B-16.4 Mitigation of trace greenhouse gases from combustion processes

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Abstract

Emission control technology of the nitrous oxide (N_2O), which is one of the green house gases, from the combustion processes was studied. Sewage sludge combustion, one of the major source of N_2O, was examined with a lab-scale circulating fluidized bed combustor in order to investigate an effective control technique at the first year of this research program. N_2O emission level had exceeded 1000 ppm in the flue gas. However, conversion ratio of nitrogen to N_2O during sewage sludge combustion was 15-20% compared with 30% when coal was burnt with the same combustor. From the detail studies, it is understood that N_2O in the sewage sludge combustion was mainly formed from the volatile matters.

Practical mitigation methods were studied from the second year. Catalytic decomposition of N_2O in flue gas, enhancement of the N_2O destruction reaction by injection of supplemental fuel gas to make hot spot in the combustor, were tried as practical methods. It was found that Rh/ZnO catalyst had high N_2O decomposition reactivity in pure system. It easily lost, however, its reactivity in the existence of SO_2 which was very common gas in the combustion processes. N_2O decomposition by making the high temperature spot in the furnace by injecting supplementary fuel gases was able to decrease N_2O emission about 40% without additional NO emission. This method seems to be an effective control technique for practical use. In the final year, tried the mitigation method by the preprocessing of the fuel to omit the volatile matter as a further decreasing method. By using this method, about 40% of N_2O emission could be decreased.

N_2O from the combustion process may be controlled by about 80% or less by combining the control methods shown in the above-mentioned.

Key Words Nitrous Oxide, Combustion, Mitigation methods

1. Introduction

Nitrous oxide (N_2O) are 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 process of fossil fuel or waste are one of the major anthropogenetic source relating the activity of human being. To reduce the N_2O emission from combustion becomes important because mitigation of the greenhouse gases are required in worldwide. In this study, emission control technology of N_2O from the combustion processes was studied.

2. Formation mechanism in sewage sludge combustion in CFBC

Experimental

Major N_2O emission in combustion processes is fossil fuel combustion. Waste incineration, however, is second biggest source among the combustion processes. Especially, sewage sludge incineration emits large amount of N_2O because of high N content and usage of the fluidized bed incinerators[1]. To establish an effective N_2O emission reduction methods for the sewage sludge incineration, N_2O emission characteristics were studied by using a lab-scale fluidized bed combustor (CFBC)[2,3].

Figure 1 shows the experimental system for combustion tests of sewage sludge. 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 injecting 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. Twenty-three taps are installed in the riser wall at intervals of 100 mm. This taps are utilized for measurement of temperature and static pressure, sampling of gas and particles from the riser, and injection of gases into the riser.

Sample fuel particles were dried and classified to 0.25 ~ 0.5 mm, and fed continuously into the main air flow by a small screw feeder. Analytical values of the sewage sludge are listed in Table

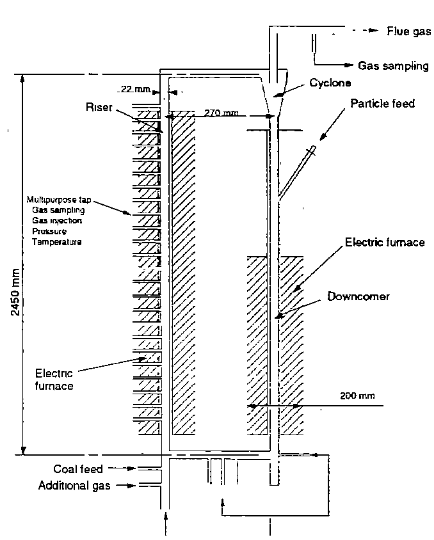

Fig. 1 Schematic diagram of lab-scale CFBC.

Table 1 Analytical data of sewage sludge.

	A	B	C
Proximate analysys (dry wt%)			
Moisture	13.46	7.47	7.67
Volatile matters	66.62	58.12	55.38
Fixed carbon	8.87	3.53	4.42
Ash	24.51	38.35	40.20
Heating value (kcal/kg)	4770	3290	3240
Ultimate analyses (dry wt%)			
C	38.20	31.65	31.14
H	4.90	4.83	4.66
N	6.27	2.76	3.46
S	1.16	0.93	1.26
O	25.01	22.17	20.20

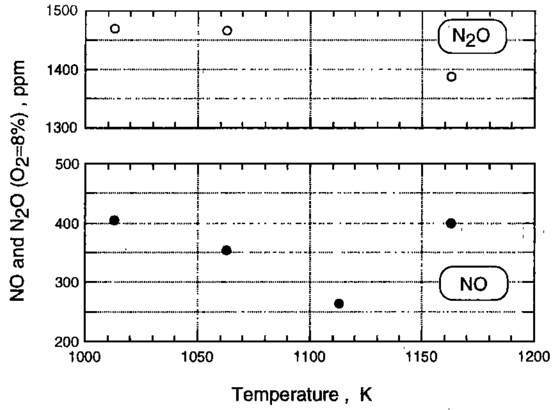

Fig. 2 NO and N_2O emission of sewage sludge combustion by CFBC.

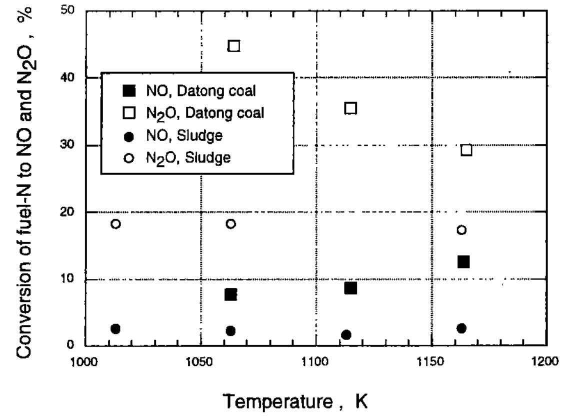

Fig. 3 Conversion ratio of fuel-N to NO or N_2O.

1. Limestone for desulfurization were 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 second.

Results and discussion

Figure 2 shows NO and N_2O emission during sewage sludge combustion by a lab-scale CFBC. N_2O concentration in flue gas exceeded 1000 ppm when combustion temperature was 1000 to 1200 K. On the other hand, NO emission was lower than that of N_2O. One can observe the emission characteristics that NO emission is increased with combustion temperature and N_2O emission is decreased when fossil fuels are burned. Almost same emission characteristics was observed when sewage sludge was burned. However, decrease in N_2O emission with combustion temperature was smaller than that of fossil fuel. NO emission was decreased with combustion temperature up to 1120 K, and then decreased with combustion temperature. Effect of excess air on N_2O emission is shown in Fig. 3. N_2O emission is increased linearly with O_2 concentration in flue gas up to 8 % when fossil fuel was burned. On the contrary, N_2O emission had a maximum value when O_2 was 3 % in sewage sludge combustion. Difference between dependency on excess air ratio of both fuel may given by combustion behaviors. Combustion of volatile matter is dominant, as shown in Table 1, in sewage sludge combustion. In order to understand clearly, more detailed study is needed.

Absolute N_2O emission level was higher than that of coal in sewage sludge combustion, because of higher nitrogen content as listed in Table 1. However, conversion ratio of nitrogen in sewage sludge to N_2O and NO was 20 % and 10 % respectively. Conversion ratio of nitrogen in coal to N_2O and NO is generally in range of 40 % and 20 % respectively. Comparing the conversion ratio of nitrogen in fuel to N_2O and NO, sewage sludge showed half value of those of coal. HCN in slow volatile, released from char, play an important role in N_2O formation[4-6]. In the case of combustion of sewage sludge, conversion ratio of nitrogen to N_2O was low because contribution of char combustion was small.

3. Emission control methods

3.1 Catalytic decomposition of N_2O in flue gas

The N_2O mitigation method by catalytic decomposition has a great advantage because this method requires very small energy. Catalytic treatment of flue gas was tried at first.

Experimental

Catalytic N_2O decomposition tests were carried out using an electrically heated quartz reactor of 23 mm I.D. and 600 mm height, equipped with a sintered porous plate, supporting a fixed bed. A schematic diagram of the experimental system is shown in Fig. 4. About 135 mg of catalyst particles with diameter of 125 ~ 250 μm and 3 g of quartz sand particles with same diameter were mixed, and was placed on the sintered porous plate to form a 7 mm height of fixed bed. Temperature was monitored by a type K thermocouple placed into the particle bed.

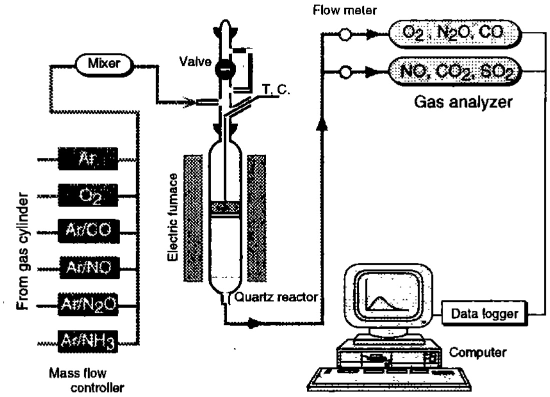

Fig. 4 Schematic diagram of fixed bed reactor using for catalyst reactivity tests.

Reactant gas, flowing in down stream, was made by mixing of N_2 / O_2 / N_2O / NO / SO_2 gases to simulate flue gas. The flow rate of individual gases were controlled by a mass flow controller to adjust the inlet concentrations. Flow rate was fixed to 3510 cm^3/min (273 K, 101.3 kPa) typically. The reactor was heated up to 973 K at the heating rate of 1 K/min to realize quasi-steady state condition. Rh/ZnO on zeolite, developed at National Institute for Resources and Environment, was used as a test catalyst[7)].

For O_2, CO_2, CO, SO_2, 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 second. In order to obtain real time acquisition, the different time lags of each analyzer response was checked. The response time of each analyzer was almost same.

Results and discussion

In order to know the basic behaviors of catalyst, N_2O decomposition in N_2/O_2/NO/N_2O was tested. N_2O concentration and decomposition rate were shown in Fig. 5 as a function of bed temperature

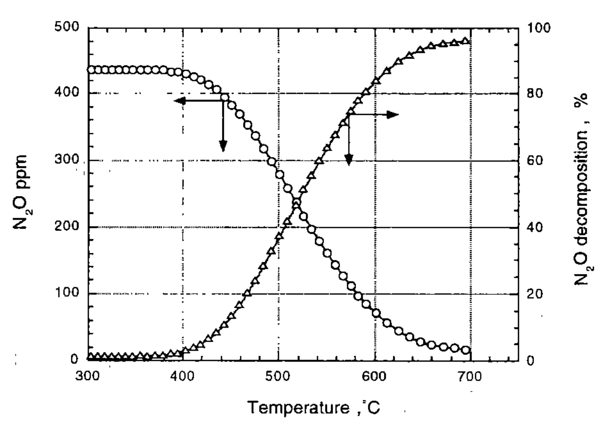

Fig. 5 N_2O decomposition as a function of bed temperature in the case of N_2/O_2/NO/N_2O mixture.

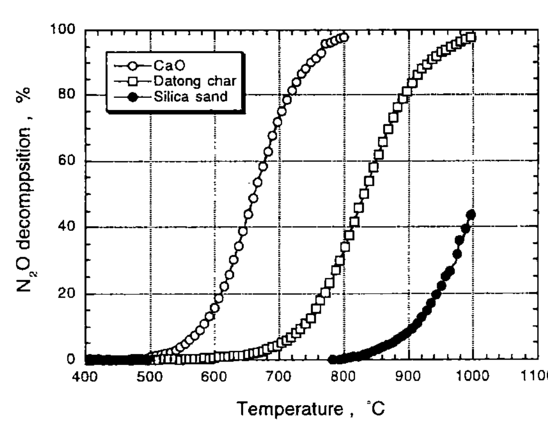

Fig. 6 N_2O decomposition of various particles as a function of bed temperature.

with inlet gas concentration of O_2=3.3%, N_2O=430 ppm, NO=420 ppm. As shown in Fig. 5, catalyst showed higher N_2O decomposition reactivity in spite of high gas velocity. Figure 6 shows the N_2O decomposition reactivities of various particles in almost same experimental conditions to compare with this catalyst. The data of silica sand particle in Fig. 6 should be gas phase homogeneous N_2O decomposition. Char particle or CaO particle has higher N_2O decomposition reactivity. Their reaction rate, however, is small below 1000 K. Comparing with those particles, this catalyst shows higher reactivity in low temperature.

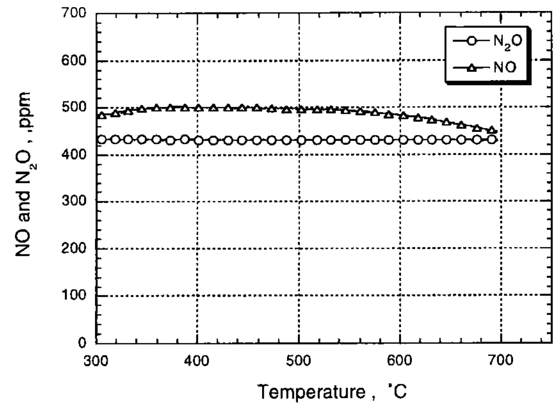

Fig. 7 NO and N_2O decomposition as a function of bed temperature in the presence of SO_2.

Flue gas from actual combustion process contains many kinds of gases such as SO_2, CO, etc. Especially, negative effect of SO_2 must be tested to evaluate the adaptability of this catalyst to actual process. Figure 7 shows N_2O and NO decomposition reactivity when 450 ppm of SO_2 was added to inlet gas. As shown in Fig. 7, catalyst lost reactivity with existence of SO_2. In order to know this manner is permanent or temporary, catalyst was treated with N_2 at 973 K in 30 min. After treatment, N_2O decomposition test was done in same experimental conditions of Fig. 8. Retrial showed that reactivity had lost though small reactivity in high temperature. So, catalyst lost N_2O decomposition reactivity permanently by existence of SO_2. In actual combustion process, SO_2 concentration do not exceed 400 ppm. It is, however, necessary to increase the tolerance to SO_2 further for practical use of the Rh/ZnO catalyst.

3.2 Injection of supplemental fuel gases to combustor

By thermodynamic consideration or the knowledge of reaction kinetics of N_2O formation and destruction, high temperature circumstance by flame should have an effect to reduce N_2O emission. N_2O reduction by injection of supplemental fuel gases to combustor was tried in CFBC.

Experimental

In this trial, the same CFBC illustrated in Fig. 1 was used. The fuel gases were injected through the taps shown in Fig. 1. Methane, propane and hydrogen gases used to inject were commercial grade and their purity was up to 99.99%. Flow rates of above gases were controlled by a mass flow controller and were injected into the center of the riser through a thin quartz tube. The coal used was Datong Coal (Chinese coal). Coal particles were usually fed to combustor from riser bottom by a specially designed pneumatic transportation type feeder. Oxygen concentration was typically kept as 8% before injection of fuel gases, and oxygen concentration in flue gas decreased according to fuel gas injection and finally reached to 2%. A temperature of 1123K was chosen to be a standard temperature in the riser at the injection of the fuel gases. In this condition, typical NO and N_2O concentration were 100 ppm and 380 ppm respectively.

Results and discussion

The reduction rate of N_2O is shown in Fig. 8 as a function of the volumetric propane injection rate in the standard temperature and pressure condition. N_2O emission was greatly decreased by injection of propane, and the reduction rate of N_2O was almost proportional to the volumetric gas injection rate. Moreover, it is shown that the third injection port is the best position from the results shown in Fig. 8. The third injection port is a position of 1/3 in the upper part of the riser and the effect of the fuel gas injection on the decrease of N_2O emission becomes smaller when fuel gas is injected in the upper or lower position than this. In injection of propane, additional small increase in NO emission was observed. However, this NO emission level was acceptable.

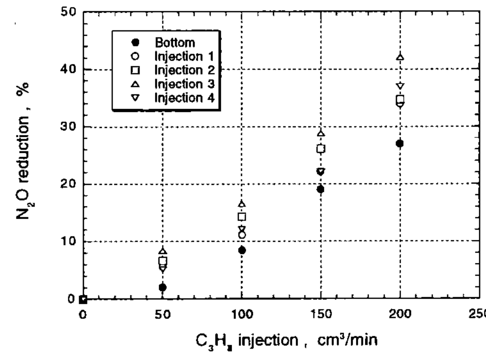

Fig. 8 N_2O reduction by propane gas injection.

When methane or hydrogen was injected, N_2O emission decreases remarkably as propane was injected. Moreover, the decrease of NO was seen for hydrogen at all injection positions. Absolute amount of gas injected has increased greatly, about six times larger than that of propane for hydrogen, two times larger for methane to obtain the same N_2O reduction rate. Both cases of propane and hydrogen injection, N_2O reduction up to 35% was achieved in this experiment. Oxygen consumption by the injected fuel gases was about 25% of whole oxygen consumption when fuel gases injected at maximum flow rate. From above results, a thermal decomposition of N_2O may be a major contribution in this N_2O reduction method.

3.3 Pretreatment of fuel

As mentioned before, one of the major source substance of N_2O in combustion process is volatile matters of fuel. If the volatile matters could be omitted or reduced, N_2O emission should be decreased. This kind of technology, pretreatment of fuel, was already developed for low rank coals. The total resources of low-rank subbituminous and lignite coals are huge. It is, however, difficult to use in usual facilities because of bad handling. An upgrading technology is required to accommodate the sustained and the increasing use of coal for electric power generation while simultaneously attempting to meet international goals for environmental protection. ENCOAL Corp. has developed an upgrading technology by mild pyrolysis[8]. This process generates two products, a solid upgraded coal product (designated as Process Derived Fuel, PDF) and a heavy liquid fuel (designated as Coal Derived Liquid, CDL). PDF has low ash content and high heating value. Pretreatment methods as a method for the reduction of N_2O emission was tried.

Experimental

Experiments were carried out by using a lab-scale CFBC illustrated Fig. 1. Sample fuel particles were classified to 0.25 ~ 0.5 mm, and fed continuously. The fuels used were PDF and parent coal of PDF (Wyoming Buckskin coal). Proximate and ultimate analysis values are listed in Table 2. Table 2 shows that volatile matters was reduced and heating value was improved in PDF comparing with those of parent coal.

Table 2 Analytical data of PDF and parent coal.

	Wyoming Buckskin coal	PDF
Proximate analysis wt%		
Moisture	29.12	8.00
Volatiles	30.64	23.50
Fixed carbon	34.95	60.50
Ash	5.29	8.00
Heating value (kcal/kg)	4527	6440
Ultimate analysis (dry %)		
C	69.26	75.33
H	4.81	3.37
N	1.02	1.20
S	0.54	0.54
O	16.92	10.87

Results and discussion

Figure 9 shows NO and N_2O emission characteristics as a function of O_2 concentration in flue gas. At the fixed temperature condition, both NO and N_2O emissions were increased with excess air for both fuel. However, emission characteristic was different. NO emission of PDF was increased as 40% higher than that of parent coal, and N_2O emission was decreased to half of N_2O emission of parent coal. Total nitrogen oxides emission of PDF was same as that of parent coal. Main reason of increase in NO emission of PDF may be as follows; 1) N content of PDF is higher than parent coal, 2) NO is mainly formed during char combustion. Decrease of N_2O emission of PDF is agree with N_2O formation mechanism by previous mentioned. As N_2O is mainly formed during volatile combustion, N_2O emission was decreased because of less volatile matters.

PDF shows higher NO emission in circulating fluidized bed combustion. Simultaneous lower NO and N_2O emission levels are required. In order to minimize NO emission level, two staged combustion technique was tried. Figure 10 shows a typical results of two staged combustion when PDF was burned. By adapting the two staged combustion, NO emission could be finally decreased to 60% of initial emission. NO emission decreased with decreasing of primary air ratio, especially the operating condition of primary air ratio less than 0.8 seems to be suitable to reduce NO emission. On the contrary, CO emission was gradually increased with decreasing of primary air ratio, and finally 40% higher emission was observed. However, this CO emission level was same as that of typical bituminous coal when this lab-scale CFBC was used. CO emission in full scale CFBC will be not high. N_2O emission was also gradually decreased with decreasing in primary air ratio. As initial N_2O emission level, however, was low enough, decreasing in N_2O emission may not so

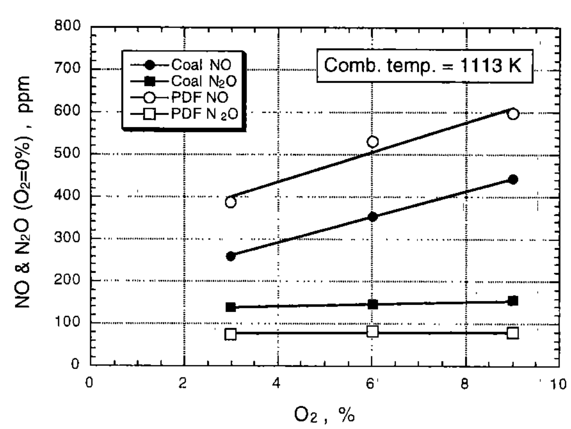

Fig. 9 NO and N_2O emission of PDF and parent coal as a function of O_2 concentration.

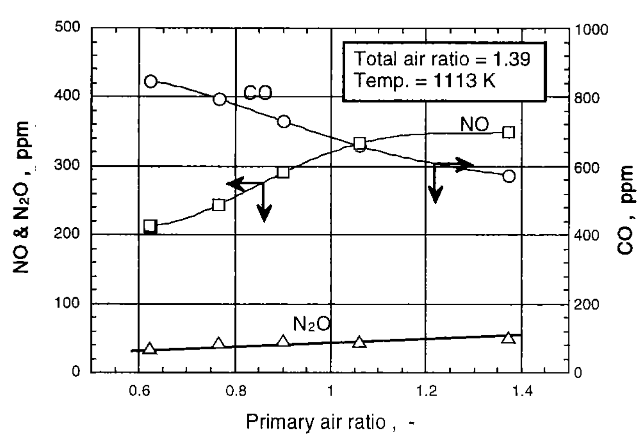

Fig. 10 Effect of two staged combustion on NO, N_2O and CO.

important. NO emission level could be successfully reduced to acceptable level by adapting conventional two staged combustion technique to PDF combustion.

4. Conclusion

Emission control technologies of the nitrous oxide from the combustion processes were studied. Sewage sludge combustion, one of the major source of N_2O, was tested with a lab-scale circulating fluidized bed combustor in order to investigate an effective control technique. N_2O emission level had exceeded 1000 ppm in the flue gas. However, conversion ratio of nitrogen to N_2O during sewage sludge combustion was 15-20% compared with 30% when coal was burnt with the same combustor. From the detail studies by using a drop tube furnace, N_2O in the sewage sludge combustion was mainly formed from the volatile matters.

Practical mitigation methods were examined. Catalytic decomposition of N_2O in flue gas, enhancement of the N_2O destruction reaction by injection of supplemental fuel gas to make hot spot in the combustor, preprocessing of the fuel to reduce volatile matters, were tried as practical methods. It was found that Rh/ZnO catalyst had high decomposition reactivity in pure system. It easily lost, however, its reactivity in the existence of SO_2 which was very common gas in the combustion processes. N_2O decomposition by making the high temperature spot in the furnace by injecting supplementary fuel gases was able to decrease N_2O emission about 40% without NO emission increase. This method seems to be an effective control technique for practical use. By using preprocessing of fuel to reduce volatile matters, about 40% of N_2O could be decreased.

N_2O from the combustion process may able to be controlled by about 80% or less by combining the control methods shown in the above-mentioned.

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