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Simultaneous Removal of Particulates and NOx Using Catalyst Impregnated Fibrous Ceramic Filters

Keywords: Ceramic Fiber Filters, Catalysts, DeNOx and Dedust

Introduction

The amount of energy consumption in Korea increase continuously in proportion to the economic growth and industrial development, and the required energy is mainly produced from the combustion of fossil fuels, which causes an emission of atmospheric pollutants. It is well known that the sulfur oxides(SOx) and nitrogen oxides(NOx) contained in flue gases are harmful to human health and also causes an acid rain and ozone formation problems in the atmosphere.

There is not a promising single technique or process which can effectively remove all of the nitrogen oxides, sulfur oxides, and particulate pollutants simultaneously.

The development of efficient, cost effective air pollution control device and processes is in great need in Korea to meet the stringent emission standards enforced by the government.

Simultaneous removal technology is one option to reduce the installation sites and to lower the installation and operating cost. This work aims to remove particulates and HAP simultaneously using catalyst impregnated fibrous ceramic candle filters.

Targeted air pollutants and removal mechanisms are particulates by filtration, NOx by SCR(Selective Catalytic Reduction), SO_2 and HCl by oxidation using limes.

Proposed process has an advantage of maintaining high temperatures to enhance oxidation reactions and eliminate reheating to meet temperature windows for effective reduction reactions. If commercialized, developed technology can substitute E.P, scrubber, absorption bed currently in use.

Although test results are limited to pilot scale, potential for commercialization is great in that results are successful on the whole.

Objective

The research is focused on the development and commercialization of high efficiency, cost effective air pollution control system, which can replace in part air pollution control devices currently in use.

In many industrial processes, hot exhaust gases are cooled down to recover heat and to remove air pollutants in exhaust gases. Conventional air pollution control devices such as bag filters, E.P. and adsorption towers withstand operating temperatures up to 300℃. Also, reheating is sometimes necessary to meet temperature windows for S.C.R. Since Oxidation reactions of acid gases such as SO_2, and HCl with lime are enhanced at high temperatures, catalyst impregnated ceramic filters can be candidate for efficient and cost effective air pollution control devices. As shown on Fig. 1., catalytic ceramic filters remove particulates on exterior surface of filters and acid gases are oxidized to salts reacting with limes injected in upstream ducts. Oxidation reactions are enhanced in the cake formed on exterior of filters.

Finally, injected reducing gas such as NH_3 react with NOx to form N_2 and H_2O interior of filters in particulate-free environment. Operation and maintenance technology is similar to conventional bag filters except that systems are exposed to relatively high temperatures ranging 300℃～500℃.

Approach

Attempts were made to remove particulates, NOx and acid gases simultaneously using catalyst impregnated 1m-long fibrous ceramic filters. Candle filter dimensions are 60 O.D ¸ 10t ¸ 1000L, which are vacuum formed from slurries of alumino-silicate fibers and pastes.

Pilot tests were made using particulates collected from Iron and Glass melting processes and NOx were injected using standard N_2 base gas bomb. Objective of this work is to commercialize the multi-filter unit, which can replace the E.P., deNOx, and deSOx units currently in use. If commercialized, installation and O&M cost can be lowered compare to the systems currently in use.

The catalytic filters can replace multi processes with one unit, which allows potential cost reduction in several environmental applications. The performances of catalytic filters were tested at different deposited catalyst amount, particulate matter loadings, lime injection rates, space velocities, operating temperatures, and NO/NH_3 mol ratios.

Catalytic ceramic filters used in this study were impregnated with CuO/Al_2O_3, V_2O_5/TiO_2, $V_2O_5/TiO_2/SiO_2\text{-}Al_2O_3$, respectively. For the experiment, NO(N_2 base) of 1,000 ～ 2,000 ppm and NH_3 of 99.9% were used. As shown on Table 1. test temperatures range 220 to 550℃, NH_3/NO mole ratios, 1～1.2, pulse pressures, 3～5 atm, and pulse cycles, 5 min. Particle collection and NO conversion efficiencies were analyzed using the aerosizer and IMR 3000P gas analyzer. Experiment were performed using filters that have 3～7 wt% V_2O_5 content and 5～9 wt% CuO content. Schematic diagram of experimental apparatus are shown on Fig. 2.

In this work target efficiencies of particulates, NOx, SOx and HCl were set to 99.5%, 90%, 80% and 50% to compete the current air pollution control devices. Also, long term experiments with 12 candle filters were performed at glass melting processes.

Project Description

This work is supported in part by the Ministry of Environment for the last three years, First years Efforts were focused on the test of disc(60O.D ¸ 10t) type catalytic ceramic filters to investigate optimum conditions, which maximizes the removal efficiencies.

For the last two years, pilot tests using one or twelve 1m long candle type catalytic ceramic filters were performed. Test results are satisfied to meet targeted removal efficiencies of particulates, NOx, SOx and HCl.

Results

Tests results are summarized by the category of air pollutants treated.

- Particulates alone

Untreated fibrous ceramic candle filters are commercialized and in good use at many industrial processes including semiconductor manufacturing processes and pyrolysis etc. for particulates removal alone. For 16 months of continuous operation, pressure drops are stable and collection efficiencies are over 99.5% in semiconductor etching processes to remove submicrometer SiO_2 particulates. Ceramic filters are suitable for the treatment of air pollutants at high temperatures in small scale processes where heat recovery system is unnecessary.

- Simultaneous removal of PM and NOx

One meter long ceramic candle filter was tested at 200℃ to 500℃ with 50℃ interval and at 1900 ~ 6600 hr^{-1} space velocities with 1000 hr^{-1} interval. NH_3 was injected at 1.1 mol ratio to NO. At 1000ppm of inlet NO with N_2 base, removal efficiencies were ~90% at near 350℃. NO conversion rates at different temperatures and space velocities are shown on Fig. 3

Similar candle filters are tested at glass melting processes for three months. Flow rates range 5 to 6 Nm^3/hr at temperatures near 350j.

Test plants are equipped with 12 catalytic candle filters mounted horizontally and is shown on Fig. 4. Operating temperature range 310j to 350j with air flow rates of 5 to 6 Nm^3/min. NH_3/NO mol ratio is 1.2 with inlet NO concentrations range 300 to 400 ppm. NO conversion rates are over 90% and are shown in Fig. 5.

- SO_2 and HCl removal test with lime injection SO_2 removal mechanisms are similar to conventional dry scrubbing system other than operating temperatures are relatively higher.

Ceramic filters can withstand up to 500℃, enhancing oxidation reactions with limes in the duct and on the cakes formed exterior of ceramic filters.

This phenomenon is shown on Fig. 6. As operating temperatures are raised up to 500℃, SO_2 conversion rates are increased up to 90%, which efficiency is seldom obtained in conventional dry scrubbing system.

Similar phenomenon is shown on Fig. 7. for HCl oxidation reactions with limes. HCl removal tests are performed at temperature ranges 360℃ to 500℃ and space velocities 2600 hr^{-1} to 6600 hr^{-1}.

- Simultaneous removal of PM, NOx and SOx using catalytic ceramic filters.

A longer term test was performed using 1m long ceramic candle filter to remove PM, NOx, SOx simultaneously. Test lasted 2 months with NO removal test for the first 30 days and SOx and NOx removal test for the last 10 days. Reducing agent and limes are injected intermittently averaging two hours a day and hot gas was flown for the rest on hours.

Test temperatures range 300℃ to 350℃ and space velocities range 2000 to 6600 hr^{-1}.

The higher the NOx removal efficiencies, the lower the space velocities, the closer the optimum temperature windows.

One meter long candle type ceramic filter tests show that simultaneous removal is as effective as conventional separate air pollution control devices. Removal efficiencies of particulates, NOx, SOx, and HCl are over 99.5%, 90%, 75%, 50% at optimum test conditions. Catalysts are slightly degraded after 2 months of operation for the simultaneous removal of particulates and NOx. Developed technology can be best applied to hot gas cleaning systems such as glass melting, semiconductor manufacturing, carbonization and pyrolysis processes.

APPLICATION

Currently, ceramic filters are supplied and in use at pyrolysis, semi conductor production lines and glass melting processes. Developed technologies are protected by 7 patents directly related to the production of ceramic filters and design of filter mounting apparatus in Korea.

FUTURE ACTIVITIES

The technology can be applied to the removal of VOCs and dioxins in future with different catalysts and sorbents utilizing technologies.

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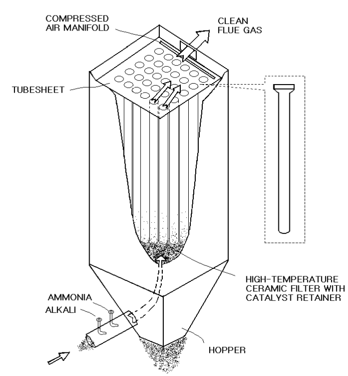
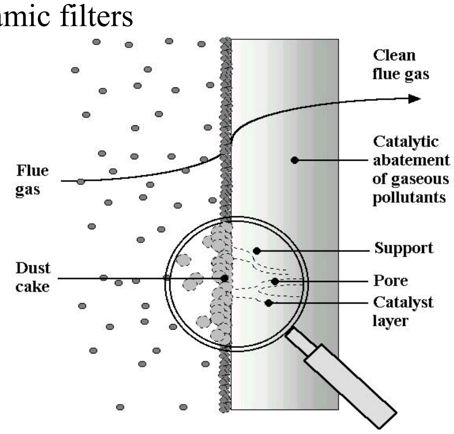
Table. 1. Experimental condition

Items	Value	Items	Value
Temperature	200 ~ 550℃	NO	1,000 ~ 2,000 ppm
Space velocity	9500 ~ 23900 hr^{-1}	NH_3	99.9% (0.2Mpa)
Oxygen	2～5%	Gas analysis	IMR 3000P
NH_3/NO mole ratio	1～1.2	Dust removal efficiency measurement	Aerosizer API Co.
SO_2/lime mole ratio	1～1.2	Dust loading	40, 100g/㎥
HCl/lime mole ratio	1～1.2	Pulse pressure	3atm
SO_2	1,000 ~ 2,000 ppm	Pulse exhaustion time	0.5 sec
HCl	1,000 ~ 2,000 ppm	Pulse cycles	5 min



(A) Simultaneous removal process of dust/NOx/SOx/HCl using catalytic ceramic filters



(B) Basic structure and mechanism of catalytic filters (de-dusting + catalytic abatement of gaseous pollutants)

Fig. 1. Catalytic ceramic filters housing and removal mechanisms

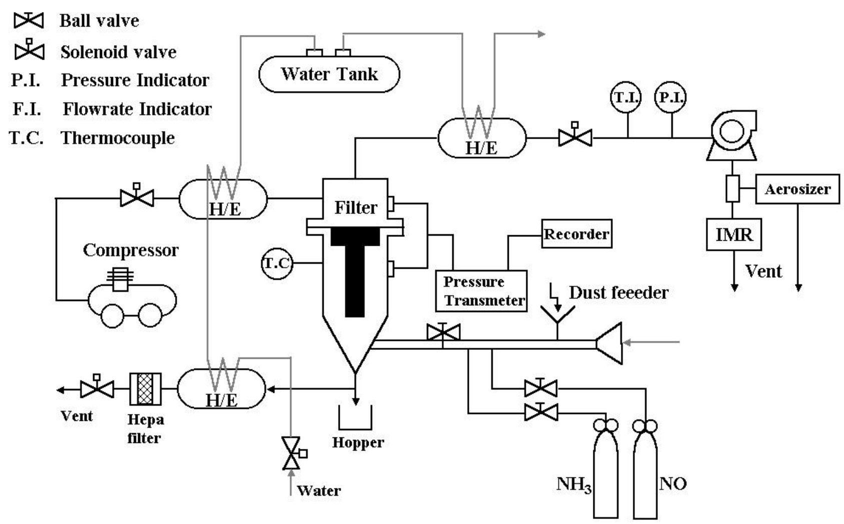


Fig. 2. Schematic diagram of experimental apparatus for simultaneous removal of particulates/Nox

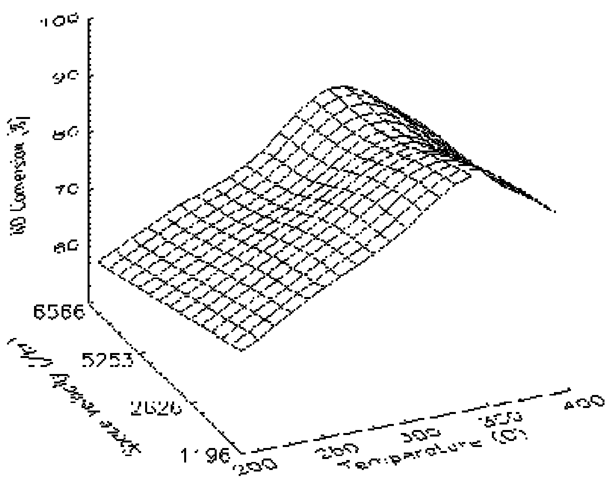
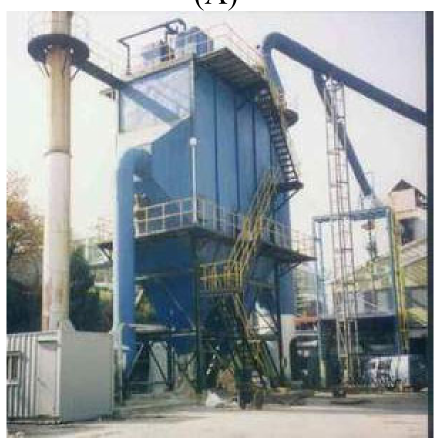


Fig. 3. 3-D diagram for NO conversion rates of G5-17 ceramic filter at different reaction temperatures and space velocities

(A)



(B)

Fig. 4. Photograph of pilot plant installed at T-company ;
(A) pilot plant (B) glass melting furnace.

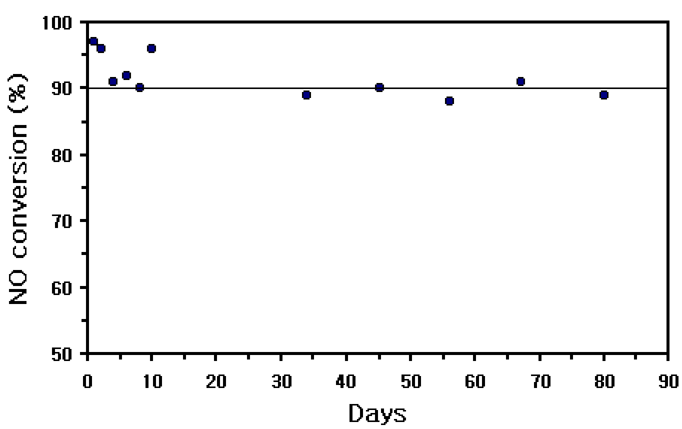


Fig. 5. NO conversion rates of CuO/Al_2O_3-SiO_2 (5wt%) ceramic filters for three months

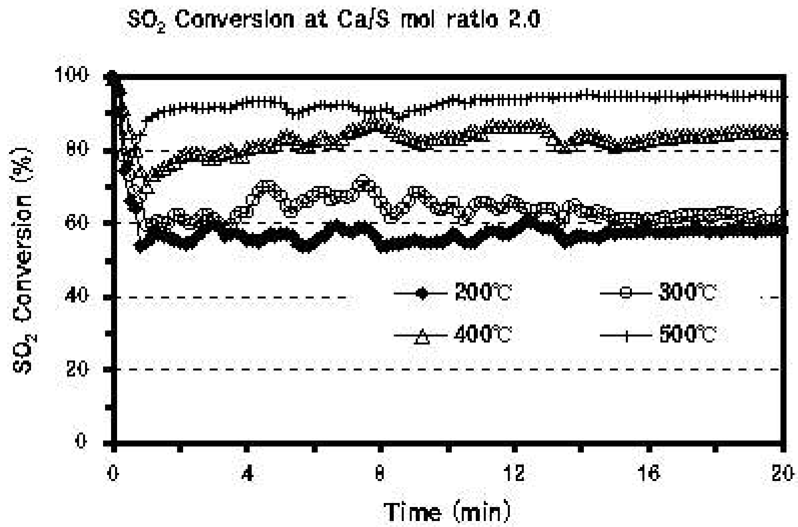


Fig. 6. SO_2 conversion rates of G3-12 ceramic filter with lime injection at Ca/S mol ratio of 2.

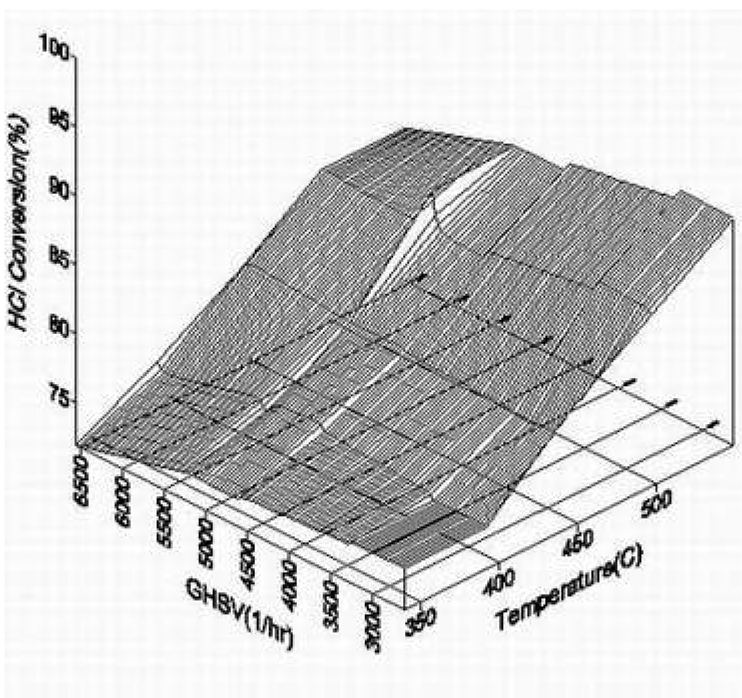


Fig. 7. HCl conversion rates of G5-14 ceramic filter at different reaction temperatures and space velocities ; (A) 350j (B) 400j (C) 500j

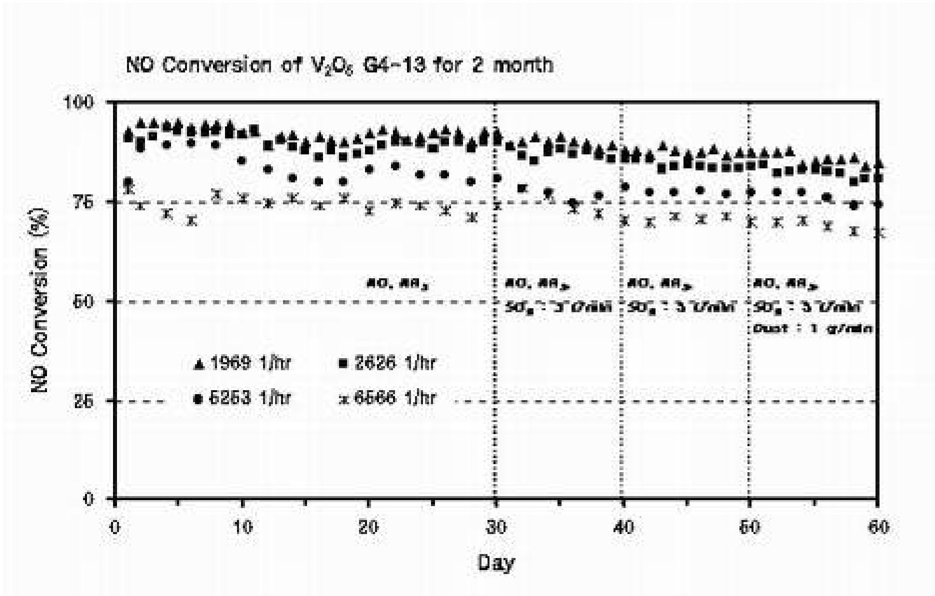


Fig. 8. NO conversion rates of G4-13 ceramic filter for 2 months test