

OXIDATION OF NO TO NO₂ IN PRESENCE OF SO₂

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Abstract

In the course of experimental research for abatement of acid gas as HCl, SO₂ and NO_x, carried out in an installed pilot plant, an interesting and promising way for oxidation of NO to NO₂ was observed during dry abatement experiment, using NaHCO₃ powder as reagent.

This oxidation occur using SO₂ contemporary with NaHCO₃, which is also used for dry abatement process and in particular on Na₂CO₃ powder present in the reactor and on the filter bags; Na₂CO₃ is due to decomposition of bicarbonate at working temperature of about 170°C. Mechanism of such oxidation is not completely clear and it will be further investigated.

Analyses for determining conversion were carried out on the inlet pipe and on the outlet pipe of bag filter. Inlet concentration of NO was about 200 ppm. Concentration of SO₂ after filtration was practically 0 ppm. The integration of dry oxidation-removal process can result a zero discharge for NO_x and SO₂ removal. Research is financially supported by T.M.E.

Introduction

NO_x are pollutants which are increasingly falling under scrutiny by regulatory agencies, because they act as a pollutants, acid gas and ozone precursors.

The oxidation of NO to higher oxidation states (NO₂, HNO₂, HNO₃) was proposed as a method for enhancing NO_x removal in flue gas by wet or dry acid gaseous pollutants (SO₂, HCl, etc.) scrubbing system.

Pulsed corona discharge, ozone oxidation, H₂O₂ oxidation are representative examples of past and present investigations on the possibility to enhance NO_x removal efficiency oxidizing NO to NO₂, which can then be removed in a wet scrubber [1].

For instance injecting H₂O₂ in to hot flue gas, the peroxide split in to OH[•] and HO₂[•] radicals at temperature of 500°C and above. The free radicals readily oxidize NO mainly to NO₂. At lower temperature, such as found in boiler exhaust fuel gases, NO oxidation by H₂O₂ need U.V. light activation [2].

On the other hand a variety of combined SO₂ (HCl) and NO_x control methods are in development, but few, if any, have been completely adapted at a commercial scale, because of high costs and/or lack of simplicity.

The possibility of interaction between SO₂ and NO in presence of chemical compounds such as Calcium Hydroxide [3,4] or Sodium Bicarbonate [5] under proper temperature conditions has already been reported in literature. Injection of such sorbents in gaseous stream containing O₂, SO₂, and NO can lead to oxidation of NO to NO₂ and to contemporary reaction between sorbent with formation of calcium or sodium sulfate and nitrate.

Until today such reactions have not been applied on incinerator waste gas treatment or conventional power plants.

Dry processes are used for waste gases treatment on MSW or RDF incineration plant as primary stages followed by a final wet stage consisting in a washing column using alkaline solution.

In incineration plants, concentration levels of SO_2 are very low, around 100 ppm, whilst concentration of NO_x are around 400-500 ppm and NO is predominant, 80-90% of total NO_x . In these cases oxidation of NO in presence of SO_2 and its abatement can be carried out by dry and wet stages already present on incineration plants [6].

Our pilot plant was used firstly to test efficiency of abatement on HCl and SO_2 and subsequently to verify the possibility for using an oxidative process to transform NO to NO_2 and its abatement by dry and wet processes.

Pilot Plant and Procedures

The experimental plant is described in Fig.1.

Fan P2 with variable speed drive, installed after final column C2, sucks air into the pilot plant. In order to simulate incinerator waste gas, air is heated in E1 up to 180°C ; NO and SO_2 are added to the gas stream for reaching the required concentration and milled NaHCO_3 is fed to gas stream before entering the decomposition reactor R1.

Air goes through the decomposition reactor where sodium bicarbonate decomposes to sodium carbonate and CO_2 and H_2O . In R1 the contact between decomposing NaHCO_3 and NO and SO_2 begins. After that, the gas goes through the filter bag F1, where reactions are completed.

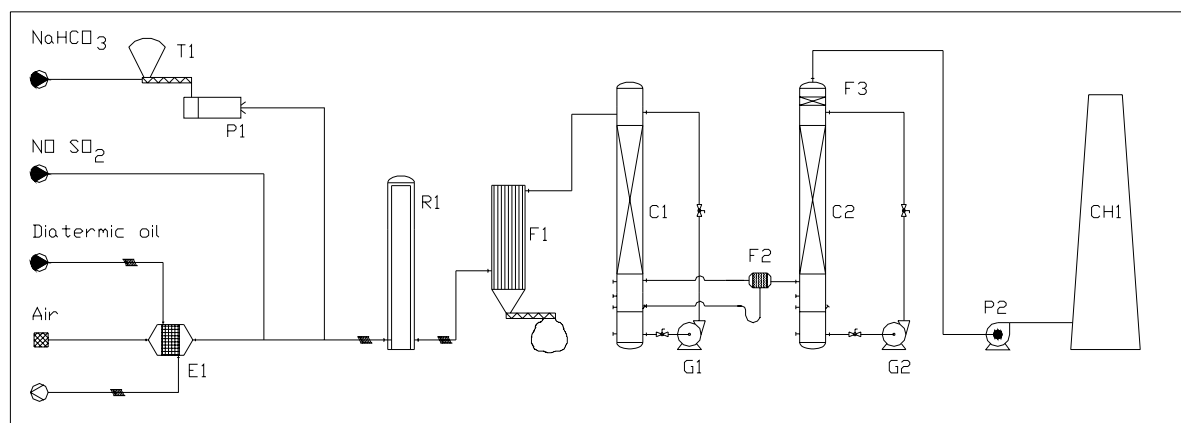


Figure 1. Simplified sketch

In the plant, gases, after dry abatement, are fed to co-current washing column C1.

After column C1 an impact entrainment separator F2 is positioned in order to minimize entrainment between column C1 and C2.

After separator F2, gas flows into counter-current column C2. The top of column C2 is equipped with a wire mesh demister F3. Inside C1 and C2 there is a NaOH water solution.

The requested concentration of NO and SO_2 in the inlet air stream was achieved by a gas-spiking system, which consists of mass flow controllers and 15 m of 0.1 m diameter stainless steel tubing, placed between air heater E1 and the sorbent injection point. SO_2 and NO are injected separately as relatively pure gases.

Air stream was analysed for SO_2 , NO and NO_2 concentration at the end of the spiking 15 m tube: upstream the sorbent injection point the NO_2 species was always absent.

Gaseous stream were continuously sampled.

During each test a computerized data acquisition system continuously records gas concentrations and system temperatures.

Gas stream temperature decreases from solid injection point to bag filter outlet, due mainly to heat loss through the walls of the filter.

Contact time between entrained decomposing sorbent and SO₂, O₂ and NO/NO₂ is of the order of eight seconds in the reactor R1 tract and subsequently in the order of minutes in the baghouse and through solid panel on the cloths.

Cleaning of the bags is performed at the beginning and at end of each test period. Solid samples from baghouse cleaning operation and from air flowing out from the reactor R1 were collected.

Characteristics of apparata are given below:

E1 Heat exchanger 65600 kcal/h;

R1 Reactor, diameter 0.700 m, height 4.5 m, volume 1,73 m³;

F1 Bag filter, tissue Nomex antistatic; filtration area 30 m²; filtration velocity 0.77 m/min;

T1 Screw conveyer, 1-10 kg/h;

P1 Mill, particles diameter 80% under 50 µm;

C1 Co-current packed tower, packing height 4 m, diameter 0.7 m, Raschig rings 2" PE;

F2 Impact type entrainment separator, Type Vico-Vane Costacurta;

C2 Counter-current packed tower, packing height 4 m, diameter 0.7 m, Raschig rings 2" PE;

F3 Wire mesh demister, Type Vico-Chevron Costacurta;

P2 Fan up to 1200 Nm³/h, head 10 kPa;

Operative conditions are given in Tab.1

Parameters	Range or value
Air flow rate	500 m ³ /h
Air inlet temperature	184 °C
Air after reactor R1 temperature	160°C
Air after bag filter F1 temperature	140°C
Inlet SO ₂ concentration	0-400 ppm
Inlet NO concentration	100-200 ppm
SO ₂ /NO mole ratio	0-2
2NaHCO ₃ /(SO ₂ +2NO)	4

Table 1

Instrumentation

Air flow rate is measured by means of a TSI Inc. hot wire anemometer Velocicalc Plus Mod. 8386(A) at the air inlet duct.

LAND Mod. Lancom III analyser for NO, NO₂ and SO₂ analysis.

Chemiluminescent analyser API Mod. 200 for NO and NO₂.

TGA (Pyris 1 Perkin Elmer Termogravimetric analyzer) for bicarbonate.

DIONEX ion-chromatograph for nitrate, nitrite, sulphate.

Spectrum One" Perkin Elmer Spectrofotometer. for FT-IR spectra on solid reacted sample.

Results and Discussion

Fig.2 shows the trends of concentrations of NO, NO₂ and SO₂ in two points of the plant: after reactor (a) and after bag filter (b) in time.

It can be observed that in correspondence with SO_2 injection concentration of NO decreases and NO_2 appears.

Conversion of NO to NO_2 up to 90% has been reached with a molar ratio SO_2/NO of 1.5.

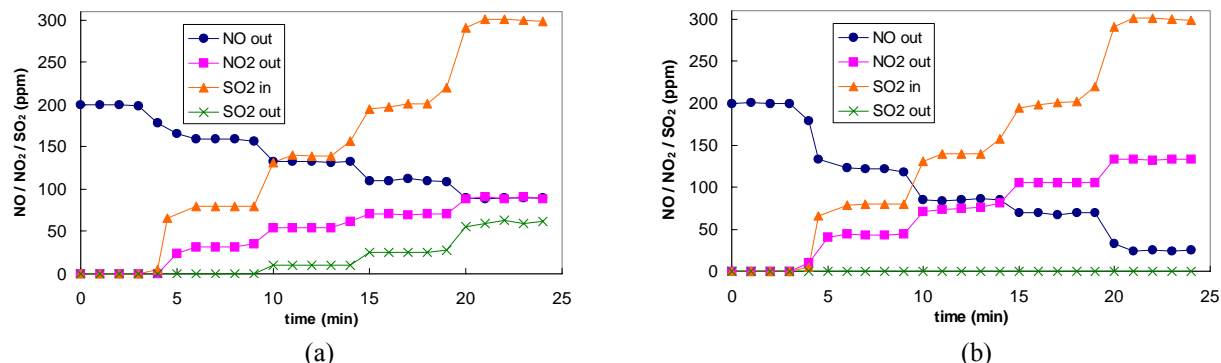


Figure 2. Time resolved profile for NO, NO_2 , SO_2 (a) after reactor and (b) after bag filter and for SO_2 at the inlet

Fig.3 shows the influence of molar ratio SO_2/NO on percentage of NO oxidation, with an inlet concentration of NO of 200 ppm.

When SO_2 is not present, after the reactor there isn't conversion, whilst after the filter a conversion of 5% is present. An interaction between NO, O_2 and sodium carbonate present on the bags of filter can be supposed.

Runs carried out, feeding to the plant NO and SO_2 without sodium bicarbonate haven't shown any interaction between them. Presence of sodium bicarbonate allows reactions in heterogeneous phase between NO, SO_2 and sodium bicarbonate during its decomposition to sodium carbonate.

In fact, samples of solid picked up after reactor and analysed by TGA show a conversion to carbonate of 60% and this is accordance with NO conversion. Samples of powder separated by bag filter analysed by TGA show a total conversion of bicarbonate to carbonate.

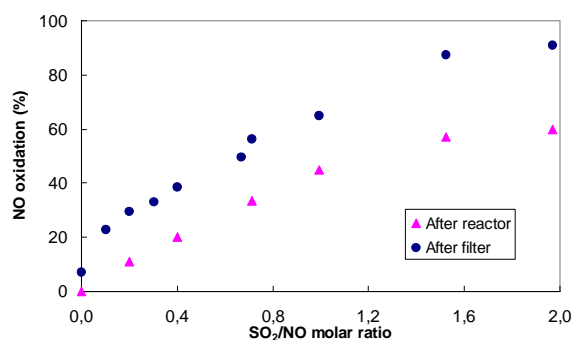


Figure 3. Percent of NO oxidation Vs SO_2/NO molar ratio after reactor and after bag filter.

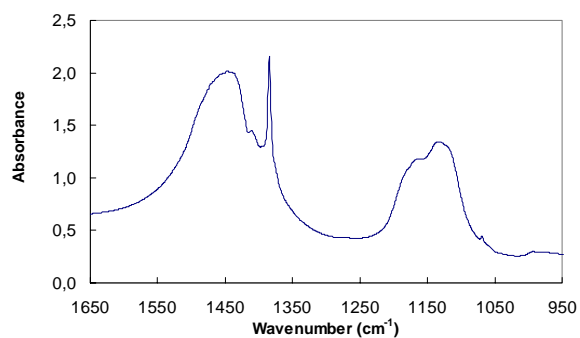


Figure 4. FT-IR spectrum of reacted sorbent on baghouse cloths.

As conversion of NO to NO_2 evaluated on inlet concentration of NO does not correspond with a quantity of formed NO_2 , a reaction of NO_2 as nitrate or nitrite in solid phase has been assumed.

Analysis of solid sample performed by ionic chromatography and by FT-IR technique seem to confirm this hypothesis as presence of nitrate and sulphate has been determined.

The FT-IR spectrum in Fig.4 exhibited a narrow strong band at 1384.4 cm^{-1} . This band is assigned to the ν_3 stretching band of the NO_3^- ion which appears as the strongest peak in most nitrates [7,4]. The band from 1100 to 1200 cm^{-1} appears in most sulphate [4].

Different concentrations of NO_2 were obtained changing NO inlet concentration between 100 and 200 ppm and SO_2 inlet concentration between 20 and 300 ppm . Obtained data have been elaborated to make evident total abatement of NO_x in the plant.

Fig.5 shows percentage of NO_2 captured by sorbent in function of NO_2 formed by oxidation.

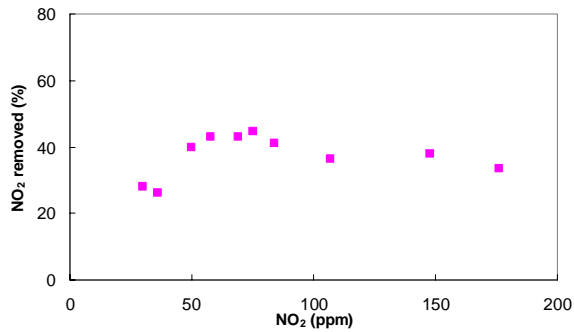


Figure 5. Percent of NO_2 removed after bag filter Vs concentration of NO_2 formed.

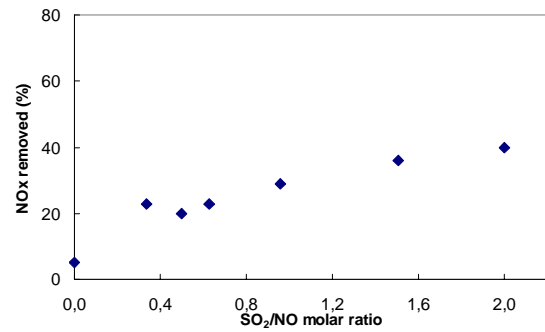


Figure 6. Percent of NO_x removed after bag filter Vs SO_2/NO molar ratio

All these data show that NO_2 dry efficiency abatement is around 40% , on the field of explored concentration, in any case, at least higher than 50 ppm of NO .

Fig.6 shows data of overall abatement of NO_x for an inlet concentration of NO of 200 ppm in function of molar ratio SO_2/NO for integrated system of oxidation and abatement.

In order to further increase abatement efficiency of NO_2 after bag filter, the gas stream is fed to column C1 and C2 operating with a caustic soda solution around 3% in weight.

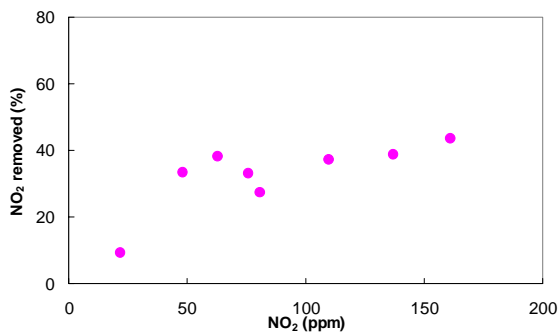


Figure 7. Percent of NO_2 adsorbed in column Vs concentration of NO_2 outlet bag filter

The effect of washing is shown in Fig.7 where, in function of filter outlet concentrations, abatement efficiency of washing system is given.

Taking into account dry and wet abatement overall efficiency of abatement is around 60% . But it is important to notice that large part of NO can be removed by this process.

According to all these experimental runs, a reaction mechanism can be suggested. As it well known, Sodium bicarbonate, injected in a gas stream, at temperature between 140

and 200°C , is decomposed to CO_2 , H_2O and sodium carbonate with very high superficial area. Sodium carbonate can react effectively with acid gas. Experimental runs have shown NO can react with system $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$ only if SO_2 is present.

Stoichiometry of reaction which can justify oxidation of NO to NO_2 and contemporary formation of sodium sulphate and nitrate is the following:



It has been shown that in excess of NO, the oxidated fraction is practically coincident with the stoichiometric one. However, either in excess of NO or in excess of SO₂, only a fraction of produced NO₂ becomes sodium nitrate, the residual fraction of NO₂ remains in gas phase.

It can be assumed (Fig.8) that, in experimental conditions, oxidation reaction passes through an intermediate compound (a) because of reaction of gaseous compounds with sodium bicarbonate or with carbonate, obtained by thermal decomposition of bicarbonate.

Intermediate unstable compound can follow reaction path (1), which leads to sodium sulphate and NO₂, or reaction path (2) reacting with sodium carbonate to give sodium sulphate and nitrate and finally path 3, where reaction between NO₂ and sodium carbonate, in sequence with path 1 is possible. It can be also supposed that higher temperatures make path 1 easier than path 2.

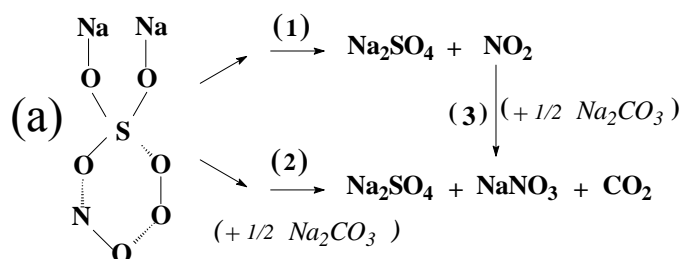
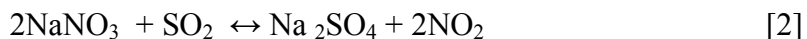


Figure 9. Reaction mechanism

When temperature increases, the reaction given below could be important, from the point of view of NO_x abatement efficiency:



Conclusions

- Presence of SO₂ in a dry abatement process using sodium bicarbonate gives oxidation of NO to NO₂;
- Optimum molar ratio SO₂/NO is around 1.5;
- Oxidation happens in heterogeneous phase and mechanism of reaction involves NO, SO₂ and sodium carbonate;
- As efficiency oxidation of NO is very high, > 90%, so real problem is abatement of NO₂;
- Consumption of SO₂ for oxidation of NO could be sufficiently high depending on concentration of NO, but limits imposed by European legislation can be respected without using thermal or catalytic reduction of NO_x.

References

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