

## Nitrous Oxide Emissions from Waste Incineration

<sup>a</sup>K. SVOBODA, <sup>b</sup>D. BAXTER, and <sup>c</sup>J. MARTINEC

<sup>a</sup>*Institute of Chemical Process Fundamentals, Academy of Sciences of the Czech Republic,  
CZ-165 02 Prague, Czech Republic  
e-mail: svoboda@icpf.cas.cz*

<sup>b</sup>*European Commission, Joint Research Center, Institute for Energy, NL-1755 ZG Petten, The Netherlands  
e-mail: david.baxter@jrc.nl*

<sup>c</sup>*Department of Thermal and Nuclear Power Plants, Faculty of Mechanical Engineering,  
Brno University of Technology, CZ-616 69 Brno, Czech Republic*

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EU energy and environmental policy in waste management leads to increasing interest in developing methods for waste disposal with minimum emissions of greenhouse gases and minimum environmental impacts.

From the point of view of nitrous oxide (N<sub>2</sub>O) emissions, waste incineration and waste co-combustion is very acceptable method of waste disposal. Two factors are important for attaining very low N<sub>2</sub>O emissions from waste incineration, particularly for waste with higher nitrogen content (*e.g.* sewage sludge, leather, *etc.*): temperature of incineration over 900°C and avoiding selective noncatalytic reduction (SNCR) de-NO<sub>x</sub> method based on urea. For reduction of N<sub>2</sub>O emissions retrofitting such plants to ammonia-based SNCR is recommendable. The modern selective catalytic reduction facilities for de-NO<sub>x</sub> at waste incineration plants are only negligible source of N<sub>2</sub>O.

Nitrous oxide is a greenhouse gas with a global warming potential approximately 300 times higher than CO<sub>2</sub>. Being chemically inert in the troposphere with a long lifetime (110–150 years), N<sub>2</sub>O can reach the stratosphere where it is destroyed by photolysis forming NO, one of the species contributing to ozone depletion. N<sub>2</sub>O contribution to global warming from anthropogenic sources is estimated to be around 4–6 % [1, 2]. N<sub>2</sub>O appears naturally in the atmosphere. Oceans, tropic and temperate soils, are believed to be the major natural sources of N<sub>2</sub>O. Nevertheless, concentration of N<sub>2</sub>O has increased by around 13 % since pre-industrial times [2]. The global (worldwide) anthropogenic emissions [3] of N<sub>2</sub>O in 1990 (3.2 Tg nitrogen/year) account for 20 % of the estimated total N<sub>2</sub>O emissions (14.9 Tg nitrogen/year, 1 Tg = 10<sup>12</sup> g).

The share of anthropogenic emissions by sector varies according to world region and the specific economic activities. Based on various studies [3–6] the approximate contribution by sectors is as follows:

i) Agriculture and land use is the highest source of

anthropogenic N<sub>2</sub>O emissions (50–70 %);

ii) Industrial sources, mainly nitric acid and adipic acid production accounts for 15–25 %;

iii) Stationary and mobile fossil fuel combustion 15–25 %.

Waste treatment and disposal is mentioned in the previous inventories as a relatively less significant anthropogenic source of N<sub>2</sub>O. Main activities with potential N<sub>2</sub>O emissions are waste water treatment, sewage sludge incineration, municipal solid waste incineration, biomass combustion for energy production, incineration of waste-based fuels with high content of nitrogen, *etc.* Quantification of their contribution to the anthropogenic N<sub>2</sub>O emissions is still difficult because they remain uncharacterized.

### *Agriculture and land use*

N<sub>2</sub>O is formed in agricultural soils mainly by the microbial process of nitrification and denitrification. These processes are enhanced by an increase of available nitrogen in soils through N-fertilization, manure application, atmospheric deposition, *etc.* Food needs

in the coming years are expected to boost N-fertilizer application and in turn to accelerate the N<sub>2</sub>O accumulation in the atmosphere [7].

Biomass burning is another source of N<sub>2</sub>O, both during the fire and by increasing soil N<sub>2</sub>O emissions through stimulation of N-mineralization. Thus, the conversion of tropical forest to agricultural land and biomass burning in tropical areas have a great impact on global N<sub>2</sub>O emissions [8]. Burning is also used to rejuvenate old pasture. It is estimated that 40 % of all savannahs are burned each year.

#### *Fossil fuel combustion*

Production of N<sub>2</sub>O from fossil fuel combustion is associated with the oxidation of the fuel-nitrogen. It is well known that N<sub>2</sub>O is formed by two different pathways, *i.e.* through gas phase reaction of nitrogenous groups in the volatiles (HCN) and also through the heterogeneously catalyzed oxidation of the char-bound nitrogen species.

N<sub>2</sub>O emissions are highly temperature-sensitive, so that N<sub>2</sub>O level in flue gas increases when temperature decreases [9, 10]. In line with this, high-temperature pulverized coal combustion technologies produce negligible N<sub>2</sub>O emissions (below 5 vol. ppm), while lower-temperature fluidized bed combustion can produce relatively high N<sub>2</sub>O emissions, even as high as 200 vol. ppm. In addition, it is known that NO<sub>x</sub> control procedures can lead to elevation of N<sub>2</sub>O emissions as a side effect.

Fossil fuel combustion in vehicles is another important source of N<sub>2</sub>O. It is generally accepted that cars fitted with a "first generation" three-way catalyst (TWC) for NO<sub>x</sub> abatement emit more N<sub>2</sub>O than old vehicles without catalyst. Measurements on vehicles with fuel economies of 6–12 l/100 km [11] have shown the N<sub>2</sub>O emission rate of 5–11 mg/km. It appears that N<sub>2</sub>O emissions are mostly formed during the light-off phase, when the catalyst is warming up. If the catalyst degrades (due to ageing), then the length of the light-off phase could be extended and the period over which N<sub>2</sub>O is emitted [12] is longer. Increase of N<sub>2</sub>O emissions from deactivated catalysts is due to a deterioration of the catalyst activity to decompose N<sub>2</sub>O rather than an increase in catalyst activity in converting NO to N<sub>2</sub>O [13].

#### *Waste treatment and disposal*

Waste treatment and disposal activities are believed to be a noticeable source of N<sub>2</sub>O. However, very little work on their characterization has been reported so far. This makes difficult any assessment of the waste management options in terms of N<sub>2</sub>O emissions.

Thermal treatment of solid waste materials achieves a reduction of waste volume while producing heat and/or power. Municipal solid waste (MSW) is one of the main waste streams in terms of mass. N<sub>2</sub>O emissions from MSW incinerators vary according to the

combustion temperature, as for coal combustion [14]. However, due to the generally low nitrogen content in the MSW, the emissions rarely exceed 20 vol. ppm in any incineration technology (*e.g.* grate technology, fluidized bed, rotary kilns). On the other hand, N<sub>2</sub>O emissions can be enhanced when NO<sub>x</sub> abatement techniques are used.

Another type of solid waste with increasing mass production is sewage sludge. Thermal treatment (combustion) of this waste is reported to lead to very high N<sub>2</sub>O emissions, reaching 350 vol. ppm [15] at lower temperatures of combustion. Thermal treatment of other wastes with high nitrogen content, such as waste leather, meat and bone meal (MBM), plastics, *etc.* could lead to punctual high emissions of N<sub>2</sub>O. Therefore an assessment of N<sub>2</sub>O emission from these processes is necessary before disposal of such waste by incineration is selected. Alternatively, abatement methods have to be identified and set in place.

N<sub>2</sub>O emission from waste biomass combustion (agricultural residues, waste wood, demolition waste, *etc.*) is also dependent on combustion temperature and nitrogen content of the fuel. In principle, the emissions are lower than in coal combustion due to lower nitrogen content in waste biomass (0.12–0.60 mass % (waf basis) compared to 1–2 mass % in coals). However, there are some exceptions of waste biomass, like malt waste (4.99 mass % (waf)), coffee husks (1.6 mass % (waf)), with high nitrogen content.

As regards other waste management options, it can be mentioned that composting of organic household waste produces low N<sub>2</sub>O emissions. *He et al.* [16] measured N<sub>2</sub>O emissions from aerated composting and detected a small peak of N<sub>2</sub>O (< 10 vol. ppm) during the first day of treatment. *Beck-Friis et al.* [17] concluded that more than 98 % of the nitrogen emissions are NH<sub>3</sub>-related and less than 2 % are N<sub>2</sub>O-related. Limited information has been found concerning N<sub>2</sub>O emissions from waste landfills. Landfill leachate can be [18] a source of N<sub>2</sub>O when it is recirculated to the landfill. The same risk can arise when leachate is used for the production of compost.

The purpose of this work is to collect comprehensive information concerning N<sub>2</sub>O emissions from thermal treatment processes of various organic waste materials: incineration and co-incineration of waste, including municipal solid waste, sewage sludge, nitrogen-containing waste, and waste biomass. The knowledge gathered is useful to reduce uncertainties inherent to the current N<sub>2</sub>O inventories. In addition, it is essential to assess the potential need of abatement measures to limit N<sub>2</sub>O emissions in future operation of waste incineration plants.

### **N<sub>2</sub>O Emissions from MSW Incineration**

Municipal solid waste (MSW) is relatively complicated heterogeneous mixture of combustible and in-

**Table 1.** Comparison of Municipal Solid Waste Composition from Thailand and UK [19]

Component	Thailand	UK
$w(\text{Paper})/\%$	13	31
$w(\text{Food waste})/\%$	39	25
$w(\text{Textiles, rubber, leather, and wood})/\%$	23	5
$w(\text{Plastics})/\%$	10	8
$w(\text{Metals})/\%$		8
$w(\text{Glass})/\%$	15	10
$w(\text{Other})/\%$		13
$w(\text{Ash} - \text{raw})/\%$	13.4	22.3
$w(\text{Moisture} - \text{raw})/\%$	58.4	32.4
HHV - raw/(MJ kg <sup>-1</sup> )	6.49	10.25
HHV - dry/(MJ kg <sup>-1</sup> )	15.59	15.17
$w_i(\text{Ultimate analyses (dry basis)})/\%$		
Combustibles	67.8	67.00
Carbon	37.14	35.81
Hydrogen	5.41	4.82
Nitrogen	0.22	0.78
Sulfur	0.09	0.41
Chlorine	0.8	0.75

combustible (inorganic) materials. The organic fraction of MSW consists of plastics, paper, textile, waste biomass (wood, plants, *etc.*), and food residues. The calorific value of the MSW is mostly dependent on two factors: organic content and moisture. The usual lower heat energy value is in the range 8–13 MJ/kg. The composition of MSW, moisture content, and heat energy value is subjected to high seasonal and regional variety [19, 20] and to long-term trends caused by various factors, *e.g.* better sorting of waste, introduction of new packaging materials. In Asian countries, the calorific value of MSW is generally lower due to the high moisture content of the food waste fraction (see Table 1). The moisture content coupled with calorific value of the MSW affects significantly the combustion process on the grate, maximum attainable local temperature, and related emissions.

Nitrogen content of the municipal solid waste is relatively low, the main sources being plastic materials (polyamides, polyurethane, *etc.*), textile (acrylonitrile, wool, *etc.*), and proteins from waste food. Typical content of nitrogen in MSW is 0.1–1 mass % (dry basis). The usual content of nitrogen in MSW [19–21] from EU countries and USA is around 0.7 mass %, dry basis. In Asian countries the content of nitrogen is usually lower.

The prevailing technology for MSW incineration in Europe and USA is grate furnace followed by post-combustion chamber with secondary air injection. Other incineration technologies like rotary kiln or fluidized bed-based technologies are still uncommon and used rather in Japan for sorted MSW. Technologies based on alternative thermal treatments for MSW (*e.g.* pyrolysis and gasification) are exception-

ally used in large scale [22]. The fuel nitrogen is under such reducing conditions converted mostly to ammonia, which can be relatively easily removed from the resulting fuel gas.

Nitrous oxide emissions in municipal solid waste incineration (MSWI) originate practically from fuel nitrogen content in MSW. The mechanisms of NO<sub>x</sub>/N<sub>2</sub>O formation and destruction in an MSW incinerator are mainly related to the operating conditions, in particular temperature, oxygen concentration, mixing of gases and catalytic effects of walls, ash particles, *etc.* The optimum temperature range for minimizing simultaneously CO, NO<sub>x</sub>, and N<sub>2</sub>O emissions is estimated to be between 850 °C and 950 °C, depending on emission requirements. Although optimization of emission is feasible, simultaneous minimization of all regulated emissions (CO, NO<sub>x</sub>, N<sub>2</sub>O, SO<sub>2</sub>, HCl, *etc.*) by applying only primary measures is in practice hardly possible.

According to measurements in 10 incineration plants in Japan [23], the concentration of N<sub>2</sub>O in flue gas (without application of SNCR for de-NO<sub>x</sub>) is between 0.5 and 8 vol. ppm. Variation of the emissions depends mainly on combustion temperature and nitrogen content in the waste-fuel. In previous measurements in various waste incinerators [24] the N<sub>2</sub>O concentrations in flue gas have been found to be lower than 20 vol. ppm (frequently 4–10 vol. ppm). In European countries [25] the nitrous oxide emissions measured in MSW incinerators were in the range of 1–12 mg/m<sup>3</sup> (*i.e.* 0.5–6 vol. ppm).

During combustion and incineration processes, a significant correlation between N<sub>2</sub>O and CO emissions has been observed, as well as a reverse trends in NO<sub>x</sub> and N<sub>2</sub>O emissions [24]. The N<sub>2</sub>O, NO, and CO emissions are influenced by the presence of alkali, alkaline earth metal compounds, and Fe<sub>2</sub>O<sub>3</sub> in the combustion chamber [26]. Presence of such compounds generally causes lower N<sub>2</sub>O emissions due to catalytic destruction of N<sub>2</sub>O [27].

Formation of N<sub>2</sub>O emissions in waste incineration facilities is principally coupled with the methods applied for reduction of NO<sub>x</sub> emissions. Especially the so-called selective noncatalytic reduction (SNCR) can be relatively significant source of N<sub>2</sub>O emissions. The conversion to N<sub>2</sub>O depends on the reagent for de-NO<sub>x</sub> reaction (*i.e.* urea or ammonia). In the case of urea, the conversion of the reduced NO<sub>x</sub> to N<sub>2</sub>O can attain about 30 %. *Tsujimoto et al.* [28] reported 20 % conversion to N<sub>2</sub>O of the reduced NO<sub>x</sub>. In the case of ammonia, the maximum conversions of NO<sub>x</sub> to N<sub>2</sub>O found are around 15 %.

The selectivity for N<sub>2</sub>O formation in selective catalytic reduction (SCR) of NO<sub>x</sub> depends on composition and age of the catalyst, on operation temperature, NO<sub>2</sub>/NO mole ratio, water vapour concentration, on deposition of ammonia salts on the catalyst, *etc.* Generally, at lower operation temperatures and

**Table 2.** Proximate and Elementary Analyses of the Wet, Semi-Dry, and Dry Sewage Sludge, Comparison with Coal [35, 15]

Analysis	Wet sludge	Semi-dried sludge	Dry sludge	Bituminous coal
<i>Proximate</i>				
$w(\text{Water (raw)})/\%$	76.0	68	13	6
$w(\text{Ash (wf)})/\%$	51.8	31	45.0	35.4
$w(\text{Volatiles (waf)})/\%$	92.4	90	92.7	43.8
$w(\text{NH}_3\text{-N (waf)})/\%$	3.2	0.9	1.19	
LCV (raw)/(MJ kg <sup>-1</sup> )	1.098	4.408	9.724	19.4
LCV (wf)/(MJ kg <sup>-1</sup> )	4.567	13.775	20.984	32.112
<i>Ultimate (waf)/%</i>				
$w_1(\text{Ultimate (waf)})/\%$				
C	51.9	47.8	53	81.6
H	7.8	7.68	7.8	5.8
O	29.8	38.4	31.13	9
N	8.8	4.6	6.5	1.3
S	1.7	0.77	1.4	2.3

wf = water-free basis, waf = water- and ash-free basis.

active, fresh catalyst, the selectivity for N<sub>2</sub>O formation is low (lower than 5 %). With significantly deactivated de-NO<sub>x</sub> catalyst the conversions of NO<sub>x</sub> to N<sub>2</sub>O in SCR can be higher, but maximally about 8 %. Modern facilities for SCR are attaining conversions of NO<sub>x</sub> to N<sub>2</sub>O on the level 1–2 % only, so their contribution to N<sub>2</sub>O emissions from waste incineration is only a few vol. ppm.

### Biomass Combustion as Biofuel

A range of biomass types can be used as fuels, such as wood, wood residues (bark, sawdust, odd-sized pieces, demolition wood), agricultural residues (straw from grains, husks from rice, coconuts, coffee, stalks from maize or cotton, bagasse from sugar cane), forestry and landscape conservation residues (thinnings and verge grass), and energy crops [29]. Typical nitrogen content in biomass between 0.12 mass % and 0.60 mass % (waf basis) has been reported [29]. Some exceptions of biofuels with higher nitrogen content are malt waste (4.99 mass % (waf)), coffee husks (1.6 mass % (waf)).

According to the literature [30] combustion of wood or other biofuels scarcely produces N<sub>2</sub>O emissions as contrary to combustion of coals. This is primarily due to the lower nitrogen content of biofuels compared to coal (1–2 %). Low N<sub>2</sub>O emissions are also due to the high content of volatile matter and water vapour. The formation of HCN (the main N<sub>2</sub>O precursor) during the pyrolysis/devolatilization stages of biomass combustion is less relevant than in the case of coal [10]. The remaining bio-char has normally only a small content of nitrogen, which could be transformed into nitrous oxide. Moreover, the bio-char is very reactive in reactions for reduction of N<sub>2</sub>O. As a result, particularly in big-scale facilities at combustion temperatures higher than 850 °C, combustion of wood and biomass produces only negligible N<sub>2</sub>O emissions (maximum 2–5 vol. ppm). On smaller combustion units

(*e.g.* stove combustion in houses) the N<sub>2</sub>O and CO emissions can be relatively significant [31, 32].

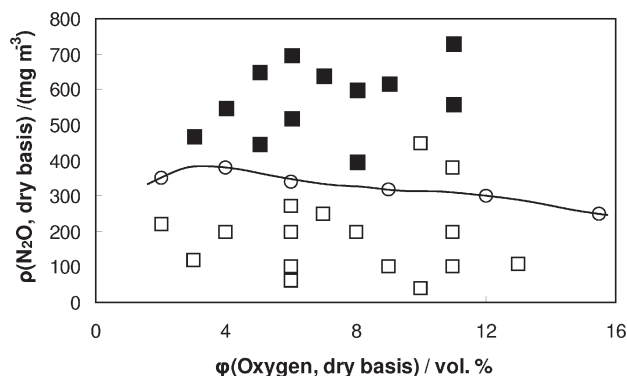
### Sewage Sludge (SS) Mono-Incineration

Sludge is formed during waste water treatment. The quantity of sludge produced worldwide is rapidly increasing. The sewage sludge production in Europe is expected to reach over 8 million tons (dry basis) in 2005 [33]. Among the disposal techniques, agricultural recycling is envisaged to be the most promising due to the favourable characteristics of the sludge compared to inorganic fertilizers. However, the presence of impurities (heavy metals, persistent organic pollutants, pathogens) is a difficulty that has to be further properly solved. Incineration accounts for 19 % of the sludge disposal in Germany [34]. Two main technologies are available for the sewage sludge, *i.e.* mono-incineration (fluidized bed, multiple-hearth furnace) and co-incineration (with coal, municipal solid waste or in other processes). Sewage sludge is characterized by high content of nitrogen (typically 5–8 mass % (waf)). This might be expected to lead to high emissions of NO<sub>x</sub> and N<sub>2</sub>O. Furthermore, substantial part of the fuel-nitrogen is bound in the form of ammonia compounds that may result in N<sub>2</sub>O emissions.

In general, three kinds of SS can be distinguished according to the pretreatment steps: wet (mechanically dewatered), dry sludge, and semi-dried sludge. Table 2 shows the elementary analysis of the sludges differing in water content (wet, dry, and semi-dry). As can be seen, the wet sludge has higher N-content than the dried sludge because part of the ammonia is released during the drying. The coal analysis data are also included for comparison.

### Fluidized Bed Combustion (FBC) of Pre-Dried Sludge

The success of fluidized bed technology for sewage



**Fig. 1.** Comparison of  $\text{N}_2\text{O}$  emissions from fluidized bed combustion of dry sludge (○), semi-dried sludge (□), and wet sludge (■) [35, 15]. Dried sludge: freeboard temp. = 850 °C, FB temp. = 850 °C. Wet sludge: freeboard temp. = 850 °C, FB temp. = 800 °C. Semi-dried sludge: freeboard temp. = 830 °C, FB temp. = 870 °C.

sludge combustion is related to advantages such as the high turbulence and large surface area for heat transfer, homogeneous combustion temperature, and quick start-up and shut-down.

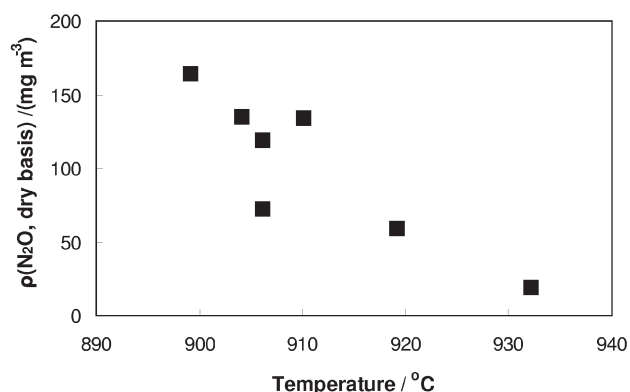
FBC of pre-dried sewage sludge [15] has exerted high levels of  $\text{N}_2\text{O}$  (250–350  $\text{mg m}^{-3}$ ) at oxygen concentrations higher than 6 vol. % and combustion temperatures about 850 °C.  $\text{NO}_x$  emissions measured under these conditions were around 1000–1200 vol. ppm [36]. The same authors [36] reported the effect of temperature and air/fuel ratio on  $\text{N}_2\text{O}$  and  $\text{NO}_x$  emissions. Just like for coals, the increase of combustion temperatures leads to higher  $\text{NO}_x$  and lower  $\text{N}_2\text{O}$  emissions. On the other hand,  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions increase with an increase in excess air ratio.

### FBC of Wet Sludge

Unlike pre-dried sludge, wet sludge appears not to exhibit similar  $\text{NO}_x$  characteristics as coals [36]. Firstly, very low  $\text{NO}_x$  are measured during combustion of wet sludge (less than 200  $\text{mg m}^{-3}$ ). Secondly, wet sludge FBC exhibits an unusual  $\text{NO}_x$  vs.  $\text{O}_2$  trend;  $\text{NO}_x$  decreases as the oxygen concentration increases and the effect of the combustion temperature is insignificant.  $\text{N}_2\text{O}$  emissions between 400  $\text{mg m}^{-3}$  and 700  $\text{mg m}^{-3}$  were measured during wet sludge FB combustion [15]. These authors found that oxygen concentration had little effect on  $\text{N}_2\text{O}$  levels during stationary fluidized bed combustion (see Fig. 1).

### FBC of Semi-Dry Sludge

$\text{NO}_x$  emissions from semi-dried sludge are closer to those of wet sludge although in some cases moderately higher, reaching 400  $\text{mg m}^{-3}$ . Like wet sludge,  $\text{NO}_x$  emissions exhibit a tendency to decrease with the increase of  $\text{O}_2$  concentration, whereas, there was no strong dependence of  $\text{N}_2\text{O}$  emissions on  $\text{O}_2$  concentra-



**Fig. 2.** Variation of  $\text{N}_2\text{O}$  emissions with freeboard temperature measured at large-scale sludge incineration plant VERA in Germany [35].

tion as shown in Fig. 1. The combustion of semi-dried sludge gave lower  $\text{N}_2\text{O}$  emissions than wet sludge [35]. Thus, typical  $\text{N}_2\text{O}$  concentrations of less than 250  $\text{mg m}^{-3}$  were measured. There was a good agreement between the results from the test rig and measurements from large-scale combustors, with emissions ranging between 30–300  $\text{mg m}^{-3}$ .

### $\text{N}_2\text{O}$ Reduction Techniques

As a result of the very high  $\text{N}_2\text{O}$  emission levels encountered during combustion of sewage sludge, it might be necessary to apply  $\text{N}_2\text{O}$  reduction techniques. Studies in this direction reached the following conclusions [15, 35, 37]:

Staged combustion of pre-dried sludge is effective in lowering  $\text{N}_2\text{O}$  emissions while such method is not effective for wet and semi-dried sludge. Varying the bed temperature while keeping the freeboard temperature constant has no influence on the  $\text{N}_2\text{O}$  emissions.

Raising the freeboard temperature proved to be the most efficient way of reducing  $\text{N}_2\text{O}$  emissions in FBC of sewage sludge. According to measurements at VERA incinerator (Fig. 2),  $\text{N}_2\text{O}$  concentrations decreased from 160  $\text{mg m}^{-3}$  to 20  $\text{mg m}^{-3}$  as the freeboard temperature raised from 900 to 934 °C.

### Incineration of Waste with High Nitrogen Content

Waste organic materials with high nitrogen content could be susceptible to produce  $\text{N}_2\text{O}$  emissions when they are disposed by means of incineration. Examples of such waste materials are leather waste, meat and bone meal, some waste plastics, *etc.* They are briefly treated here although very limited knowledge concerning  $\text{N}_2\text{O}$  emissions is currently at hand. The composition and heat energy value of some wastes with potential use for energy recovery by incineration are compared and assessed in Table 3.

**Table 3.** Typical Composition of Waste Organic Materials with High Nitrogen Content [38—41]

	Polyamide-6	Polyurethane foam	Urea-based glue	MBM	Leather waste
<i>Proximate</i>					
<i>w</i> (Water (raw))/%	3.7	1.8	32.8	3.5	13.3
<i>w</i> (Ash (wf))/%	0.03	0.3	0.1	28.7	5.25
<i>w</i> (Volatiles (waf))/%	99.8	88.2	87.4		76.55
LHV (wf)/(MJ kg <sup>-1</sup> )	28.70	27.00	13.40	17.00	18.30
<i>w<sub>1</sub></i> (Ultimate (waf))/%					
C	62.6	63.2	32.5	40.4	54.9
H	9.9	6.7	5.8	6.4	5.1
O	15.2	13.5	24.1	40.1*	19.2
N	12.1	6.6	37.4	7.8	14.4
S	< .01	0.01	0.01	0.5	1.4

\*By difference, LHV = lower heat energy value.

Footwear waste is an industrial waste with potential use for energy recovery. The heat energy value of this waste is in the range 12.5—21 MJ/kg and the content of volatile matter is similar to common biomass (~ 65 mass %). This waste leather is characterized by the high nitrogen content (14 mass % (waf)) mainly coming from the proteins (amino acids) of the animal skin. *Bahillo et al.* [39] explored the suitability of fluidized bed combustion as a disposal option for this kind of waste. They have found N<sub>2</sub>O emissions of 200—250 vol. ppm at FBC temperature about 850 °C. An important decrease of N<sub>2</sub>O emissions to values about 100 vol. ppm was detected for combustion temperature about 900 °C.

Meat and bone meal (MBM) is being destroyed in the EU due to the possibility of being responsible for the transmission of spongiform encephalopathy (BSE). Thermal treatments, incineration or gasification, are considered to be appropriate for the destruction of BSE pathogens by allowing enough residence time and adequate oxygen supply. The MBM is a fuel with high heat energy value (17 MJ/kg), with nitrogen content around 7.8 mass % (waf). Dedicated incineration plants are being set up in England, although the most common method seems to be co-incineration, mainly in cement kilns [38]. Co-combustion of Biomal (crushed animal rests) together with wood chips, sorted municipal waste and peat has also been tested in fluidized bed boilers [40]. It resulted in relatively low NO<sub>x</sub> emissions and probably low N<sub>2</sub>O emissions as well. To authors knowledge, no specific studies concerning N<sub>2</sub>O emissions from MBM combustion have been published. It could be presumed that the high Ca-content present in this waste might act as a catalyst in the reduction of N<sub>2</sub>O to N<sub>2</sub>.

Nitrogen (up to 5 mass %) is present in the plastic waste fractions of MSW [41]. Polymers with high nitrogen content are nylons/polyamides, polyurethane foam, and urea-based glues widely used for wood. Composition and nitrogen content of the mentioned materials is shown in Table 3. Investigation of combustion of these plastic waste materials in fluidized

bed has confirmed NH<sub>3</sub>, HCN, and N<sub>2</sub>O among the decomposition products from the plastics.

### Co-Combustion of Waste (MSW, Sewage Sludge, and Biomass)

Substitution of a fraction of coal by another fuel such as waste or biomass has an important effect on operation conditions, *e.g.* temperature distribution, ash properties (particle sticking and agglomeration in FBC), and emissions (CO, NO<sub>x</sub>, N<sub>2</sub>O, SO<sub>2</sub>, HCl, heavy metals, persistent organic pollutants, *etc.*) [31, 36, 40, 42—48]. Emissions during co-combustion of coal with various waste and biomass in existing coal power plants depend generally on waste/biomass composition (nitrogen, sulfur, heavy metals, and others) and content of water. Table 4 compares typical compositions of bituminous and sub-bituminous (lignite) coal with those of wood, MSW, and sewage sludge. As can be seen, bituminous coal properties (volatiles, nitrogen, ash contents, *etc.*) are substantially different in comparison with waste or biomass-based fuels. Nitrogen content of mature, hard biomass (*e.g.* wood) is typically very low. Growing biomass (*e.g.* leaves, grass) and straw contains somewhat higher percentage (0.4—1 mass %) of nitrogen resembling more the nitrogen content in coals. Nitrogen content of MSW is similar or slightly lower than in coals. Very high values (4—10 mass %) of nitrogen are commonly found in dry sewage sludge. Ash content of MSW and sewage sludge is relatively high, comparable with lignite coals. In the case of biomass, it is fairly low although it depends on the type of biomass. Plant, grass and straw-based biomass has generally higher ash content than wood.

The effect of waste or biomass-based residues co-combustion on N<sub>2</sub>O emissions is basically influenced by i) waste—coal mass ratio, ii) waste composition, iii) coal composition, particularly volatile and ash content, and iv) combustion technology (*e.g.* powdered coal combustion, FBC, grate or stove combustion). The combustion technology affects maximum temper-

**Table 4.** Typical Composition and Properties of Various Coal-Based and Waste-Based Fuels

Property of fuel (conditions)	Hard, bituminous coal	Brown, subbitum. coal	Wood	MSW	Dried sewage sludge
LHV (raw)/(MJ kg <sup>-1</sup> )	27	15	12.4	12	10.6
w(Moisture (raw))/%	7.1	36	33	35	3
w(Volatiles (wf))/%	24.8	43	83.2	65	50.5
w(Ash (wf))/%	7.7	24	0.34	30	46.1
w(Fixed C (wf))/%	67.5	33	16.5	5	3.4
<i>w<sub>i</sub></i> (Ultimate (wf))/%					
C	72.5	53.7	48.7	33	25
H	5.6	4.4	5.7	4	4.9
N	1.3	0.8	0.13	0.6	5.2
S	1.0	0.63	0.04	0.2	0.7
Cl	0.1	0.016	< 0.03	1.0	0.1
O	11.1	16.6	45	31	17.7
Ash fusion temp./°C	1280	1200	~ 1100	~ 1150	~ 1000

ature attained during the combustion process and residence time of flue gas [30, 49–52].

As a thumb rule, co-combustion of mixtures of biomass waste-based fuel and coal with energy input of the biomass up to 10 % causes slight decrease of N<sub>2</sub>O emission and only very mild or practically no operational (mostly ash related) problems. The NO<sub>x</sub> and N<sub>2</sub>O emissions reduction is small in case of lignite and subbituminous coals with high volatile content [53]. More significant effects are observed for N<sub>2</sub>O emissions in co-combustion of biomass or waste with bituminous coals [36, 51].

Principal combustion technologies that are used for co-combustion of coal with waste, sewage sludge, and biomass are: Pulverized coal combustion, cycloid combustion, FBC (stationary, circulating, atmospheric, and pressurized combustion), stove, grate, and rotary kiln combustion (used mainly for special technologies, *e.g.* production of cement). Below, there is a summary of co-combustion studies of the various wastes and coal by means of the mentioned technologies. Operation scale is another important factor. Generally, CO and N<sub>2</sub>O emissions measured in smaller stoves and smaller FBC facilities are higher [31, 32, 35, 54] than in bigger facilities with more uniform temperature distribution in the furnace and longer residence time of flue gas in the combustion/incineration chamber.

### Co-Combustion of MSW with Coal

The co-combustion is technically difficult due to the nature of MSW (bigger pieces, content of metals, ceramics, glass, *etc.*). This is the reason why practically only co-combustion of coal with sorted MSW or with refused derived fuels (RDF) containing mainly plastics, paper, and textile has been studied [43, 48, 52, 55]. The RDF contains approximately 0.7 mass % nitrogen and ash content is usually lower than 10 mass %. Due to special properties and composition of MSW, the main technology applied for mixed MSW is

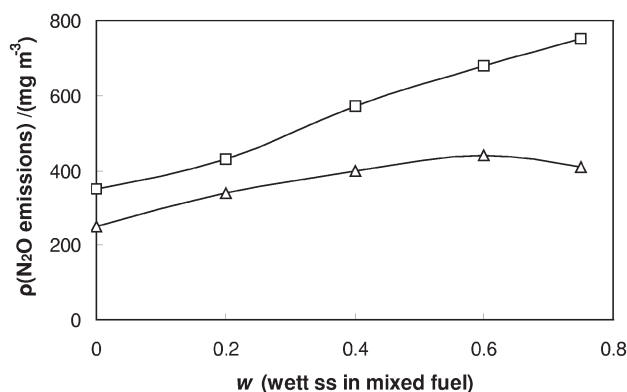
grate combustion with proper, sophisticated flue gas cleaning [20]. Co-combustion of sorted MSW or RDF in cement production rotary kilns is possible under assumption that especially chlorine and heavy metals contents are limited and guaranteed. Due to very high temperature at least in the part of cement-producing rotary kiln, the N<sub>2</sub>O emissions are practically negligible, but NO<sub>x</sub> emissions are very significant.

### Co-Combustion of Biomass, RDF, and Sewage Sludge in Pulverized Coal Combustion

Due to relatively high temperature in a pulverized coal combustion furnace, the emissions of nitrous oxide are very low. *Splithoff* and *Hein* [44] found N<sub>2</sub>O emissions below 10 vol. ppm during pulverized coal co-combustion with biomass. The main parameters affecting N<sub>2</sub>O emissions are nitrogen content in waste biomass, construction of burners, and biomass feeding system (separate or mixed with coal dust). Similar emission can be expected from RDF with nitrogen content below 1 mass %. Slightly higher N<sub>2</sub>O emissions can be supposed in pulverized and cycloid co-combustion of waste with high content of nitrogen (*e.g.* dried sewage sludge, MBM, *etc.*).

### Co-Combustion of Biomass and RDF in Fluidized Bed (FB)

The generally observed trend in N<sub>2</sub>O emissions from any fluidized bed-based co-combustion technology of coal and mature biomass or RDF with low nitrogen content is reduction of N<sub>2</sub>O emissions [51, 43, 48]. The reduction of the nitrous oxide emissions is more pronounced in the case of hard (bituminous coal) co-combustion with biomass than for lignite coals with higher content of volatiles. The effect of biomass FB co-combustion on N<sub>2</sub>O emissions is weaker for reactive lignite coals with high content of volatiles and with coal ash containing catalytically active compounds



**Fig. 3.** Dependence of N<sub>2</sub>O emissions in FB co-combustion of wet sewage sludge (SS) with bituminous coal on fraction of wet sewage sludge in the mixed fuel under different conditions for limestone desulfurization (effect of Ca/S mole ratio) [57]. Ca/S = 0 □; Ca/S = 3 △.

(e.g. CaO, Fe<sub>2</sub>O<sub>3</sub>, etc.) causing low emissions in FB single combustion of the reactive coal [49, 53].

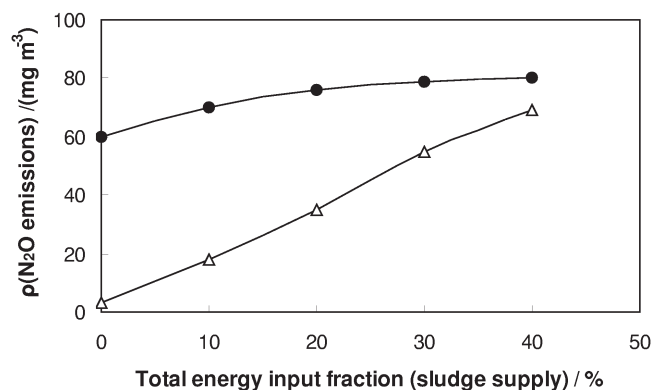
Very special kind of biomass waste is the newly produced meat and bone meal (MBM) and other animal waste such as “Biomal” (crushed, thermally treated, pulpy animal waste). Co-combustion of both kinds of animal waste differing substantially in water content and calorific value is possible in fluidized bed boilers. The relatively high content of nitrogen in such waste (around 7 mass % in dry matter) can lead to higher N<sub>2</sub>O and NO<sub>x</sub> emissions. But, as practical FB co-combustion experience with wood and sub-bituminous coal has shown [40, 56], the NO<sub>x</sub>, CO, and N<sub>2</sub>O emissions are below 100 mg (norm. m)<sup>-3</sup> in FB co-combustion with wood and lignite coal, probably due to higher content of calcium and special thermal behaviour of the animal waste nitrogen.

### Co-Combustion of Sewage Sludge in Atmospheric FB

Sewage sludge can be found in three different forms concerning water content and pretreatment: wet, dry, and semi-dry. N<sub>2</sub>O emissions from co-combustion of wet and dry sewage sludge with coal and wood in FB combustion are shown in Figs. 3 and 4.

Co-combustion of wet sludge with bituminous coal in atmospheric circulating fluidized bed combustor leads to an increase in N<sub>2</sub>O emissions [36, 57]. Main parameters affecting N<sub>2</sub>O emission are: nitrogen content in the sludge, coal characteristics, coal ash composition, limestone addition for *in situ* desulfurization, freeboard temperature distribution, and gas residence time (gas velocity). Increasing bed and freeboard temperature results in reduction of N<sub>2</sub>O emissions. Nevertheless, CO and N<sub>2</sub>O can be as significant as 100 vol. ppm or even 200 vol. ppm.

Co-combustion of semi-dried and dried sewage sludge in atmospheric fluidized bed is known to produce higher NO<sub>x</sub> emissions than in the case of FB



**Fig. 4.** Dependence of N<sub>2</sub>O emissions in FB co-combustion of dry sewage sludge with bituminous coal and wood on sludge supply expressed as fraction of total energy input of the mixed fuel [46]. Coal-sewage sludge ●; wood-sewage sludge △.

co-combustion of wet sewage sludge [35, 36, 46]. The N<sub>2</sub>O emissions in semi-dried sludge co-combustion are generally lower than in wet sludge co-combustion, but still on the levels 20–100 vol. ppm. FB co-combustion of dried sewage sludge with bituminous coals leads to slight elevation of N<sub>2</sub>O emissions on levels around 50 vol. ppm. Simultaneous wood and dried sewage sludge FB co-combustion with bituminous coal can offer further reduction of N<sub>2</sub>O emission on levels between 10 and 40 vol. ppm [46]. Similar results and effects can be expected in FB co-combustion of dried sewage sludge with lignite coals. Higher freeboard temperature (over 900–930 °C) is proved to be a relatively simple method for reduction of N<sub>2</sub>O emissions. N<sub>2</sub>O concentrations below 20 vol. ppm in flue gas are attainable at freeboard temperatures above 930 °C. Unfortunately, NO<sub>x</sub> emissions are relatively high in FB co-combustion with high dried sludge/coal mass ratio, even under convenient air staging conditions.

### Co-Incineration of Sewage Sludge in MSW Incinerators

It is suitable and employed technology for thermal destruction of sewage sludge especially in Germany, where the gas cleaning in MSW incineration is sufficiently dimensioned and flexible to manage higher concentrations of heavy metals and nitrogen oxides [36]. Due to high temperature in post combustion chamber (typically over 900 °C) the N<sub>2</sub>O emissions are only slightly elevated and are generally low (below 20 vol. ppm) in sewage sludge co-incineration with MSW.

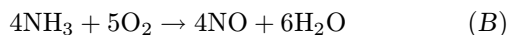
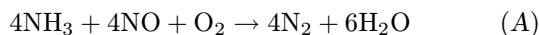
### SNCR as Source of N<sub>2</sub>O Emissions

#### Brief Description of SNCR and Factors Affecting its Efficiency

Selective noncatalytic reduction (SNCR) is a widespread secondary measure for NO<sub>x</sub> control. In this



process NO is reduced to N<sub>2</sub>, in the presence of O<sub>2</sub>, by injection of a reducing agent, such as ammonia, urea or cyanuric acid. The process is characterized by a selectivity in the reaction pathways as shown by the overall steps [58–60]



The selectivity towards N<sub>2</sub> or NO (reactions (A) or (B)) mainly depends on temperature and gas composition. The optimum temperature for the reduction to N<sub>2</sub> is between 900 °C and 1000 °C. Oxidation of NH<sub>3</sub> to NO becomes increasingly important when the maximum temperature is exceeded. Below the optimum temperature window the selective reduction reactions are too slow, resulting in undesired high ammonia slip. Other factors affecting process efficiency are ammonia stoichiometry to NO (*i.e.* NH<sub>3</sub>/NO mole ratio), concentrations of oxygen, CO and H<sub>2</sub>O in flue gas, and residence time.

Sufficient residence time within the temperature range is required for allowing chemical reactions and for proper mixing between the reagent and flue gas. Certainly, when reactions are fast, mixing may be the rate-limiting step. The minimum residence time is around 0.2–0.5 s [58]. Residence times in excess of 1 s yield optimum NO<sub>x</sub> reductions.

Concerning the O<sub>2</sub> concentration, both very high concentrations in flue gas (over 9 vol. %) and very low ones (typically below 2 vol. %) were found to be an obstacle for attaining high NO reduction efficiencies [59]. At increasing oxygen concentrations, the temperature range for NO reduction is widened (mainly towards lower temperatures), but the NO reduction potential decreases [60].

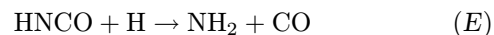
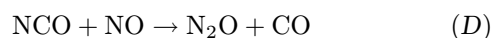
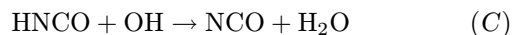
Increasing CO concentration in flue gas shifts the selectivity towards oxidation of NH<sub>3</sub> to NO, as well as increases the kinetic rate of this reaction. At higher CO concentrations, the optimum temperature for SNCR is displaced towards lower temperatures [61].

### Conversion of NO<sub>x</sub> to N<sub>2</sub>O

Wojtowicz *et al.* [9] reported conversion ratios of  $m(\text{N}_2\text{O})/m(\text{NO}_x)$  between 5 % and 50 % for coal combustion. However, the last figure seems high compared with later studies. Thus, the maximum conversions of NO<sub>x</sub> to nitrous oxide under well-controlled conditions of SNCR with ammonia are below 5 % and in many cases below 2 % [62].

Utilization of urea instead of ammonia as reducing agent leads to a higher portion of NO converted into N<sub>2</sub>O (typically > 10 %). In terms of the formation mechanism, studies suggested that HNCO (one of the products of the initial decomposition of urea) reacts

according to the following sequence [14]



Comparison of urea and cyanuric acid as reducing agents shows that urea generates less N<sub>2</sub>O under equivalent conditions. This is consistent with the previous reaction mechanism, as all cyanuric acid is converted to HNCO after injection.

Under poorly controlled SNCR conditions, such as too high temperature with oxidation of surplus ammonia and with quick quenching of gases (low residence times for thermal destruction of N<sub>2</sub>O) the conversions to N<sub>2</sub>O may attain 20–25 %. The use of promoters (CO, C<sub>2</sub>H<sub>6</sub>) to shift the optimum temperature to lower one appears to increase the fraction of NO converted into N<sub>2</sub>O [14].

### Selective Catalytic Reduction (SCR) as Source of N<sub>2</sub>O Emissions

#### Brief Description of SCR and Factors Affecting its Efficiency

Depending on nitrogen content in waste or biomass and on combustion conditions, particularly temperature and the NO<sub>x</sub> concentrations in flue gas can vary in a broad range. For combustion of waste/biomass with high content of nitrogen (above 1–2 mass %) and for combustion processes with temperatures above 1000 °C the NO<sub>x</sub> concentrations in flue gas can be relatively high, over 300 mg (norm. m)<sup>-3</sup> [36]. This is especially true for FB combustion or co-combustion of dry sewage sludge or some waste with high N-content and low moisture content (< 10 %). For reduction of NO<sub>x</sub> (NO + NO<sub>2</sub>) emissions either selective non-catalytic reduction (SNCR) or selective catalytic reduction (SCR) by ammonia can be used. The SCR achieves a more efficient reduction of NO<sub>x</sub>, with common conversions of NO<sub>x</sub> between 80 % and 90 %.

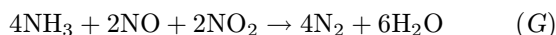
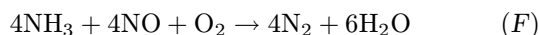
The usual position of SCR in the flue gas cleaning system of an MSW incinerator is behind wet gas cleaning system (scrubbers + demister). Only in exceptional cases it is located behind electrostatic precipitator (ESP). The position of SCR behind wet cleaning of flue gas has advantage of lower concentration of dust, heavy metals, SO<sub>2</sub>, and HCl. It means, under such conditions, the catalyst in SCR technology will be less deactivated (poisoned) by deposition of fine dust, deposition of volatile compounds of heavy metals (*esp.* arsenic compounds), and by deposition of ammonium salts, like ammonium sulfate and bisulfate.

A disadvantage of the position of SCR behind wet gas cleaning lies in requirements on reheating

of gases. The older (former) generation of de-NO<sub>x</sub> catalysts (mostly based on TiO<sub>2</sub>—V<sub>2</sub>O<sub>5</sub>—WO<sub>3</sub>) had usual range of operating temperature between 250 °C and 350 °C. The newer generation of SCR catalysts is characterized by lower operating temperature – about 200 °C (with less energy necessary for reheating of gases). Such low-temperature SCR is usually coupled with lower emissions of N<sub>2</sub>O, but on the other hand, relatively low temperatures can bring some difficulties with formation and deposition of ammonium salts on the surface of the catalyst.

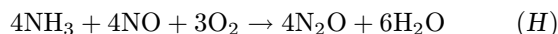
### Overall Reactions for NO<sub>x</sub> Reduction and Side Reactions Leading to N<sub>2</sub>O Formation

Selective catalytic reduction of NO<sub>x</sub> is mainly based on reactions (F) and (G) where, particularly at temperatures between 200 °C and 250 °C, the reaction (G) is faster than reaction (F) [63, 64].

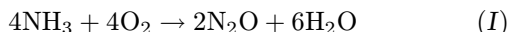


The NO<sub>2</sub>/NO mole ratio increases with decreasing temperature, but for the sufficiently high NO<sub>2</sub>/NO ratio catalytic oxidation is needed upstream the SCR catalyst [64]. In laboratory studies a number of side reactions in SCR leading to N<sub>2</sub>O formation have been identified. Temperature is one of the most important parameters influencing the potential mechanisms.

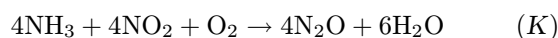
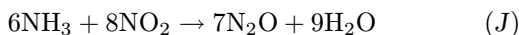
At high temperatures (> 350 °C), where the fraction of NO<sub>2</sub> is low and at low space velocities of gas, N<sub>2</sub>O can be formed mainly according to reaction (H) [65]. For SCR catalyst based on V<sub>2</sub>O<sub>5</sub>—TiO<sub>2</sub> the selectivity of N<sub>2</sub>O formation from NO<sub>x</sub> is increasing under temperatures over 350 °C.



In addition, ammonia can be partially oxidized to N<sub>2</sub>O at temperatures over approximately 350 °C according to the following reaction [65]



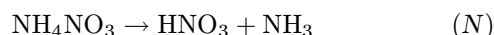
At intermediate temperatures (250—350 °C) the following reactions in the presence of NO<sub>2</sub> can be supposed to be potentially significant source of N<sub>2</sub>O



At low temperatures (< 250 °C) and higher NO<sub>2</sub>/NO ratio, reaction mechanism involving transient formation of NH<sub>4</sub>NO<sub>3</sub> and its decomposition to N<sub>2</sub> and NO is supposed [65]



At temperatures below 200 °C the formation and deposition of solid ammonium nitrate on SCR catalyst according to reaction (L) was experimentally demonstrated [63]. Presence of water vapour and slow heating rates causes preferable formation of HNO<sub>3</sub> and NH<sub>3</sub> in decomposition of NH<sub>4</sub>NO<sub>3</sub> (*i.e.* lower N<sub>2</sub>O formation selectivity)



### Conversion of NO<sub>x</sub> to N<sub>2</sub>O in Big-Scale SCR Units

The catalytic activity of catalysts based on TiO<sub>2</sub>—V<sub>2</sub>O<sub>5</sub>—WO<sub>3</sub> depends mainly on content, interactions, surface, and catalytic properties of vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>). Higher concentrations of V<sub>2</sub>O<sub>5</sub> in the catalyst usually cause higher catalytic activity in de-NO<sub>x</sub>, but simultaneously higher sensitivity to deactivation at expositions to higher temperatures (especially above 400 °C). At higher concentrations of V<sub>2</sub>O<sub>5</sub> in the catalyst, it seems that the conversion of NO<sub>x</sub> to N<sub>2</sub>O in SCR is higher [66].

The conversion of nitrogen from NO<sub>x</sub> to N<sub>2</sub>O in SCR is dependent mainly on temperature [65, 67], catalyst ageing (deactivation), and water vapour concentration in the gas [68]. At temperatures 250—300 °C the conversions of nitrogen from NO<sub>x</sub> to N<sub>2</sub>O are below 5 %, at temperatures below 250 °C (for modern new catalysts) the conversion to N<sub>2</sub>O is lower than 3 %. In modern SCR units with fresh catalyst and water vapour concentration above 4 vol. % the conversion of NO<sub>x</sub> to N<sub>2</sub>O is commonly below 1 % [24, 68]. The conversions of NO<sub>x</sub> to N<sub>2</sub>O in SCR units are summarized in Table 5.

From various catalyst and carrier compositions the best performance and lowest N<sub>2</sub>O concentrations have been attained by V<sub>2</sub>O<sub>5</sub>—WO<sub>3</sub>—TiO<sub>2</sub>-based catalysts [67]. For low-temperature SCR (< 200 °C) various new catalysts on the basis of Fe—Mn oxides on TiO<sub>2</sub> and Mn—Ce—O<sub>x</sub> oxides have been tested [69, 70]. The new catalysts proved very low N<sub>2</sub>O formation selectivities. At low temperatures (150—200 °C) carbon impregnated with Cu or Cu—Fe exhibits very high catalytic activity in SCR reduction of NO<sub>x</sub>, higher than conventional catalysts [71], but the big-scale applications and selectivities for N<sub>2</sub>O formation are not described. Zeolitic catalysts [72—74] for destroying of N<sub>2</sub>O at higher temperatures are intended mainly for industrial processes (*e.g.* production of nitric acid). Their working temperature is normally above 300 °C or even above 350 °C. From the point of view of application in modern waste

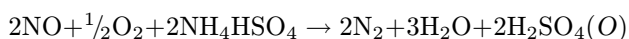
**Table 5.** Approximate Conversions of NO<sub>x</sub> to N<sub>2</sub>O [67, 68]

Temperature range/°C	Conversion of NO <sub>x</sub> to N <sub>2</sub> O in SCR <i>x</i> (NO <sub>x</sub> )/mole %	Notice, catalyst, conditions, <i>etc.</i>
< 180	> 1	Inconvenient temperature range, formation and deposition of ammonium salts.
180—220	0.7—2	Low-temperature SCR, higher NO <sub>2</sub> /NO ratio needed, N <sub>2</sub> O emission increases with NO <sub>2</sub> /NO ratio over 0.6.
220—300	1—3	Classical SCR – in MSWI high energy needed for gas reheating, older generation of SCR catalysts.
300—400	< 5	Inconvenient SCR for MSW and waste incineration (higher costs for gas reheating, higher N <sub>2</sub> O emissions).

incineration units the needed temperature seems to be too high. Another disadvantage of such catalysts is sensitivity to some acid gases (*e.g.* SO<sub>2</sub>, HCl, *etc.*).

#### Side Effects of SCR of NO<sub>x</sub>

The SCR can simultaneously oxidize reactive hydrocarbons and partly oxidize even benzene, toluene, and PAH, where the conversions depend on catalyst composition, operating temperature, *etc.* [75—77]. At lower temperatures (< 180 °C) depending on NO<sub>2</sub> and NH<sub>3</sub> concentrations in flue gas [64] ammonium nitrate can be formed and deposited within catalyst. Simultaneously, at presence of SO<sub>2</sub> in the gas at concentrations above about 10 mg/m<sup>3</sup> the probability of formation and deposition of ammonium bisulfate and sulfate increases. In the case of SO<sub>3</sub> (H<sub>2</sub>SO<sub>4</sub>) presence in flue gas, even very small concentrations (1—3 vol. ppm) can contribute to formation of the ammonium salts and their deposition. The deposited ammonium salts are decomposed by reaction with NO under absence of NH<sub>3</sub> in gas



Such decomposition, as it is obvious, leads temporarily to higher sulfuric acid concentration in flue gas and higher corrosion in the units (*e.g.* heat exchangers) behind the SCR.

#### Multifunctional Catalytic Filters (MCF's)

The MCF's are designed for simultaneous reduction of dust emissions together with catalytic destruction of NO<sub>x</sub>, volatile organic compounds (VOC) and polychlorinated organic compounds (PCDD/F) emissions [78—80]. The catalyst dispersed into the filter structure, *i.e.* fibers, grains or felt, has to be multifunctional, often modified in comparison with common SCR catalyst. Catalytic oxidation of VOC's can be elevated by inclusion of Ni, Cu, Mn or other catalytically active metals. There are two basic kinds of

MCF's used in MSW and other waste incineration facilities:

a) Teflon (PTFE) based felt filters with membrane [78, 81]. Such filters have operating temperature typically between 180 °C and 230 °C.

b) Ceramics fiber based MCF's [80, 82] with possible operating temperature between 220 °C and 350 °C. Advantage of such ceramic MCF's is possibility of removal of deposits of volatile inorganic/organic compounds from the filters by short-time heating to temperatures over 500 °C.

The MCF's have usually somewhat different optimum temperature range for SCR of NO<sub>x</sub> and destruction of PCDD/F and/or VOC's. Therefore, their operating temperature is mostly a matter of compromise and acceptable conversions of all catalytic destructions. The selectivities for N<sub>2</sub>O formation in such MCF's are not stated in open literature, but probably, the conversions to N<sub>2</sub>O are relatively low.

In reality, in big, modern plants for MSWI the SCR of NO<sub>x</sub> contributes typically only by a few vol. ppm to elevation of N<sub>2</sub>O concentrations in flue gas [24].

### CONCLUSION

1. MSWI and biomass incineration in big-scale facilities with proper controlling of the combustion process are negligible sources of N<sub>2</sub>O emissions.

2. Combustion of biomass and waste in small (esp. stove, grate, and FB) facilities without secondary combustion chamber and at lower freeboard temperature leads usually to higher CO and N<sub>2</sub>O emissions [31, 32].

3. Mono-combustion and co-combustion of sewage sludge and waste with high N-content (> 3 mass %) under temperatures lower than approx. 900 °C (typically FB combustion and co-combustion) can be relatively significant source of N<sub>2</sub>O emissions. Temperatures over 900 °C cause substantial decrease of N<sub>2</sub>O emissions and they are widely practically employed for reduction of N<sub>2</sub>O emissions.

4. Co-combustion of common biomass and RDF in pulverized and FB coal combustion facilities leads to

reduction of N<sub>2</sub>O emissions, particularly for bituminous coals with lower content of volatiles.

5. SNCR and SCR of NO<sub>x</sub> by ammonia under carefully controlled conditions is elevating only slightly the N<sub>2</sub>O emissions in MSW, waste and biomass combustion units. The conversions of NO<sub>x</sub> to N<sub>2</sub>O are usually lower than 5 % (or the N<sub>2</sub>O concentration contribution is in units of vol. ppm).

6. SNCR of NO<sub>x</sub> by urea is practically the only significant source of “de novo” created N<sub>2</sub>O emissions in MSW and waste/biomass incineration facilities. Nevertheless, the conversions of NO<sub>x</sub> to N<sub>2</sub>O are usually lower than 20 % (usual contribution in content in flue gas being in tens of vol. ppm).

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