

B-16.1 Reduction technologies of N₂O emitted from stationary sources

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Key Words Nitrous oxide, stationary sources, reduction technology

Abstract

A reduction method of nitrous oxide (N₂O) emission from fluidized bed combustion by addition of particles, which decompose N₂O in the combustor, to bed materials was tested. Al₂O₃ particles was mixed with sand particles and recirculated in the combustor. N₂O emission was decreased to 2/3 of original value at mixing ratio of 35% by weight when coal was burned. NO emission was not changed in this mixing ratio. N₂O was reduced efficiently at higher mixing ratio. However, two times higher NO emission was observed at higher mixing ratio.

Catalytic N₂O decomposition and simultaneous SO₂ absorbing by CaO and several kinds of ceramic particles were examined to use cheaper additives in the fluidized bed combustion. The particle containing CaO and Al₂O₃ destruct N₂O rapidly in reducing condition. In oxidizing condition, Ca mainly decomposes N₂O. When Ca or Al exists as a silicate, however, catalytic N₂O decomposition becomes slow. It means that the ceramic mainly consists of Ca and Al has N₂O destruction ability. For example, cement particle can be used as N₂O destruction additive.

Key Words Nitrous Oxide, Combustion, Mitigation methods

1. Introduction

Nitrous oxide (N₂O) is one of the greenhouse gases and its concentration in the atmosphere is increasing year by year. The sources are natural and anthropogenic. The contributors are estimated in many reports recently due to the importance for the roll in the climate change. Combustion processes of fossil fuel or wastes are one of the major anthropogenetic sources relating the activity of human being. To reduce the N₂O emission from combustion becomes important because mitigation of the greenhouse gases is required in worldwide. Although N₂O inventory from the stationary sources is small, reduction in N₂O seems to be sure.

Recent 15 years, many field measurements were done for N₂O emission from the stationary sources. It is clearly shown that only the fluidized bed combustors (FBC) emit N₂O with higher concentration among the stationary sources. Another major types of combustors emit N₂O in

slightly higher than atmospheric concentration or become a N_2O sink. N_2O reduction technology is required only for FBC. The reason why N_2O emission becomes very high in FBCs is almost understood by fundamental studies. Main reason is relatively low combustion temperature, 1000 ~ 1150K, to reduce NO_x formation and to promote in-situ desulfurization by limestone. In this temperature range, N_2O production reactions much exceed destruction reactions.

Many technologies to control N_2O from FBC are proposed. For example, making hot spot in the gas stream and destruct N_2O , flue gas treatment with N_2O destruct catalyst are tested. In this study, addition of active particles into fluidized bed to control N_2O emission was studied. This method can be widely used in many types of FBCs such as fossil fuel combustion, waste incineration.

2. N_2O destruction by additives in circulating fluidized bed combustor

2.1 experimental

Figure 1 shows a laboratory scale circulating fluidized bed combustor (CFBC) used in this study. The main parts of this CFBC (a riser, a downcomer, a cyclone and an L-valve) are made of quartz. The riser is 23 mm in inside diameter and 2300 mm in height. The diameter of the downcomer is equal to that of the riser. Downcomer and riser are connected with an L-valve. Both riser and downcomer were divided into five sections. In the riser section, all sections are covered by electric furnaces. In the downcomer, lower three sections are covered by electric furnaces, and upper two sections are covered by heat insulators. Power supplied to each electric furnace was controlled independently.

Circulation of solid particles was driven by injection of the air into the L-valve from two positions. Silica sand particles, the average diameter of 0.1 mm, were used as a bed material. A typical circulating rate was 20 ~ 30 $kg/m^2.s$. This value is almost same as that of full scale CFBC. Fuel, Jellinbah East coal, particles were dried and classified to 0.177 ~ 1.0 mm, and fed continuously into the main air flow by a small screw feeder. Limestone for desulfurization was not added in this experiment. For O_2 , CO_2 , CO , NO and N_2O , on-line analyzers were used. Analog output data from gas analyzers and thermocouple were converted to the digital data and were recorded on a computer in every 2 seconds. Additive for N_2O reduction was alumina (g-alumina) particle and its mean diameter was 0.160mm.

2.2 Results and discussion

NO and N_2O emission are shown in Figs. 2 and 3 as a function of O_2 concentration in flue gas when alumina particle was added to the bed materials as 100% and 35% by weight respectively. When whole bed material was

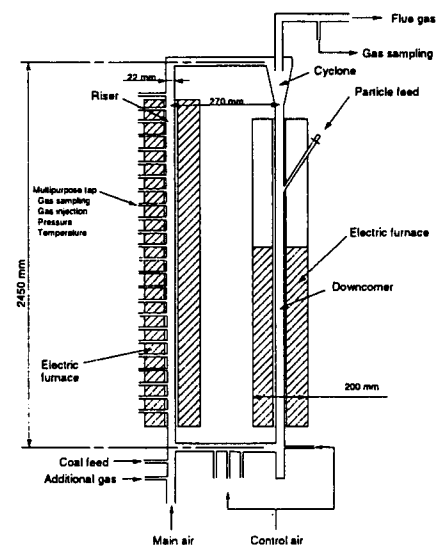


Fig. 1 Laboratory scale CFBC.

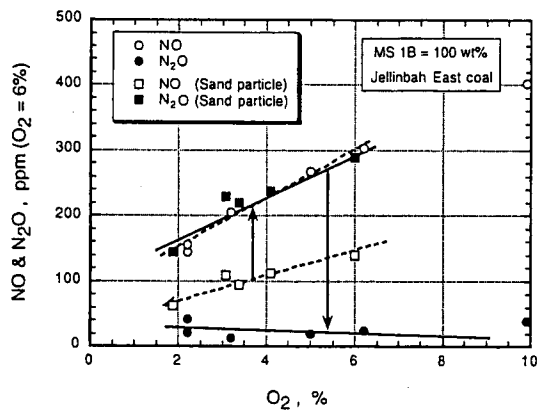


Fig. 2 NO and N₂O emission when whole bed material was replaced by alumina particles.

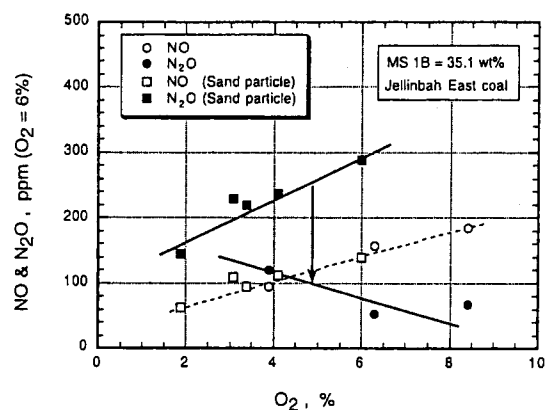


Fig. 3 NO and N₂O emission when alumina was added as 35% by weight to bed materials.

replaced by alumina particle, N₂O emission was dramatically reduced as shown in Fig. 2. However, NO emission increased double as a trade-off. When alumina particle was added to bed material in 35% by weight, N₂O emission was reduced to 120 ppm from original value of 180 ppm at O₂=3%, and no increase in NO emission was observed. Only N₂O emission was decreased selectively. Dependency on oxygen concentration in flue gas was also changed. Without alumina additive N₂O emission increased with oxygen concentration. On the contrary, N₂O emission decreased with oxygen concentration in flue gas. This may be explained as follow. As alumina works as the oxidizing catalyst, source substances of N₂O, such as HCN and NH₃, formed during the pyrolysis of fuel are oxidized to NO. Alumina requires oxidizing condition to work as an oxidizing catalyst. More than 2 % of oxygen concentration in flue gas was needed to reduce N₂O by alumina as shown in Fig. 3. As combustors including FBC are usually operated with higher than 3% of oxygen concentration, N₂O reduction by alumina particles to bed material is possible in actual FBC.

In order to find the optimum condition of alumina addition without "trade-off", effect of mixing rate on N₂O emission was examined. Figure 4 shows the dependency of NO and N₂O emission on the mixing rate of alumina to bed material. In the region less than 35% by weight, there was

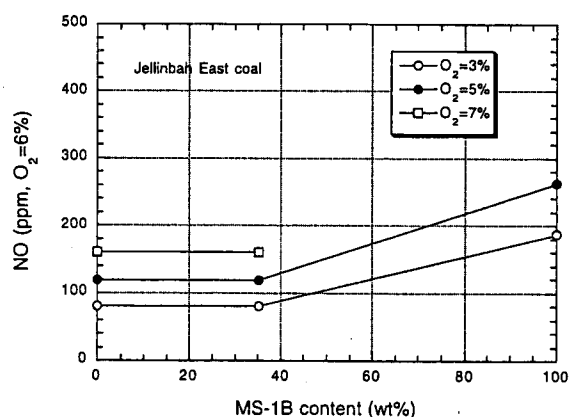
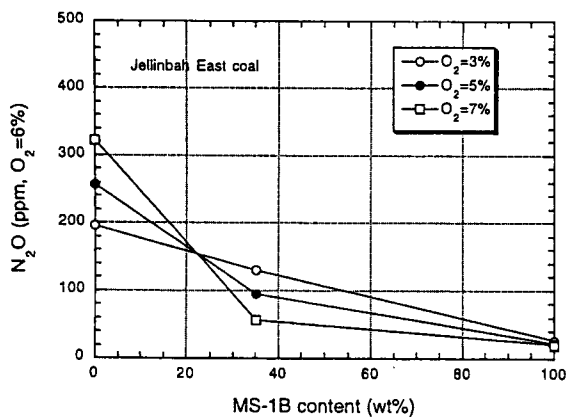


Fig. 4 Effect of mixing rate on N₂O and NO emission.

no trade-off. From these results, addition of alumina at 30% by weight may be the optimum mixing rate to reduce N₂O effectively. In this condition, 33% (O₂=3%) to 75% (O₂=5%) reduction in N₂O emission is expected. Though life test could not be done, alumina is so stable and tough material that N₂O reduction by addition of alumina particle into the bed material is good method in practical use.

3. Screening tests of ceramic particle for N₂O destruction and simultaneous SO₂ absorbing

Addition of alumina particle into the bed material is good method as described above. Alumina, however, is not cheaper material. Separation from ash and reuse is required for practical use. If cheaper particles having same reactivity as alumina can be used as the additive, one time use can be possible. Reactivity of several kinds of ceramic particles was examined to find cheap and good additives to reduce N₂O emission in actual FBC. As SO₂ is generally absorbed by sorbent in the bed in FBC, simultaneous SO₂ absorbing is also tried.

3.1 Experimental

Experimental setup employed in screening test is shown in Fig. 5. Sample ceramic particles of 0.2g and inert quartz particles of 0.5g were mixed well and put into a reactor to form a fixed bed above sintered quartz plate. A type-K thermocouple was immersed in the fixed bed and monitored the bed temperature. Reactor was heated up to typical temperature of 850°C with nitrogen gas stream and sample particle was calcined, if occurred, then switched to reactant gas mixture. Basic gas composition was 10vol%

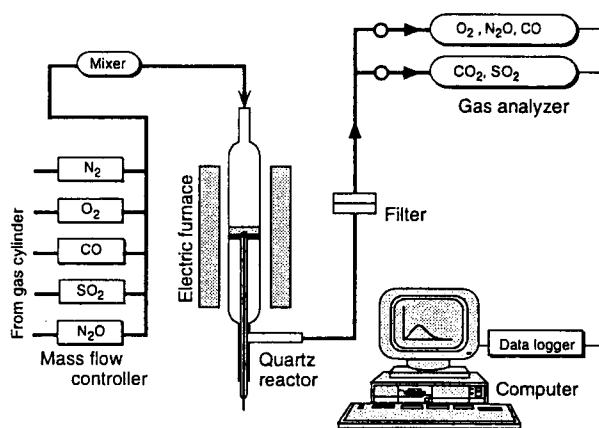


Fig. 5 Experimental setup for screening tests.

Table 1 Chemical composition of tested ceramic particles.

		Alumina cement	Cement A	Zeolite	Wollastonite	Slag cementic	Cement B
Ignition loss	wt%	0.2	0.8	11.3	2.1	<0.1	0.2
Si(SiO ₂)	wt%	6.1	<0.01	40	50.5	34.2	0.01
Al(Al ₂ O ₃)	wt%	4.8	80.8	33.6	0.59	14.7	71.1
Ca(CaO)	wt%	37.2	18	14.5	44.8	41.3	28.4
Pb	wt ppm	32	5	<1	11	3	27
Zn	wt%	0.09	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	wt%	0.06	0.01	0.01	<0.01	<0.01	0.11
As	wt ppm	<0.5	<0.5	<0.5	1.8	<0.5	<0.5
Se	wt ppm	<0.6	<0.5	<0.5	<0.5	1.3	<0.5
Hg	wt ppm	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd	wt%	<0.4	<0.4	0.8	0.8	<0.4	<0.4
T-Cr	wt%	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Mo	wt%	0.06	<0.01	<0.01	<0.01	<0.01	<0.01
H ₂ O	wt%	<0.1	0.1	<0.1	<0.1	<0.1	<0.1

of CO₂, 1500ppm of SO₂, 500ppm of N₂O in N₂. To achieve oxidizing and reducing condition, 4vol% of O₂ and 4vol% of CO was added exclusively. Experimental time was 20 minutes and 30 minutes in oxidizing condition and reducing condition respectively. Outlet gas composition was monitored continuously by gas analyzers. Chemical composition of ceramic particles is listed in Table 1.

3.2 Results and discussion

3.2.1 N₂O destruction and SO₂ absorbing behaviors among the ceramic particles

(1) Limestone

In oxidizing condition, N₂O was decomposed catalytically and SO₂ was absorbed as following reactions,



According to the proceeding of reaction (3), CaO surface is covered by CaSO₄ and pore is plugged by CaSO₄ because of higher molar volume. Hence, contact of CaO and N₂O was prevented and catalytic N₂O destruction was decreased and finally stopped. In reducing condition, CaS was formed by a reaction between CaSO₄ and CO. Because molar volume of CaS is smaller than that of CaSO₄, cracks form or pore plugging is broken and contact of CaO and N₂O can be recovered. Following reaction of N₂O destruction may also take place.



In reducing condition, N₂O destruction efficiency was kept very high. As actual combustor is operated under a oxidizing condition, this high N₂O destruction efficiency can not be expected.

(2) Alumina cement

SO₂ absorbing reaction took place, but N₂O destruction did not take place in oxidizing condition. Because alumina cement contains 37.2 wt% of CaO, N₂O reduction reaction is expected to take place with the consideration of the results of limestone. This may be caused by physical structure and existing chemical composition. On the contrary, both N₂O destruction reaction and SO₂ absorbing reaction took place in reducing condition as same as limestone. Because increase in CO₂ concentration was observed, reaction (4) should also occur.

(3) Cement A

Both N₂O reduction reaction and SO₂ absorbing reaction took place only in the beginning of the experiment in oxidizing condition. This may be caused the little CaO content of 18wt%. In reducing condition, both N₂O destruction reaction and SO₂ absorbing reaction suddenly started at 800 second after switching from oxidizing condition to reducing condition. It means surface reactivity was changed in reducing condition. Al₂O₃ should work as a catalyst for N₂O destruction

reaction.

(4) Zeolite

Both N_2O destruction and SO_2 absorbing reaction took place slightly in oxidizing condition and neither N_2O destruction nor SO_2 absorbing reaction took place in reducing condition. As Zeolite contains 14.5 wt% of CaO and 33.6wt% of Al_2O_3 , reactions in oxidizing condition should be driven by CaO. However, physical structure or chemical composition may prevent the reactions in reducing condition.

(5) Wollastonite

As same as zeolite, both N_2O destruction and SO_2 absorbing reaction took place slightly in oxidizing condition and neither N_2O destruction nor SO_2 absorbing reaction took place in reducing condition. Wollastonite contains 44.8 wt% of CaO and 0.59wt% of Al_2O_3 . Reactions in oxidizing condition should be driven by CaO. Although wollastonite has almost same content of CaO, N_2O destruction reaction and sulfur absorbing reaction does not occur as CaO. Especially in reducing condition, no reactions took place. It means physical structure or chemical composition may prevent the reactions in reducing condition as same as zeolite.

(6) Slag cement

Behavior of slag cement was as same as zeolite and wollastonite. Physical structure or chemical composition may prevent the reactions.

(7) Cement B

Slight sulfur absorbing reaction took place, but no N_2O destruction reaction took place in oxidizing condition. On the contrary, slight N_2O reduction reaction took place, but no sulfur absorbing reaction took place in reducing condition. This behavior can not be explained by chemical composition.

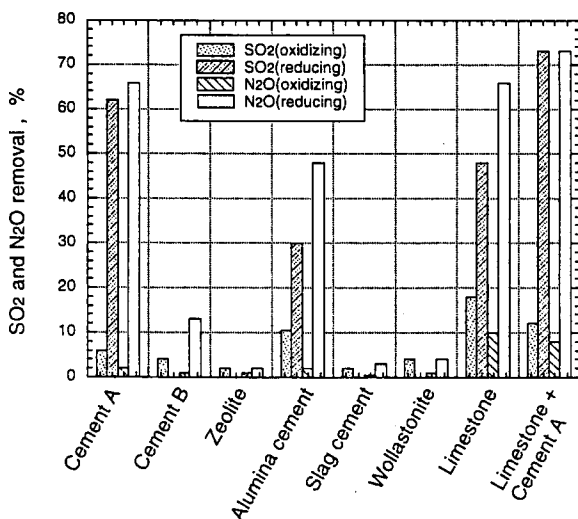


Fig. 6 N_2O destruction and sulfur absorbing efficiency of each particles.

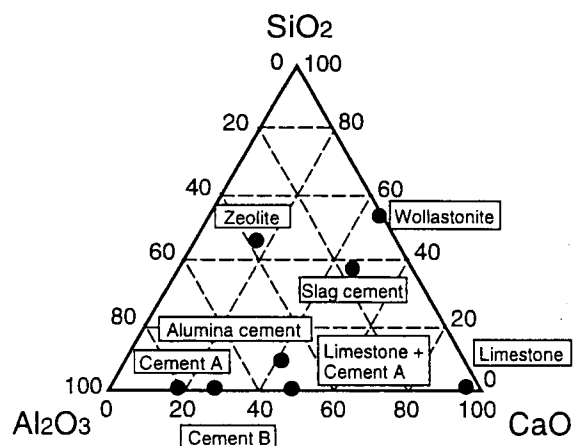


Fig. 7 Triangular composition diagram of tested particles.

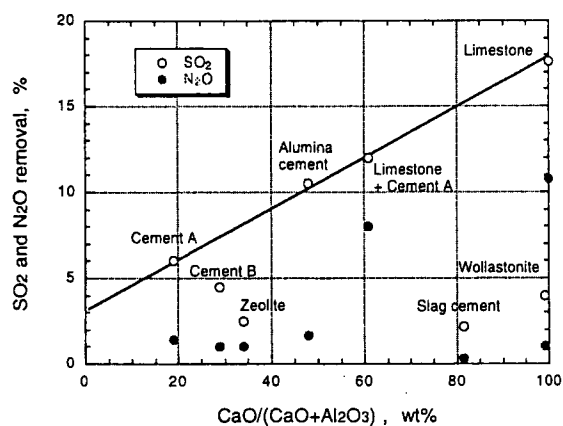


Fig. 8 SO_2 removal and N_2O destruction efficiency as a function of $\text{CaO}/(\text{CaO} + \text{Al}_2\text{O}_3)$ in oxidizing condition.

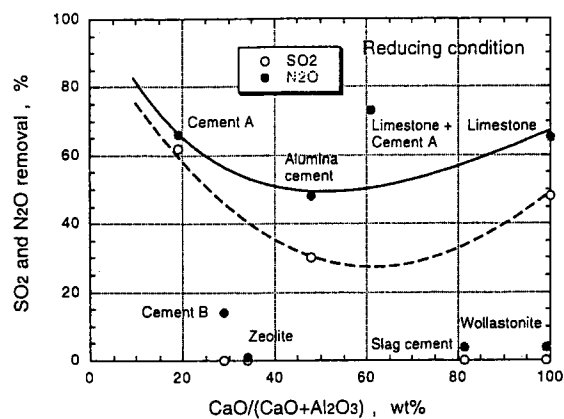


Fig. 9 SO_2 removal and N_2O destruction efficiency as a function of $\text{CaO}/(\text{CaO} + \text{Al}_2\text{O}_3)$ in reducing condition.

(8) Mixture of limestone and cement A

A mixture of 0.1g of limestone and 0.1g of cement A, which showed high sulfur absorbing and N_2O destruction efficiency in oxidizing condition and reducing condition respectively, was tried. In oxidizing condition, N_2O destruction and sulfur absorbing reactions were mainly controlled by limestone. However, limestone and cement A worked in different region and total N_2O reduction and sulfur absorbing efficiency became higher than those when limestone and cement A was used individually.

3.2.2 Effect of the chemical composition of the particles on N_2O destruction and SO_2 absorbing
Data analysis by chemical composition was tried. Figure 6 shows N_2O destruction and sulfur absorbing efficiencies for each particle in oxidizing and reducing conditions. Limestone and cement A shows maximum efficiency in oxidizing and reducing conditions respectively. Moreover, a mixture of limestone and cement A shows highest N_2O reduction and sulfur absorbing efficiency in reducing condition.

Correlation among Ca, Al, and Si was considered. Figure 7 shows a triangular composition diagram of tested ceramic particles. Tested ceramics consist of mainly Ca-Al except zeolite, wollastonite, and slag cement as shown in Fig. 7. Sulfur absorbing and N_2O destruction efficiencies in oxidizing and reducing conditions are shown as a function of $\text{CaO}/(\text{CaO} + \text{Al}_2\text{O}_3)$ in Figs. 8 and 9 respectively. In oxidizing condition, a good correlation of N_2O reduction and SO_2 absorbing efficiency between $\text{CaO}/(\text{CaO} + \text{Al}_2\text{O}_3)$ except wollastonite and slag cement. However, ceramics with high SiO_2 content, zeolite, wollastonite and slag cement, has no reactivity irrespective of the content of CaO. In reducing condition, sulfur absorbing and N_2O reduction efficiency were high in the regions of low Al_2O_3 content and high Al_2O_3 content. This means that CaO and Al_2O_3 content control sulfur removal and N_2O reduction. The ceramic particle having higher CaO or Al_2O_3 content shows higher reactivity. As well as in oxidizing condition, ceramics with high SiO_2 show low reactivity. Although cement B contains almost same quantity

Table 2 Physical structure of Ca and Al determined by X-ray analysis.

Ceramic particle	Crystal composition
Wollastonite	CaSiO ₃
Zeolite	CaAl ₂ SiO ₃
Slag cement	Non crystal structure

Table 3 Physical structure of Ca and Al in cement A and B.

Ceramic particle	Crystal composition
Cement A	α -Al ₂ O ₃
	CaAl ₂ O ₄
	CaAl ₄ O ₇
Cement B	CaAl ₂ O ₄
	CaAl ₄ O ₇
	trace α -Al ₂ O ₃

of Al as cement A, no reactions took place. This may be caused by the difference in physical structure.

3.2.3 Effect of the physical state of Ca and Al on N₂O destruction and SO₂ absorbing

It was impossible to explain reactivities of ceramic particles by chemical composition only as described above. An X-ray analysis was done to examine the effect of physical structure on reactivity. The results of X-ray analysis of three ceramics, which show low reactivity, are listed in Table 2. Both Ca and Al exist as not CaO or Al₂O₃ but silicate or non-crystal structure in zeolite, wollastonite and slag cement. From this analysis, Ca should exist as CaO for N₂O reduction.

It is still not clear why cement A and B show completely different behaviors in reducing condition although they have almost same CaO and Al₂O₃ content. Table 3 shows an X-ray analysis of cement A and B. Cement A has α -Al₂O₃ mainly and has CaAl₂O₄ and CaAl₄O₇. On the contrary, cement B has CaAl₂O₄ and CaAl₄O₇ and trace α -Al₂O₃. From this result, it is obvious that α -Al₂O₃ is a key component for sulfur absorbing and N₂O reduction in reducing condition. From X-ray analysis, not only chemical composition and physical structure are very important to evaluate the reactivity of ceramic particles.

3.2.4 Conclusions of screening tests

Following results were obtained in the screening tests of various ceramic particles.

- (1) There is a good correlation between N₂O reduction efficiency and Ca content in oxidizing condition.
- (2) Sulfur absorbing and N₂O reduction efficiency become high in Ca rich region and Al rich region in reducing condition.
- (3) α -Al₂O₃ works as a catalyst for N₂O reduction reaction in reducing condition.
- (4) When Ca or Al exist as silicate, reactivity of sulfur absorbing and N₂O reduction reaction become slow.
- (5) When Ca or Al exist in non crystal state, reactivity of sulfur absorbing and N₂O reduction reaction become slow.

4. Conclusions

A reduction method of nitrous oxide (N_2O) emission from fluidized bed combustion by addition of particles, which decompose N_2O in the combustor, to bed materials was tested. Al_2O_3 particles was mixed with sand particles and recirculated in the combustor. N_2O emission was decreased to 2/3 of original value at mixing ratio of 35% by weight when coal was burned. NO emission did not changed in this mixing ratio. N_2O was reduced efficiently at higher mixing ratio. However, two times higher NO emission was observed at higher mixing ratio.

Catalytic N_2O decomposition and simultaneous SO_2 absorbing by CaO and several kinds of ceramic particles were examined to use cheaper additives in the fluidized bed combustion. The particle containing CaO and Al_2O_3 destruct N_2O rapidly in reducing condition. In oxidizing condition, Ca mainly decomposes N_2O . When Ca or Al exists as a silicate, however, catalytic N_2O decomposition becomes slow. It means that the ceramic mainly consists of Ca and Al has N_2O destruction ability. For example, cement particle can be used as N_2O destruction additive.

References

- 1) Suzuki, et al., Proc. 6th symposium on Circulating Fluidized Beds, pp. 135 (1993) (in Japanese).
- 2) Suzuki, et al., Proc. 7th symposium on Circulating Fluidized Beds, pp. 153 (1994) (in Japanese).
- 3) Takeishi, et al., Doboku Kenkyusho Kyo-do Kenkyu Houkoku-sho, Vol 109, 1994 (in Japanese).
- 4) R.A. Newby, D.L. Keairns, Proc. of 11th Int. Conf. on FBC, Vol. 1, pp. 65 (1991).
- 5) P.F.B. Hansen, K. Dam-Johansen and L.H. Bank and K. Ostergaard, Proc. 11rd Int. Conf. on FBC, Vol. 1, pp. 73 (1991).
- 6) P.F.B. Hansen, K. Dam-Johansen and K. Ostergaard, Chem. Eng. Sci., **48**, pp. 1325 (1993).
- 7) A. Lyngfelt, B. Leckner, Chem. Eng. Journal, **44**, pp. 207 (1989).
- 8) A. Lyngfelt and L.E. Åmond, *idem*, **40**, pp. 59 (1989).
- 9) A. Lyngfelt, B. Leckner, Chem. Eng. Journal, **48**, pp. 1131 (1993).

Related publications

- 1) Suzuki Y., "N₂O Emission from Stationary Sources in Japan and Reduction Technologies for combustion processes", Proc. of the Int. Workshop on the Atmos. N₂O Budget, Tsukuba, pp. 22, (1999).
- 2) Yasumoto, et al., Proc. of the 64th Annual meeting of the SCEJ, K318 (1999).
- 3) Yasumoto, et al., Proc. of the 65th Annual meeting of the SCEJ, H116 (2000).