Nitrogen Oxide Emission Control — A Review

by

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ABSTRACT

The problems due to nitrogen oxide emission have been stressed and sources identified. A few recent measures for reduction of nitrogen oxide emissions are enumerated. Current developments in dry denitrification techniques viz. catalytic, non-catalytic and adsorption techniques are outlined and a detailed comparative account of wet absorption of nitric oxides by various absorbents has been given. Importance of a few simultaneous desulfurisation and denitrification techniques has also been incorporated. Lines of future research relating to specific denitrification techniques are proposed.

INTRODUCTION

The problem of ambient air pollution in industrial and metropolitan areas is a consequence of rapid industrialization. The oxides of nitrogen are the second most abundant air contaminants found in industrial environment. Nitrogen oxides result from a variety of high temperature combustion processes, such as in thermal power plants, automobile engines, chamber process of sulfuric acid manufacture and from the manufacture of nitric acid. Nitric acid conversion of nitrogen oxides in the concentration range of 4000 ppm or less is not an economic proposition. However concentration of nitrogen oxides above 200 ppm (i.e. 0.02% by volume) in the effluent gas constitutes a potential air pollution problem and warrants the incorporation of suitable abatement measures for the gaseous effluent streams.

SOURCES OF NITROGEN OXIDE EMISSION

Conventional coal and MHD power plants emit upto 2000 and 5000 ppm of nitrogen oxide respectively. The tail gases of a nitric acid plant contain around 3000 ppm of nitric oxides. A two-ton electric steel making furnace emits upto 44 kg of nitrogen oxides per day. However, the major source of nitrogen oxide pollution originates from gasoline-powered motor vehicles

The emission problem due to motor vehicles, scooters and three-wheelers is critical for some of the crowded cities of India. Around 86000 motor vehicles and a number of scooters and three-wheelers plying over an area of 600 sq. kilometers of Greater Bombay and the industries taken together contribute significantly to nitrogen oxide emission. The average concentration of nitrogen oxide estimated from ten key industrial sectors of Bombay was found to be 45 micrograms per cubic metre.

EFFECTS OF NITROGEN OXIDE EMISSION

Nitrogen dioxide ($NO_2 \rightleftharpoons N_2O_4$), which is a reddish brown gas, causes irritation to the upper respiratory tract of human beings, leading to other physiological problems. In combination with moisture in the atmosphere, nitrogen oxides form droplets of nitric acid. These acidic mists and smog cause corrosion to metallic structures in the plant and its vicinity.

NITROGEN OXIDE EMISSION STANDARD

Standards for nitrogen oxide emission prevalent in different countries vary considerably in nature The standards for emission of nitrogen oxide as determined by the environment agency in 1973 in Japan are given in Table 1. The standard values have further been strengthened.

Table- 1: Emission standards for nitrogen oxides on existing facilities in Japan.

(Gas flow rate of 100,000 Nm^3/h and over)

Kind of facilities	Standard values existing facilities, ppm
1. Boiler- Gas firing	130
Coal firing	750
Solid-fuel firing	600
Oil tar firing	280
2. Metal heating furnaces	220
3. Oil heating furnaces	210

In U. S. as found by Lyman, plant life becomes damaged when the No_x concentration reaches about 25ppm while the safe limit for human beings is about 5ppm. In India, concentration above 0.02 per cent by volume (i.e. 200 ppm) constitutes a potential air pollution problem.

MEASURES FOR REDUCTION OF NITROGEN OXIDE EMISSION

Viewing the effects of omission of nitrogen oxide and safe limits of its concentration in air, measures for its reduction are quite essential. But the control of nitrogen oxide pollution has proved to be difficult and no widely applicable methods have so far been developed for commercialization.

However, countermeasures involving the use of low nitrogen fuel, cleaning up of exhaust gases through the use of catalytic converters (e.g. iron-chromium catalyst on silica-alumina support) improved methods of combustion (staged combustion) and engine remodelling by manufacturers are being promoted in some advanced countries. But these countermeasures are not sufficient to reach the safe limit of this pollutant concentration. Hence suitable denitrification techniques must be considered, particularly for the nitrogen oxides-rich exhaust gases.

EXHAUST GAS DENITRIFICATION TECHNIQUE

Reduction of nitrogen oxides from combustion flue gases to below 100 ppm will require flue gas denitrification techniques which are either of the dry or the wet type.

Dry Processes

Catalytic Reduction

A) Solid Reductant: Iron ore (93.33% Fe_2O_3 and 2.48% SiO_2) was successfully tested for nitrogen oxide reduction in internal combustion engines. This cheap and inexpensive material can be a potential catalyst for dry denitrification of flue gas in due course. A recent investigation reveals that quantitative conversion of nitric oxide (Conc. below 6000 ppm) into N_2 and CO_2 is possible above 440°C by a composite nickel or cobalt catalyst substrate with small amount of rare earth xiade and platinum metal as co-catalyst supported on active carbon without addition of any reductive gases.

(B) Gaseous Reductant: Reducing agents like ammonia, hydrogen, carbon monoxide and methane can reduce nitrogen oxides to nitrogen and water in the temperature range of 300-400°C in presence of catalysts. Oxides of iron, copper, vanadium and chromium supported on an alumina carrier are effective as catalysts for 'clean gas' and alumina is sulphated by sulphur oxides for dusty gas. The reactions involved are:

$$6\,NO + 4\,NH_3 \rightarrow 5\,N_2 + 6\,H_2O \quad \ldots \quad \ldots \quad (1)$$

$$6\,NO_2 + 8\,NH_3 \rightarrow 7\,N_2 + 12\,H_2O \quad \ldots \quad \ldots \quad (2)$$

This denitrification reaction is accelerated by the coexistence of oxygen in flue gases. The reaction is

$$4\,NO + 4\,NH_3 + O_2 \rightarrow 4\,N_2 + 6\,H_2 \quad \ldots \quad . \quad (3)$$

Ammonia as the reductant has the unique advantage of selective reaction with nitrogen oxide inspite of the presence of oxygen.

The process, being a dry one, does not pose any waste water problems due to reaction water. However problems associated with the process are :-

(1) Processing of flue gases is necessary in the optimum reaction temperature range of 300-400°C.
(2) Reduction of catalyst activity by sulphur dioxide and particulates;
(3) Plugging of catalyst bed by particulates.

Non-catalytic reduction by Ammonia

According to the Exxon Research and Engg. Co. ammonia can react selectively with nitrogen oxide to produce nitrogen and water in the temperature range of 900-1100°C. However the limitations of the method are as follows.

a) Low denitrification efficiency of the order of 50% approximately.
b) Variation of denitrification efficiency with change in boiler load factor.
c) The danger due to the emission of unreacted ammonia along with the flue gases.

A recent study shows that nitric oxide reduction with ammonia can be accelerated in presence of hydrogen peroxide, in the temperature range from 500°C to 600°C under one atmospheric pressure. In the absence of oxygen, nitrogen oxide reduction ratio of more than 90% has been obtained for NH_3/NO = 1.5 and H_2O_2/NO = 1 at 550°C.

Adsorption-desorption techniques

Suitable adsorbents like active carbon and synthetic zeolites can be used as adsorbents for removal of nitrogen oxides. Active carbon adsorption will be unsuitable for flue gases where oxygen is present However synthetic zeolites can retain NO_x effectively, which can be recovered as enriched NO_x and nitric acid by regenerating the bed at elevated temperature with air and/or steam.

This technique, when employed in an acid plant, not only reduces the NO_x emmission in the waste gas stream but partly adds to the acid production also. About 4 to 5 tons of 60% HNO_3 could be added to a 300 tons per day acid plant.

Wet processes

More than 90% of the nitrogen oxides emitted from stationary combustion sources being nitric oxide, its removal from the flue is more important as compared to that of nitrogen dioxide. The efficiency of removal of nitric oxide by the wet scrubbing processes is very much affected by its low solubility (0.00376 g in 100 g of water at 50°C) in absorbents.

Various absorbents and absorption systems to remove nitric oxide are presented below. Some of the processes are still in the development stage.

Gas phase oxidation process

In view of its low solubility NO is oxidized to NO_2 or the anhydride of nitric acid (N_2O_5) before absorption by ozone or chlorine dioxide as oxidizing agent.

A 100,000 Nm^3/hr pilot plant has been successfully operated, the method being that of recovering dilute nitric acid by adding ozone to the flue gases of a natural gas-fired boiler to yield the anhydride of nitric acid which is then absorbed by water.

Main drawbacks of the process are:

i) difficulty in utilizing the dilute nitric acid produced when contaminated with SO_2 and particulates.
ii) enormous electric power requirement to produce ozone.

Liquid phase oxidation-absorption process

Nitrogen oxides are absorbed with high efficiency by aqueous solutions of oxidizing substances such as potassium permanganate and sodium chlorite either in a neutral or in an alkaline solution.

The absorption of NO in aqueous solution of $KMnO_4$ was carried out in a batch stirred vessel with a plane gas-liquid interface. The reaction involved is

$$NO + MnO_4 \longrightarrow NO_3 + MnO_2 \quad \ldots\ldots (4)$$

The reaction for absorption of lean NOx from flue gases in an aqueous alkaline solution of $NaClO_2$ and NaOH is written in ionic form as $4NO + 3ClO_2^- + 4OH \longrightarrow 4NO_3 + 3Cl^- + 2H_2O$ (5)

The absorption of NO in aqueous mixed solution of $KMnO_4$ and NaOH was also performed with a batch stirred vessel with a plane gas-liquid interface

The reaction involved is : $NO + MnO_4^- + 2OH^- \longrightarrow NO_2^- + MnO_4^{2-} + H_2O$ ... (6)

The reaction between NO and $KMnO_4$ in neutral as well as alkaline solutions was found to be first order with respect to both NO and $KMnO_4$.

The specific rates of absorption of nitric oxide in aqueous alkaline solutions of sodium dithionite and sodium sulfide have been measured and the order of reaction and the rate constant have been determined.

The method of alkaline absorption is suitable for treatment of exhaust gases from the acid cleaning, metal plating and nitric acid units where nitrogen dioxide and nitric oxide are nearly in equal proportions.

Gas phase oxidation-reduction process :

This process utilizes zone oxidation to yield nitrogen dioxide and subsequent reduction by an aqueous solution of sulphite or urea to nitrogen. In addition nitrous oxide, sodium salt or imido disulphonic acid nitrites and nitrates are also formed according to reaction conditions.

This method is suitable for supplementing the effectiveness in removing nitrogen oxides of existing flue gas desulphurization facilities. Since a variety of products are formed in this process, the disposal of waste liquids still poses a serious problem.

Complex salts formation-absorption process:

In view of the low solubility of nitric oxide the only method for its direct absorption by wet process is complex salts formation-absorption process as is widely adopted in Japan.

Complex salts are formed in the following manner : Nitric oxide is absorbed by ferrous sulphate so that

$$FeSO_4 + NO \rightleftharpoons Fe(NO)SO_4 \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

The significant disadvantage of waste liquor is overcome since the absorbent can be easily regenerated.

As an improvement on the above, ferrous chelate compounds of ethylene diamine tetraacetic acid can be effectively used as an absorbent along with sodium.

Ammonium sulphite performs the functions of regeneration of complex reaction products to the active absorbent.

Absorption of nitrogen oxides in nitric acid

A mathematical model has been devised for the absorption of nitrogen oxide into dilute nitric acid and has been tested in a laboratory three stage sieve plate column.

The overall chemical reaction involved in the steady state absorption of NOx compounds into water or dilute HNO_3 are represented as :

$$O_2 + 2NO_2\,(g) \rightleftharpoons N_2O_4\,(g) \quad \ldots\ldots (8)$$

$$N_2O_4\,(g) \rightleftharpoons N_2O_4\,(l) \quad \ldots\ldots (9)$$

$$N_2O_4 + H_2O\,(l) \longrightarrow HNO_3\,(l) + HNO_2\,(l) \quad \ldots (10)$$

$$3HNO_2(l) \rightleftharpoons H_2O(l) + HNO_3(l) + 2NO\,(g) \quad \ldots (11)$$

$$2NO(g) + O_2\,(g) \longrightarrow 2NO_2\,(g) \quad \ldots \quad \ldots \quad (12)$$

The investigations revealed that the conversion of NOx varies directly with the gas and liquid flow rates and the partial pressure of NO_2 ($NO_2 + N_2O_4$, a mixture of nitrogen dioxide).

Recent studies on the absorption rate and mechanism of NO_2-N_2O_4, gas mixtures diluted with nitrogen into nitric acid solutions at 20°-30° indicate that N_2O_4, which is continuously in equilibrim with NO_2, is preferentially absorbed into diluted nitric acid (25-40% W) as well as into concentrated nitric acid.

However, more investigations are necessary in order to commercialize the process.

Simultaneous desulphurization and denitrification techniques:

In the recent past, the tendency towards complex pollution by different kinds of pollutants has been observed. Among these, the major ones being sulfur dioxide and nitrogen oxides, a few techniques have been developed for a simultaneous desulphurization and denitrification.

Absorption in alkaline/sulfite solutions:-

Simultaneous absorption of SO_2 and NO_2 has been conducted from an SO_2 - NOx- N_2 mixture into an aqueous solution of NaOH and Na_2SO_3 in an agitated vessel with plane interface. The rate of NO_2

absorption into aqueous NaOH solution was enhanced more than in the absence of SO_2, while for aqueous Na_2SO_3 solution the rate was reduced. The rate equations for absorption of NO_2 and SO_2 have been given. It has also been suggested that a possible process may be developed for removing SO_2 and NOx simultaneously from stack gases by an alkaline solution after oxidation of NO and NO_2 which requires prior attention for development.

Simultaneous absorption of SO_2 and NO_2 on solid additive:

Combustion of fossil fuels in a fluidized bed of limestone or dolomite additive has been studied to determine the effects of operating variables on the reaction of pollutant SO_2 and NOx. The level of NOx emission was found to be affected only by a change in temperature.

Further the decrease of NOx emissions with increase of SO_2 emissions indicated the possibility of interaction between NO_2 and SO_2. Use of partially sulfated lime (a reaction product of lime and SO_2) caused a reduction in NOx emissions proportiona to the average concentration of SO_2 in the mode combustor.

The reactions involved are-

$$CaO + SO_2 \rightarrow Ca\,SO_3 \quad (13)$$
$$CaSO_3 + 2NO \rightarrow CaSO_3\,(NO)_2 \quad (14)$$
$$CaSO_3\,(NO)_2 \rightarrow Ca\,SO_4 + N_2 + \tfrac{1}{2}\,O_2 \quad (15)$$

Dry-regenerative adsorption by alkalized alumina

For the simultaneous removal of sulfur dioxide and nitrogen oxide from power plant flue gases, a dry-regenerative adsorption process with alkalize-alumina as the adsorbent was carried out in a labord atory radial flow fixed bed (RFFB) reactor at temperatures between 100-150°C. The process in appreciably exothermic and strong interaction between NO, and SO_2 uptake was apparent. Presence of NO was found to affect the adsorption of SO_2 and absorbent saturation capacity. Regeneration of adsorbent with H_2 at 600°C without appreciable loss of activity is an advantage.

CONCLUDING REMARKS

Most of the nitrogen oxide abatement measures, wet or dry, have yet to pass the laboratory scale of development in the United States. In Japan a few processes viz. the activated carbon process, electron beam radiation, catalytic reduction with ammonia and wet scrubbing have been developed and tested at pilot plant level for simultaneous removal of sulphur dioxide and nitrogen oxides. But many technical problems remain unsolved and impose constraints for ful commercial exploitation of the process. These ot be resolved until further research points the w he tasks that confront the environmental technolo of the world are to utilize effectively the by-p ts generated from the effluent gas denitrification to establish measures for waste water treatment

Bibliography

1. T. Ohtsuka and Y. Ishihara, "Emission control technology for sulphur oxides and nitrogen oxides from flue gas in Japan," *Journal of the Institute of Fuels*, June 1977, p. 82.
2. L. A. Haas, C. Anderson & S. E. Khalafaka, "Decomposition of NO in a silent discharge", *Ind. Eng. Chem, Process Res. Develp.*, Vol 18, No. 1, 1979, p. 143.
3. K. Wark & C. F. Warner, "Air pollution, its origin and control" IEP, A Dun-Donnelley Publisher, New York, p. 357.
4. E. Sada, H. Kumuzawa, and N. Hayakawa, "Absorption of NO in Aqueous Solution of $KMnO_4$" *Chem. Engg. Sci.*, Vol. 32, No. 10, 1977, P. 1171.
5. E. Sada, H. Kumuzawa, I. Kudo & T. Kondo, "Absorption of lean NO_x in Aqueous Solutions of $NaClO_2$ and NaOH", *Ind. Eng. Chem. Process Res. Dev.*, Vol. 18, No. 2, 1979, p. 275.
6. R. M. Counce & J. J. Perona, "A mathematical model for NO absorption in a sieve plate column" *Ind. Eng. Chem. Process. Res. Dev.*' Vol-19, No. 3, 1980, p. 426.
7. R. M. Counce & J. J. Perona, "Gaseous Nitrogen Oxide absorption in a sieve plate column", *Ind. Eng. Chem. Fund.*, Vol. 18, NO. 4, 1979, p. 400.
8. J. M. Tarbell & C. A. Petty, "Combustion Modifications for the control of No_x emissions", *Chem. Engg. Science*, Vol. 32, No. 10, p. 1177.
9. Kalback, W M. Sliepcevich, "Kinetics of Decomposition of Nitrous Oxide", *Ind. Eng. Chem. Fund* Vol. 17, No. 3, 1979, p. 165.
10. K.C. Salooja, "Combustion with high efficiency and low pollution emission", *Energy World*, Vol. 54, No. 12, p.6.
11. F.P.M. Candles, K M. Hodgson, R.H. White and J D. Bowman, "Reduction of Nitric Oxide with Metal Sulfides", *Ind. Chem. Process Res. Dev.* Vol. 19, No. 1, 1980, p. 108.
12. D.W. Pershing & J.O.L. Wendt-"Relative contributions of volatile nitrogen and char nitrgen to NOx emissions from pulverized coal flames", ibid, Vol. 18, No. 1, 1979, p. 60.
13. H Takeuchi, M. Ando & S. Kizawa, "Absorption of Nitrogen Oxides in Aqueous Sodium sulfite & Bisulfite solution", ibid, vol 16, No. 3, 1977, p. 303.
14. H. Takeuchi, K. Takahashi, N. Rizawa, "Absorption of No_2 in sodium sulfite solution from air as a Diluent", ibid, Vol. 16, No. 4, 1977, p. 386
15. P. S. Rao, M.K.G. Babu and B.S. Murthy, "Prediction of Nitric Oxide Emission from Diesel Engines", *Indian Journal of Technology*, Vol. 16, May 1978, p. 178,

16. B Nagalingam, K.V. Gopalkrishnan & B.S. Murthy, "Use of Iron Ore pebbles as catalysts for reduction of NO in Automobile exhaust", *Indian Journal of Technology*, Vol. 15, No.12,1977, p. 521.

17. J.B. Lefers and P.J Vander Berg, "Absorption of NO_2/N_2O_4 into diluted and concentrated nitric acid", *Chem. Eng. Journal*, Vol. 23, March 1982, p. 211.

18. S. Azahata, H. Akimoto & Y. Hishinuma, "Effect of Hydrogen peroxide on homogeneous gas phase NO reduction reaction with NH_3", *AICHE Journal, Chem, Eng. Research & Dev.*, January 1982, p. 7.

19. T: Inui, T. Otowa & Y. Takegaml, "Complete conversion of No over the composite catalyst supported on Active Carbon", *Ind. Eng. Chem. Proc. Res Dev*, Vol. 21, No. 1, 1982, p. 6.

20 J.R. Mudakavi, "Pollution Problems in Fertilizer Industry", *Chemical Age of India*, Vol. 31, No. 12, 1980, Eco-1/5.

21 H. Takeuchi & Y. Yamanaka, "Simultaneous absorption of SO_2 and NO_2 in Aqueous solutions of NaOH and Na_2SO_3", *Ind. Eng. Chem. Process Res. Dev*, Vol. 17, October 1978, p. 389.

22 A.A. Jonke, G.J. Vogel et al, "Pollution control capabilities of fluidized-bed combustion", Air pollution and its control-AIChE Symposium series, Vol 68, No. 126, p. 241.

23 G A Hammons and A. Skopp, "A regenerative limestone process for fluidized coal combustion and desulfurization", Air pollution and its control -AIChE Symposium series, Vol. 68, No. 126, p. 252.

24. B.B. Sundaresan, "Removal of Oxides of Nitrogen from waste gas streams in nitric acid manufacture", Souvenir of Chemical Engineering Association of Coimbatore Institute of Technology, 1971, p. 31.

25. T.Furusawa, T.Hondā, J.Takano & D. Kuni, "Nitric acid Reduction in an Experimental fluidized bed coal combustor" Fluidization, Proceedings of the 2nd Engineering Foundation Conference, Cambridge, England, April 1978,p.314.

26 F.J Pereira & J.M. Bue, "A mathematical model of NO formation and destruction in Fluidized combustion of coal" ibd, P.401.

27. U.C.Mishra, "Instrumental Approach to air pollution monitoring", *Chemical Engineering World*, Vol. 17, No 5, p.53.

28. C.Syamala Rao, "Sulphur dioxide pollution control" ibid, Vol.14,No.6, P.47.

29. G.K.Roy & K.C.Biswal, "Sulphur dioxide pollution control by wet-scrubbing methods", *Journal of the Institution of Engineers (India)*, (Environmental Engineering Division), Vol. 62, pt. EN3, June 1982, p. 120.

30. R.N.Lahiri, "Absorption of Nitric oxide in Aqueous alkaline solution of sodium dithionite and sodium sulfide", *Indian Chemical Engineer*, Vol. XXIII, No. 4, Nov-Dec 1981, p.44.