acids and Fertilizers*, European Commission, 2007.
- [14] *Spatial Planning and the Environment, Dutch Notes on BAT for the Production of Nitric Acid*, Ministry of Housing, Infomil, The Hague, The Netherlands, 1999.
- [15] *Nitrous Oxide Reduction at Agropolychim Fertilizer Plant*, Ministry of Environment and Energy, Danish Cooperation for Environment in Eastern Europe, Joint Implementation Project Design Documentation, DEPA File M124/000-0043t, 2004.
- [16] French Standardization, BP X 30-331, *Protocol for quantification for nitrous oxide emissions in the manufacture of nitric acid*, 1999.
- [17] HOUGHTON J.T., JENKINS G.J., EPHRAUMS J.J., *Climate Change, The IPCC Scientific Assessment*, Cambridge University Press, Cambridge 1990.
- [18] *Directive 2003/87/EC of the European Parliament and of the Council of 13 October 2003 Establishing a scheme for Greenhouse Gas Emission Allowance Trading within the Community and Amending Council Directive 96/61/EC*, OB L 275, 25.10.2003, Brussels 2003, 32.