An Innovative Injection Device to Enhance NO_x Abatement by SNCR in Waste Combustion Flue-gases

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ABSTRACT

Nitrogen oxides (NOx) are critical atmospheric pollutants that can affect both human health and the environment. A significant reduction of the quantity of NO_x inevitably formed by a combustion process with air can be achieved by both an accurate control of the combustion reaction, and adapted emission control technologies, like flue-gas denitrification. Selective non-catalytic reduction (SNCR) technology was applied and optimized to reduce NO_x emissions on our 16t/h waste incineration plant, in accordance with French legislation fixing maximal emission level at 200 mg/Nm^3. By injecting granular urea at six locations within the *post*-combustion zone through an innovative transport and injection device mediated by gravitary outflow, we achieved a yield of denitrification of 70 % for a molar N-urea/NO_x ratio close to 2, at 1223 K, without any leak of ammonia at the stack. This innovative retrofitted multi-point injection system allowed substantial savings in both investment and running costs (factor 5), while raising the whole technical performances of the equipment.

Keywords: Waste, Incineration, Flue-gas denitrification, Urea, Greenhouse effect

1. INTRODUCTION

Nitrogen oxides (NO_x) is a generic term for a group of highly reactive gases containing nitrogen and oxygen in varying amounts, that form in any high-temperature combustion process, due to chemical reactions between oxygen from air, and nitrogen from either air or the combustible. NO_x can contribute to a wide variety of health and environmental impacts, like ozone and acid rain formation (greenhouse effect) or human respiratory pathologies /1/. Selective non-catalytic reduction (SNCR) of nitrogen oxides is an interesting simple and low-cost technique /2/ that involves the injection of a reducing agent (ammonia, urea, cyanuric acid, *etc.*) able to liberate a NH_2-radical in a precise point in the combustion or in the *post*-combustion zones. Indeed, in presence of oxygen, within a narrow temperature range (1123 to 1273 K), such a radical will reduce NO and NO_2 molecules, to produce harmless nitrogen gas (N_2) and steam /1/. Our paper focuses on an optimization procedure and related equipments for selective non-catalytic NO_x reduction (SNCR) in waste incineration plants, to render stack gas less polluting when discharged to the atmosphere, thus contributing to a minimisation of health and greenhouse effects. More particularly, we present herein an innovative retrofitted multi-point injection system mediated by gravitary

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outflow to introduce solid reducing reagents, more efficiently and at far lower cost than SNCR systems based on the use of aqueous reagent forms.

2. THEORETICAL APPROACH

2.1. NO_x formation mechanisms

The chemistry and thermodynamics involved in NOx formation in high temperature combustion processes are complex. When any fuel burns with air, negligible *prompt* NO primarily forms, then followed by more abundant forms, namely, *thermal* NO_x and *fuel* NO_x /3,4/.

Prompt nitric oxyde results from the reaction in the flame of hydrocarbon radicals with air nitrogen, through the general equation /4/:

$$CH_4 + O_2 + N_2 \rightarrow NO, NO_2, CO_2, H_20, \text{trace species} \quad (1)$$

Thermal NO_x (mainly NO) result from the cleaving of N_2 present in the air into two N molecules (through a reaction called Zeldovich mechanism /4/ : $N_2 + O_2 \rightarrow NO, NO_2$), that readily combine with either atomic oxygen (originating from the dissociation of gaseous oxygen); or with -OH radicals (originating from water dissociation). *Thermal* NO_x formation is mainly dependent on temperature, oxygen content and residence time within the combustion zone. Temperatures required for significant formation of *prompt* and *thermal* NO tend to be higher than 1473 K.

Fuel NO_x are formed by the nitrogen that is contained within the fuel itself, which is rendered free during the combustion process under the form of either low molecular-weight molecules, like NH_3, or free radicals, behaving as precursors in NO formation. These nitrogen forms can readily combine with any oxygen in presence. *Fuel* NO_x formation is supposed to be the major source of NO_x during incineration of wastes. It occurs through the previously described complex process, at temperatures below 1073 K and with excess oxygen.

The relative contribution of these mechanisms to NO_x emissions is dependent on thermodynamics, combustion parameters such as fuel, temperature, combustion system size and residence time of the combustion gases /4,5/. NO is the predominant species of NO_x in flue-gases. NO_2 formation from NO occurs in conditions where rapid cooling takes place.

2.2 Primary and secondary NO_x reduction mechanisms

The control of NO_x in exhaust emissions from waste incineration is a key issue. The limit of 200 mg/Nm^3 at 11% O_2 dry as daily average, prescribed by the European Waste Incineration Directive (WID) and the French regulation /6,7/ implies that the plants have to develop and/or combine specific abatement strategies to reduce the NOx, categorized as : *i)* modification of the combustion configuration, *ii)* injection of reduction additives into the flue-gases, *iii)* treatment of the flue-gas by *post*-combustion denitrification processes.

In-furnace control methods can contribute to reduce the amount of NO formed during combustion, for example by means of : optimized stoichiometry-based air-to-fuel ratio, low-NO_x burners, low nitrogen content fuels, pure oxygen instead of air, staged combustion, flue-gas recirculation, reburning, or steam/water injection to reduce temperature /8-10/. Reduction of NO_x directly at the source of formation in the combustion process can be a strategy, but current emission standards often require the use of flue-gas clean-up. Furthermore, if such primary measures can be easily applied to peculiar combustion systems like gas turbines, their implementation on waste incinerators is limited, due, for example, to the high heterogeneity of the waste feed and to the necessity to operate such combustion systems at high temperature and turbulence, and with a sufficient residence time (the "3 T's rule" : Time, Temperature and Turbulence), and with a large excess of air, as prescribed by regulation /6,7/.

Post-treatment removes NOx from the exhaust gases after the NOx has already been formed in the combustion chamber. Most of the *post*-treatment methods are relatively simple to retrofit to existing plants, but they are capital intensive and may have high operating costs. The general strategy is to inject a reducing agent, typically ammonia or urea, to remove the oxygen from the NO and convert it into N_2 and O_2.

To denitrify flue-gases, the SCR method (Selective

Catalytic Reduction) is often used in waste incineration plants. SCR can be implemented after cleaning the flue-gas for acid components at a temperature of approximately 520 to 700 K /11/. In the SCR process, ammonia (mixed with water or, more frequently, in an anhydrous form), is injected into the flue-gas before a catalyst, *i.e.* a substance that speeds up a chemical reaction without undergoing a chemical change itself. The NO_x and NH_3 react on the surface of the supported catalyst (vanadium, titanium, platinum, zeolites /8/) at a stoichiometric ratio of 1, to form N_2 and H_2O, thus requiring moderate ammonia consumption. But the cost for reheating the flue-gas and maintaining the catalyst can be important, as it can be poisoned or deactivated under certain conditions, and as its activity declines over time. The overall ammonia reaction equation is represented by /11/;

$$2NO + 2NH_3 + 1/2O_2 \rightarrow 2N_2 + 3H_2O \qquad (2)$$

To avoid supplying additional energy for reheating, some plants integrate the SCR process directly downstream of the boiler, where the flue-gas temperature is still sufficiently high, but where dust content is also high. Ammonia must be metered with accuracy, in accordance with real time nitrogen oxide concentrations. The quantity of unreacted ammonia entering the gas (referred to as ammonia slip) must be kept to a minimum (< 2 mg/m^3), while always ensuring an effective denitrification process by sufficient reagent introduction in the system.

Selective non-catalytic reduction (SNCR) also called *Thermal DeNOx*, is a technology with lower costs than SCR, which takes place at a higher optimum temperature window (1220-1340 K), with injection of NOx reducing chemicals, such as ammonia or urea, at a higher stoichiometric level. The detailed chemistry is complex and involves free radical reactions /8,9,12/. No catalyst is involved in the process, which is one advantage over SCR. In the case of urea, the overall reaction for NO reduction can be written /8,12/:

$$H_2NCONH_2 + 2\,NO + 1/2O_2 \rightarrow 2N_2 + CO_2 + H_2O \qquad (3)$$

2.3 SNCR process parameters and performance

Although it is often considered quite simple to install and operate, SNCR has a complex chemistry and requires specific operational conditions, based on well-mastered process parameters. Indeed, the appropriate narrow temperature window required to allow SNCR reactions is fluctuant, depending on several parameters, particularly on oxygen and unburned combustible concentrations in the flue-gas /13-15/. In a hazardous waste incineration plant, such parameters, as well as temperature profiles, are usually variable with time, and difficult to control, due to the high heterogeneity of the admitted waste. Furthermore, hazardous waste incineration plants operate with high excess of combustion air, inducing a higher residual O_2 concentration in the flue-gas, and thus a shift of the optimal temperature window for SNCR, compared with other combustion plants.

The performance of the SNCR process is strongly infuenced by four main parameters: *1)* flue-gas temperature at the reagent injection zone; *2)* flue-gas residence time in the relevant temperature range; *3)* reactant dosage, *i.e.* nitrogen-urea/NO_x molar ratio; and *4)* mixing conditions. Practically, in full-scale waste incineration plants, it is possible to change the reagent injection position and/or to vary its dosage (Nitrogen-urea/NO_x molar ratio) to improve the efficiency of the process.

When increasing N-urea/NO_x molar ratio, a higher NO_x reduction efficiency can be achieved at a determined optimal temperature, but the fraction of unreacted residual nitrogen may increase too much with the increase of this ratio. As an undesirable consequence, an increase in nitrogen content of stack gases may occur, possibly under the form of various compounds (NO, ammonium compounds). Such a negative effect is obviously unacceptable above determined limits, and it can also occur if the overall parameters controlling the process are not set within the narrow range required for SNCR optimal performance. In particular, if the upper temperature of the window is reached in excess of injected nitrogen, the SNCR may result in the formation of NO_x rather than their removal, while at lower temperatures most of the nitrogen injected may prove ineffective for NO_x reduction.

Playing with relatively high N-urea/NO_x molar ratios thus appears relatively critical, but, at least up to now, it was frequently required to reduce NO_x at levels below emission standards.

Rapid mixing conditions of the reagent with the flue-gas stream are also of great impact on the NO_x reduction efficiency, mainly when high efficiency of NO_x removal is required, *i.e.* in the range of 50-70%, as a NO_x removal over 70% is not required in most waste incineration plants. Mixing conditions are dependent on the physical form of the reactant, as well as on the conception and positioning of the injection system. NO_x reductant compounds may be injected in either solid, liquid, or gaseous forms. Solid and liquid forms require a longer residence time compared with gaseous forms, to achieve sublimation or vaporisation.

A deep knowledge of the equipment and the process parameters is required when implementing a SNCR system on a waste incineration plant. Optimal regions for SNCR reagent injection must be accurately mapped, through both computational-modeling of the combustion zone and real temperature measuring, particularly when different thermal charges are introduced in the kiln.

3. FULL-SCALE SNCR IMPROVEMENT TRIALS: EXPERIMENTAL CONDITIONS

Our full-scale SNCR experimentations were carried out at the *TREDI Salaise III* waste incineration plant, located at Salaise-sur-Sanne, 38150 – France. Within the *TREDI Salaise* site, three specialized facilities are able to carry out incineration of industrial wastes with energy recovery. Two out of three units are dedicated to thermal treatment of hazardous industrial wastes, while the third unit, called *Salaise III*, is dedicated to the thermal treatment of soiled packagings, infectious clinical wastes, non-recoverable banal wastes and household wastes.

TREDI Salaise III incineration unit can process 16 tons of wastes per hour, with a lower calorific value of about 18,828 kJ/kg, which is high enough to carry out combustion without additional need of fossil energy resources. During combustion of such wastes, much energy is given off in the form of heat, that is recovered by conversion in steam and/or electricity through a boiler coupled with a steam-turbine producing about 60 t of steam per hour. The nominal electrical capacity of the plant is 14 MWe. The electric power produced in the *TREDI Salaise III* unit corresponds to the annual consumption of a city with 40,000 inhabitants. The thermal capacity of the plant is maintained as constant as possible, considering the heterogeneity of the waste feed, chiefly banal industrial wastes or soiled materials with a low proportion of household wastes.

The thermal treatment occurs in a peculiar grid kiln with injections of excess air, allowing both the conveyance and the complete combustion of the wastes. *TREDI Salaise III* waste incinerator is designed to provide and maintain a high degree of gas turbulence and mixing, as assessed by high Reynolds numbers within the different parts of the system.

The maximal flue-gas flow is 200,000 Nm^3/h at the stack. The unit is equipped with full air-pollution control systems, and water treatment plant. A global scheme of the waste incineration plant is presented in Figure 1. The urea-based SNCR process is employed on the plant to control NO_x emission below 200 mg NO_2/m^3, in compliance with current French and European environmental regulation /6,7/.

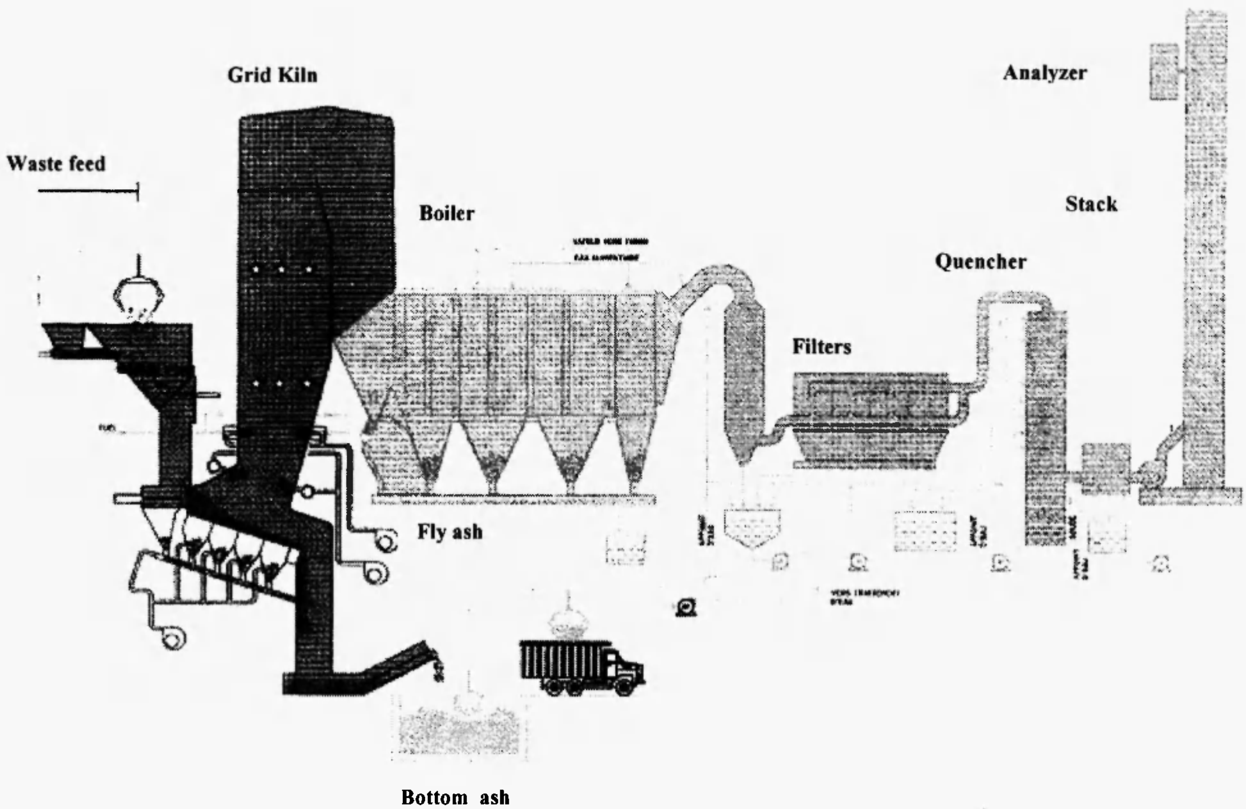

Fig. 1: Flow sheet of TREDI Salaise III Waste Incineration Plant, Salaise-sur-Sanne, France. Stars (☆) indicate the 6 urea injection points in the *post*-combustion zone

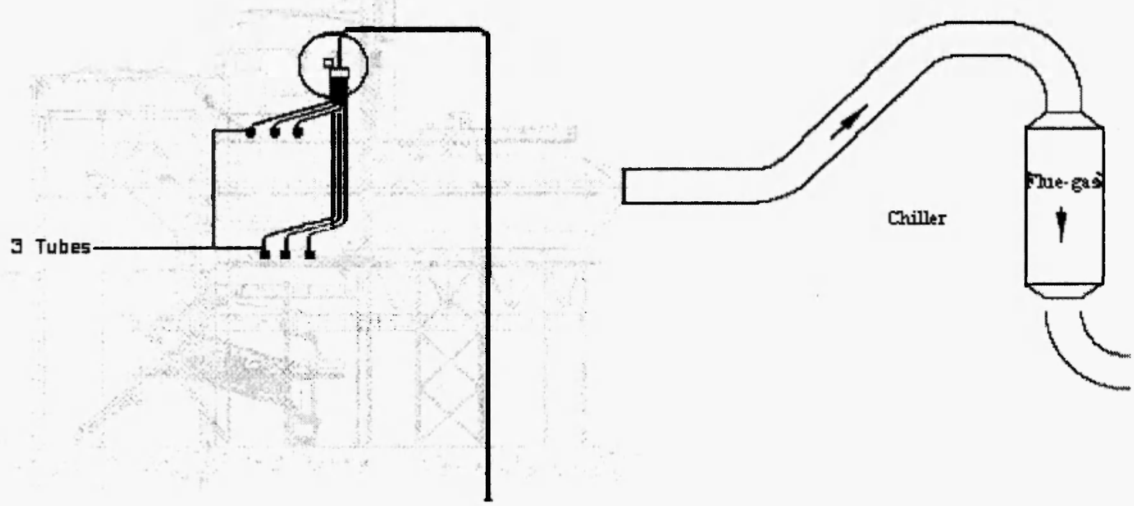

Fig. 2: Gravitary outflow multipoint-injection device within the *post*-combustion zone, equipped with 3 nozzles located in the upper part, and 3 in the lower part.

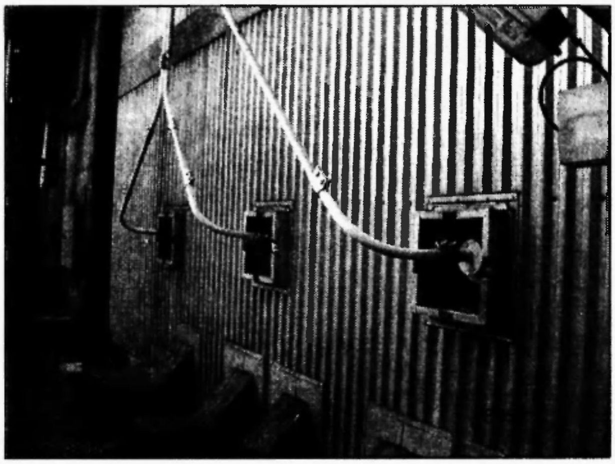

Fig. 3: Details of the three lower injection nozzles.

Experimental tests were conducted at the nominal operation conditions of the incineration plant, each test lasting about 1 hour. The whole innovative pneumatic transport and gravitary-outflow multipoint injection system shown in Figures 2 and 3 is patented by TREDI, Group SECHÉ ENVIRONNEMENT /16/. Granular 46%N urea (1.5 to 2.2 mm) is injected with a propulsion speed of about 25 m/s, at 3 or 6 points within the *post*-combustion zone (up/down, Figures 2 and 3), at a flue-gas temperature of approximately 1273 K and an O_2 concentration monitored to about 10% (gas oxygen content after the boiler is fixed at 8.8 %). These injection locations have been chosen as the best possible injection zones for the optimum NO_x reduction, after modeling of the *post*-combustion zone, coupled with real temperature measuring. The urea injection rate can be regulated and retrofitted in real-time, as it is enslaved to NO_x and NH_3 on-line continuous measurements at the stack, through a multicomponent analyzer (IR, Sick Maihak, model MCS 100 E HW). Gas sampling is performed in radial mode, through a line heated at 458 K, preventing any condensation in the sampling line. No significant difference in NO_x concentrations was observed between axial and radial axis, the exhaust gas flow being fully turbulent. The MCS 100 E Multi-Component Measuring System is a IR photometer system with gas filter correlation method, for simultaneously measuring up to 8 IR-sensitive gas components (HCl, H_2O, SO_2, NOx, CO, CO_2, NH_3 and O_2), with high statistical representation in terms of accuracy, precision and reliability /17/. The MCS 100 E multi-component analyzer is a certified system for continuous emission monitoring of incineration plants (*e.g.* UK MCERTS compliance).

4. RESULTS AND DISCUSSION

When performing the full-scale trials, initial NO_x concentrations, expressed as NO_2 in the raw flue-gas, were in the range 230 to 290 mg/Nm^3 (related to 11% O_2, dry and standard temperature and pressure) and flue-gas flows varied between 130,000 and 144,000 Nm^3/h.

Table 1 shows NO_x reduction efficiencies as function of the N-urea/NO_x molar ratio, when 3 out 6 injection nozzles are placed in the upper part of the post-combustion zone. As expected based on theory, No_x reduction increases with increasing N-Urea/NO_x molar ratio at a constant temperature (~ 1223 K) within the SNCR window. NH_3 emission at stack slightly increased with N-Urea/NO_x molar ratio (trials 1 to 3, Table 1), but it remains far below 10 ppm even for high urea charges, indicating well-choosen and mastered operating conditions.

Table 1

Injection of granular urea (25 kg) mediated by gravitary outflow at 3 injection points located in the upper part of the *post*-combustion zone. Evaluation of NO_x abatement in relation with N-urea/NO_x molar ratio at ~ 1223 K.

Trial	Time (min)	Molar ratio N-urea/$_{NOx}$	NO_x abatement rate (%)	NH_3 content in stack gas (mg/Nm^3)
1	49	2	28	1.12
2	27	2.9	45	1.39
3	23	3.7	83	2.15

NO_x reduction rates are presented in Table 2 as a function of temperature, when 3 out of 6 injection nozzles are activated in the lower part of the *post*-combustion zone. Above 1273 K, around 50% NO_x reduction is achieved reproducibly (trials 5 to 7, Table 2) at N-urea/NO_x molar ratio of 1.5, without any incidence on nitrogen compounds emission at stack (ammonia, NO –data not shown).

Table 2

Injection of granular urea (25 kg) mediated by gravitary outflow at 3 injection points located in the lower part of the post-combustion zone. Evaluation of NOx abatement in relation with temperature at N-urea/NO_x molar ratio < 2 (1.5 to 1.7).

Trial	Time (min)	Temperature (K)	NO_x abatement rate (%)	NH_3 content in stack gas (mg/Nm^3)
4	43	1177	39	3.25
5	24	1326	47	3.15
6	44	1328	47	3.32
7	26	1329	45	3.26

Table 3

Evaluation of NO_x abatement during gravitary-outflow injection of granular urea (25 kg) at 6 injection points located in the upper and in the lower parts of the post-combustion zone.

Trial	Time (min)	Temperature (K)	Molar ratio N-urea/ NO_x	NO_x abatement rate (%)	NH_3 content in stack gas (mg/Nm^3)
8	35	1268	2.6	70	2.8
9	37	1212	1.9	67	2.9

Table 3 shows NO_x abatements and ammonia emissions at stack when granular urea is injected at 6 points distributed both in the upper and the lower parts of the *post*-combustion zone. Our innovative multipoint injection system allows a drastic reduction of NO_x of about 70% at temperatures below 1273 K (1212 to 1268 K) with a low N-urea/NO_x ratio of about 2, and with no consequence on loss of ammonia at stack (trials 8 and 9, Table 3). Such high abatement rates (above 50%) are difficult to achieve in conventional SNCR systems, for example by using peculiar and high-cost reducing additives to generate radicals /18,19/. Injecting urea at six points up and down the *post*-combustion zone rather than at three points only allows to increase by a factor > 2 the NO_x reduction efficiency at N-urea/NO_x ratio around 2 and temperature around 1223 K (67% trial 9 - Table 3, versus 28% in trial 1 – Table 1). Optimal NO_x reduction efficiency of ~70% is achieved by injecting urea at six points within the *post*-combustion zone (up and down), with N-urea/NO_x ratio of ~ 2 and at temperature around 1223 K.

By selecting such a mode of introduction of urea under a solid form, we have avoided its dissolution in an agitated tank, its pumping towards injection nozzles, and also the energy consumption required in *post*-combustion to vaporize water, which is the usual solvent of urea. The yield of denitrification achieved with this modified process is 70 % for a N-urea/NO_x molar ratio close to 2 at 1223 K, and without any incidence of ammonia emission at the stack.

5. CONCLUSION

We described herein a full-scale experimental study to improve the performance of NO_x reduction through conventional SNCR in real waste incineration conditions. We patented an innovative retrofitted gravitary-outflow multipoint injection system for the introduction of solid reductant compounds, making it possible to achieve 50 to 70% NO_x emission reduction by SNCR in stack gases from waste incinerators. Optimal NO_x abatement of 70% was achieved with granular urea pneumatically injected at 6 points within the *post*-combustion zone, at a temperature of ~ 1223 K and with a N-urea/NO_x ratio of ~ 2. No incidence of ammonia emission was observed. Such an injection system is designed to distribute the reagent with maximum coverage and quick mixing with the flue-gas stream, ensuring optimal residence time under the conditions favouring SNCR reactions. Our injection device can easily be adapted to existing SNCR systems whatever the solid reducing reagent used, allowing substantial savings in terms of both investment and running costs (factor 5).

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