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PURIFICATION OF WASTE COMBUSTION GAS IN HIGH TEMPERATURE REGIONS USING ECOFUNCTIONAL CERAMICS

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ABSTRACT

Hydroxyl sodalite ($Na_8Al_6Si_6O_{24}(OH)_2$) and hydrogrossular ($Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$) were investigated for the purpose of developing new ecofunctional ceramics with removal performance for toxic substances present in waste combustion gas. It was found that these materials had functions of chlorine fixation, copper fixation and the control of dioxin formation. Hydroxyl sodalite had nanometer-sized micropores (β-cage) in the structure, and the chloride ions were fixed in the pores above 400°C. The amount of chlorine that was fixed increased with increasing reaction temperature and was greatest, 7.3 wt%, at 800°C. The fixation of the copper progressed by the substitution with sodium ion, and the substitution quantity increased with increasing reaction temperature. The amount of copper fixed as CuO at 900°C was 10.5 wt%. On the other hand, hydrogrossular changed to the mayenite phase ($Ca_{12}Al_{10}Si_4O_{35}$) after heating to above 700°C. Mayenite had micropores in the structure, which were fixed by the chloride ions. A drastic decrease in the concentration of dioxins was confirmed by introducing the ecofunctional ceramics, hydroxyl sodalite and hydrogrossular, in the municipal solid waste incineration.

Keywords: chlorine, copper fixation, dioxin, hydrogrossular, hydroxyl sodalite, oxidative catalyst, waste combustion gas.

1 INTRODUCTION

Recently, environmental pollution by dioxins has become a serious issue in Japan. It is important to purify the waste combustion gas discharged from the municipal solid waste incineration, because emissions of dioxins can be formed in the incineration of many forms of wastes [1–4]. To date, extensive research has been carried out on the removal of toxic substances present in waste combustion gas and the results of these studies have been put to practical use. Some of the examples are – the removal of HCl gas using calcium compounds such as lime and limestone [5–9], the adsorptive removal of dioxins using high surface area activated carbon [10–14], the decomposition removal of dioxins using catalysts [15–22] such as $V_2O_5-WO_3-TiO_2$, CrO_x-TiO_2/Al_2O_3 and noble metals, and the elution prevention by stabilization of heavy metals adsorbed on fly ash. These purification technologies are processing technologies at low temperatures of about 200°C or at ambient temperatures because of the heat resistance of the bag filter. However, there are many advantages if the purification treatment of waste combustion gas could be realized in the high temperature region. Some of the advantages of high temperature purification include: (1) improvements in the efficiency and lifetime of the heat exchanger and the incinerator by controlling the high temperature corrosion caused by acid gases, (2) control of the formation of dioxins by the removal of dioxin precursors such as HCl, hydrocarbons, chlorobenzene, phenol, unburned carbon, etc., and (3) recovering the fly ash with less pollution by controlling the formation of dioxins and by the removal of heavy metals. We have investigated that using ecofunctional ceramics, i.e. hydroxyl sodalite and hydrogrossular, in the high temperature range over 400°C, HCl, hydrocarbons and $CuCl_2$ present in waste combustion gas could be removed in order to purify it and control the formation of dioxins.

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2 EXPERIMENTAL METHOD

2.1 Sample preparation

The hydroxyl sodalite ($Na_8Al_6Si_6O_{24}(OH)_2$) was prepared using kaolinite ($Al_2(Si_2O_5)(OH)_4$) as the source of Al and Si, and NaOH as the source of Na. A mixed paste of kaolinite and NaOH was prepared in the molar ratio of 3 : 10. The ratio of NaOH added was considerably in excess than that theoretically required. The hydroxyl sodalite was synthesized by heat treatment (100°C, 24 h) of the mixed paste in an oven. It was then washed with a large amount of distilled water to remove the excess NaOH.

Hydrogrossular ($Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$) was synthesized by the hydrothermal treatment of a stoichiometric mixture of alumina-sol, amorphous silica and CaO. The mixture was put in a Teflon-lined stainless steel autoclave with distilled water. The water to solid ratio by weight was 12 : 1. The autoclave was placed in a temperature-controlled oven, and the temperature was controlled to increase from room temperature to 200°C in 2 hours. The mixture was then kept at 200°C for 15 hours. The solid product was separated by filtration and dried at 110°C for 24 hours.

2.2 Reaction with HCl gas at high temperature

2.2.1 A small-sized fixed bed reactor

A small-sized fixed bed reactor (Fig. 1) was used to examine the reaction between dry HCl gas, hydroxyl sodalite and hydrogrossular in the temperature range 400–900°C. A quartz glass tube packed with a sample of 0.5 g was placed in a tubular electric furnace and the sample was heated to the desired temperature in flowing dry N_2. After the sample reached the desired temperature, HCl gas of 1000 ppm was flowed for 3 hours at a flow rate of 200 ml/min.

2.2.2 A medium-sized vertical reactor

The experiment was started by heating the vertical tubular furnace to 700°C or 800°C with air flowing at 45 l/min. The synthetic gas, HCl: 1000 ppm, O_2: 10 vol%, CO_2: 10 vol%, H_2O: 10 vol%, and N_2: balance, was introduced into the quartz glass reactor of diameter 0.1 m and length 4.5 m.

Hydrogrossular was introduced into the reactor at the rate of 0.4, 0.8, 1.2 and 1.6 g/min. A rough drawing and photograph of the reactor are shown in Figs 2 and 3 respectively.

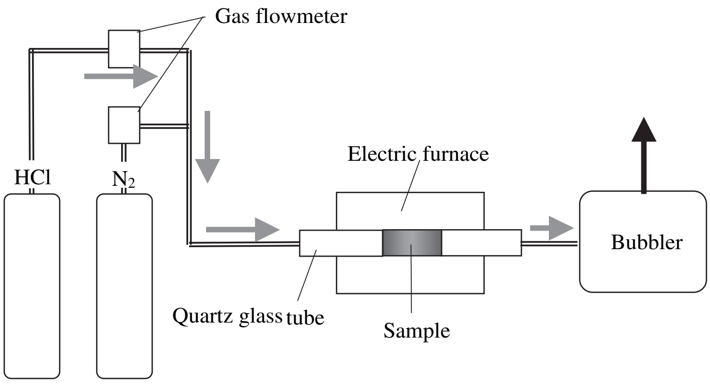

Figure 1: Rough drawing of a small-sized fixed bed reactor.

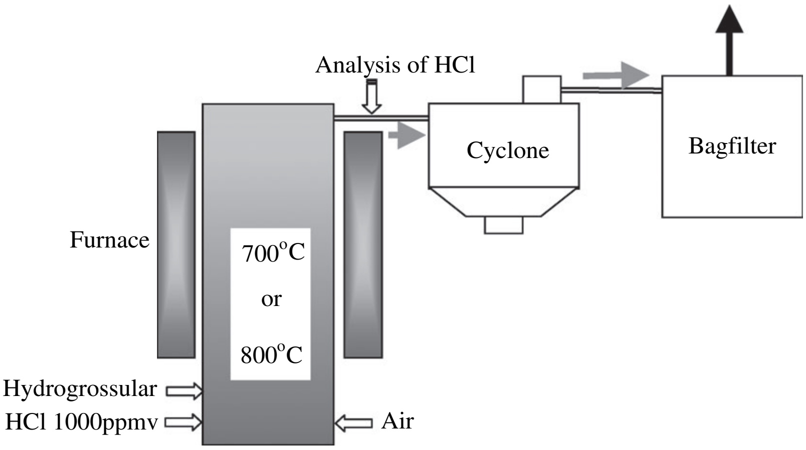

Figure 2: Rough drawing of a medium-sized vertical reactor.

Figure 3: A photograph of a medium-sized vertical reactor.

2.2.3 A large-sized fluidized bed combustor

A rough drawing of the combustor used is shown in Fig. 4. Refuse derived fuel (RDF) made from a mixture of polyvinyl chloride, plastics waste and paper was burnt in a 1.2 × 1.2 × 9 m bubbling type fluidized bed combustor. The gas flow rate was 500 N m^3/h and the temperature of combustion was 750 ± 50°C. The concentration of HCl was continuously recorded. Hydroxyl sodalite and hydrogrossular powder were introduced into the combustor at 6.2 kg/h, respectively.

2.3 Reaction with $CuCl_2$ at high temperature

The reactor is shown in Fig. 5. Two alumina boats, one filled with 0.5 g hydroxyl sodalite and the other containing 0.5 g $CuCl_2$, were loaded into the tubular electric furnace. The reaction of the hydroxyl

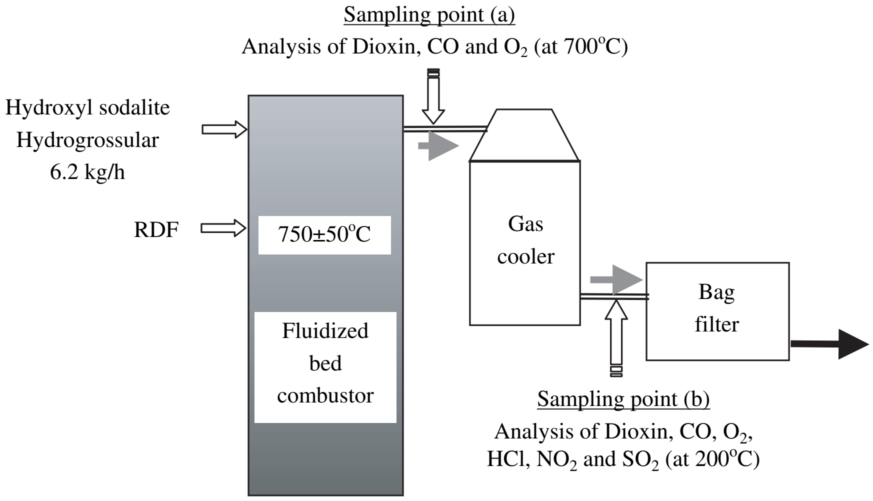

Figure 4: Rough drawing of a large-sized fluidized bed combustor.

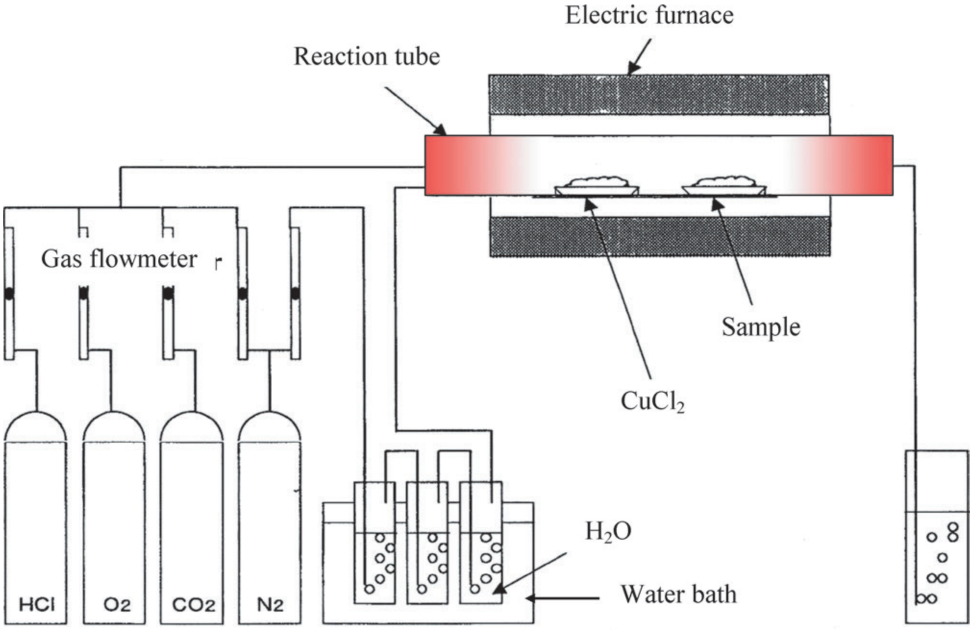

Figure 5: Rough drawing of a reactor for examining the reaction between the sample and $CuCl_2$.

sodalite and $CuCl_2$ was carried out in the temperature range 400–900°C, with a mixed gas consisting of 10 vol% O_2, 10 vol% CO_2, 10 vol% H_2O, 1000 ppm HCl and N_2 (balance) flowing through the furnace. The flow rate of the mixed gas was 500 ml/min, and the reaction time was one hour. After the reaction was complete, the hydroxyl sodalite recovered was analyzed by XRF after washing with distilled water.

2.4 Measurement

Thermal decomposition behavior, crystal structure and chemical composition of the samples before and after the reaction were examined by TG-DTA, XRD and XRF, respectively.

3 RESULTS AND DISCUSSION

3.1 Fixation performance of Cl^- using a small-sized fixed bed reactor

3.1.1 Hydroxyl sodalite

When hydroxyl sodalite reacts with HCl gas, OH^- ions are replaced with Cl^- ions in the β-cage of the sodalite structure and it becomes sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) (eqn (1)) [23]. The lattice constant (a_0) of the sodalite structure increases from 8.86 to 9.04 Å due to the substitution of smaller OH^- (ionic radius: 1.32 Å) by the larger Cl^- ion (1.81 Å).

$$Na_8Al_6Si_6O_{24}(OH)_2 + 2HCl \rightarrow Na_8Al_6Si_6O_{24}Cl_2 + 2H_2O \tag{1}$$

The relationship between the amount of Cl^- fixed in the sodalite structure and the reaction temperature is shown in Fig. 6. The weight ratio of the Cl^- ion was measured by XRF, and the weight ratio to the sodalite (wt%) was regarded as the amount of Cl^- fixed. The amount of Cl^- fixed increases with increasing reaction temperature, however it drastically decreases after reaching the highest value at 800°C. Consequently, the amount of Cl^- fixed at 900°C was almost zero. The amount of Cl^- fixed at 800°C was 7.3 wt%, and this value corresponds to the Cl^- weight ratio in the sodalite. At 900°C, the crystal phase changed from the sodalite structure to carnegieite ($NaAlSiO_4$).

According to the measurement result of TG-DTA of hydroxyl sodalite, the dehydration reaction for OH^- occurred at 260°C (eqn (2)) with the endothermic peak, and hydroxyl sodalite underwent a phase change to carnegieite at 877°C (eqn (3)) with the exothermic peak. Carnegieite cannot react with HCl at all.

$$Na_8Al_6Si_6O_{24}(OH)_2 \rightarrow Na_8Al_6Si_6O_{25} + H_2O \quad \text{at } 260°C \tag{2}$$

$$Na_8Al_6Si_6O_{25} \rightarrow 6NaAlSiO_4 + Na_2O \quad \text{at } 877°C \tag{3}$$

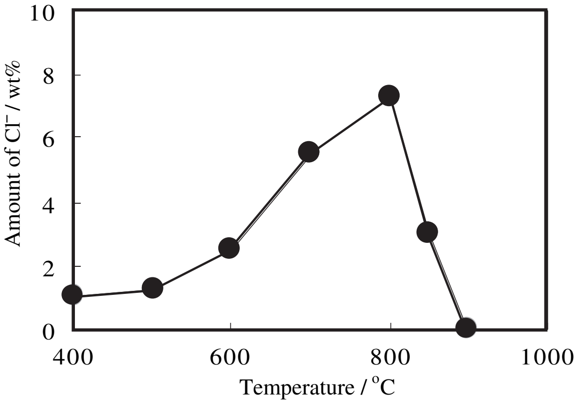

Figure 6: The relationship between the amount of Cl^- fixed in the sodalite structure and the reaction temperature.

3.1.2 Hydrogrossular

From the TG-DTA measurement of hydrogrossular, the following fact became clear: the endothermic peaks at 320°C and 680°C recorded in DTA could be attributed to the release of OH radical. The hydrogrossular phase is transformed into anhydrous mayenite ($Ca_{12}Al_{10}Si_4O_{35}$) through the hydrous mayenite ($Ca_{12}Al_{10}Si_4O_{32}(OH)_6$) phase. The ideal phase transition of hydrogrossular with increasing temperatures has been described as shown in eqns (4) and (5), respectively [24, 25].

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{32}(OH)_6 + 3CaO + 19H_2O \quad \text{at } 320°\text{C} \tag{4}$$

$$Ca_{12}Al_{10}Si_4O_{32}(OH)_6 \rightarrow Ca_{12}Al_{10}Si_4O_{35} + 3H_2O \quad \text{at } 680°\text{C} \tag{5}$$

The XRD patterns of hydrogrossular reacting with HCl were measured under ambient conditions after cooling from each reaction temperature to room temperature. At the reaction temperature above 400°C, the main phase recorded was wadalite ($Ca_{12}Al_{10}Si_4O_{32}Cl_6$), and a second phase corresponding to $CaCl_2 \cdot 2H_2O$ was also observed. Since $CaCl_2$ is highly hygroscopic, it could take up moisture and form $CaCl_2 \cdot 2H_2O$. The chemical composition of the sample, after removing the second phase ($CaCl_2 \cdot 2H_2O$) by washing in distilled water, was $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ (Wadalite), which had a chlorine content of 13.2 wt%. The HCl gas was efficiently removed from the inlet gas as $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ and $CaCl_2$ above 400°C.

On the basis of the results obtained, the reaction formula of hydrogrossular and HCl is shown in eqns (6) and (7) [24, 25].

$$\begin{aligned} Ca_{12}Al_{10}Si_4O_{32}(OH)_6 + 3CaO + 12HCl \rightarrow\ & Ca_{12}Al_{10}Si_4O_{32}Cl_6 \\ & + 3CaCl_2 + 9H_2O \quad \sim 400-650°\text{C} \end{aligned} \tag{6}$$

$$Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 12HCl \rightarrow Ca_{12}Al_{10}Si_4O_{32}Cl_6 + 3CaCl_2 + 6H_2O \quad \text{above } 700°\text{C} \tag{7}$$

3.2 Hydrogen chloride removal performance using a medium-sized vertical reactor

In the medium-sized vertical reactor with flowing synthetic gases, the concentration of HCl at 700°C and 800°C with the introduction of hydrogrossular was ~0.4–1.6 g/min. The HCl was efficiently removed from the inlet gas, and the concentration decreased with increasing the concentration in the inlet. In Fig. 7 the result of introducing hydrogrossular of 0.4 g/min (a) and 1.6 g/min (b) is shown. The amount of HCl removed at 800°C was only half the quantity compared to that removed at 700°C. This result could be attributed to the fact that at 800°C, H_2O suppresses only $CaCl_2$ formation but not the wadalite formation [26–28].

3.3 Reaction of hydroxyl sodalite and $CuCl_2$

After the reaction of hydroxyl sodalite and $CuCl_2$ in the temperature range 400–900°C was complete, the hydroxyl sodalite recovered was analyzed by XRF after washing with distilled water. The result of the analysis is shown in Fig. 8 and Table 1. It can be seen that the Al_2O_3 and SiO_2 contents before and after the reaction are almost the same. However, the content of Na_2O decreases with increasing reaction temperature. It is also observed that the CuO content increases with the decreasing Na_2O content exhibiting a reverse correlation as shown in Fig. 8. The result of a similar experiment using sodalite ($Na_8Al_6Si_6O_{24}Cl_2$) showed that the CuO content at 700°C was 5.0 wt%, which is almost equal to that observed using hydroxyl sodalite (5.3 wt%). From these results, it can be concluded

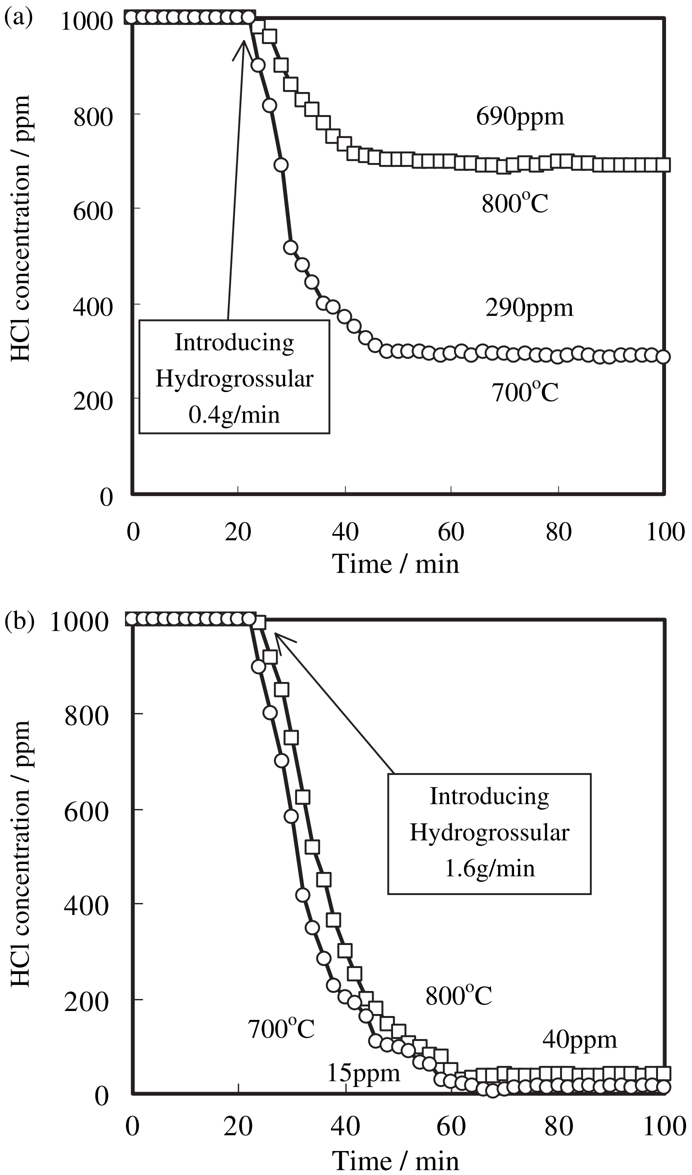

Figure 7: The effect of hydrogrossular introducing of 0.4 g/min (a) and 1.6 g/min (b) for HCl concentration reduction.

that hydroxyl sodalite and sodalite could react with $CuCl_2$ at high temperatures over 400°C, and Na cations in hydroxyl sodalite and sodalite could be substituted by Cu cations.

Although the existence of Cl in hydroxyl sodalite is evidenced, it is unclear if all the Cl^- ions are captured from HCl or also from $CuCl_2$. In any case, the existence of $CuCl_2$ is very important in the formation of dioxins. $CuCl_2$ present in fly ash fulfils the role as a catalyst for the formation of dioxins [29–31]. Therefore, it seems to be possible to realize the control of the formation of dioxins by removing $CuCl_2$ at high temperature.

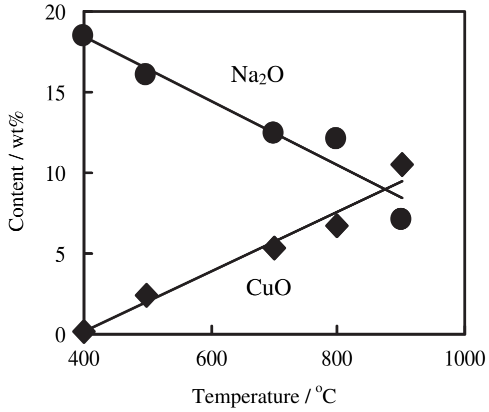

Figure 8: The relationship between the Na_2O and CuO content in hydroxyl sodalite and the reaction temperature.

Table 1: Analysis result of hydroxyl sodalite after reaction with $CuCl_2$.

Reaction temperature (°C)	Reaction time (hour)	Analysis value (wt%)				
		CuO	Na_2O	Cl	Al_2O_3	SiO_2
400	1	0.2	18.4	0.4	32.2	48.8
500	1	2.4	16.0	0.7	32.3	48.5
700	1	5.3	12.5	3.2	31.1	46.5
800	1	6.7	12.0	3.3	30.9	45.5
900	1	10.5	7.1	1.1	31.6	48.0

3.4 Waste combustion gas purification performance using a large-sized fluidized bed combustor

Table 2 summarizes the composition of waste combustion gas from RDF in the large-sized fluidized bed combustor. After introducing hydroxyl sodalite or hydrogrossular, the HCl concentration decreased from 174 ppm to 13 ppm for the former and to 35 ppm for the latter.

The concentration of dioxins at the sampling point (a) with the introduction of hydrogrossular (1.2 ng-TEQ/N m^3) is significantly higher than that observed in the absence of hydrogrossular (0.21 ng-TEQ/N m^3). A more oxidizing condition for combustion, as a higher CO concentration (1010 ppm versus 687 ppm) suggested, could be a possible cause for the reduction in the formation of dioxins. It has been noted that the formation of dioxins at the inlet of the gas cooler is suppressed more effectively with the use of hydrogrossular than without it, although the combustion conditions differ from each other. This suppression should result from capturing Cl^- with hydrogrossular at high temperatures, by which the formation of digoxins could be avoided. It is also probable that the oxidative decomposition of dioxins would occur even if it is formed during the combustion of RDF. This is because mayenite ($Ca_{12}Al_{10}Si_4O_{35}$), which is formed by the thermal decomposition of hydrogrossular, has the ability for the oxidative decomposition of chlorinated compounds to CO_2 and H_2O probably due to the superoxide anion (O_2^-) and peroxide anion (O_2^{2-}) present in it [32, 33].

Table 2: Composition of waste combustion gas.

	Blank	Hydroxyl sodalite	Hydrogrossular
Sampling point (a)			
Dioxin (ng-TEQ/N m^3)	0.21	0.06	1.2
O_2 (%)	2.4	3.7	2.3
CO (ppm)	687	999	1010
Sampling point (b)			
Dioxin (ng-TEQ/N m^3)	12	4.2	4.6
HCl (ppm)	174	13	35
O_2 (%)	3.2	3.7	2.3
CO (ppm)	741	1020	>1100
SO_2 (ppm)	0	0	0
NO_2 (ppm)	18	11	21

On the other hand, since hydroxyl sodalite also has the possibility of occluding the oxygen radicals, it is considered that a similar phenomenon occurs even in hydroxyl sodalite. Research is in progress to clarify this. In any case, it has been confirmed that the amount of dioxins could be decreased by simply introducing hydrogrossular or hydroxyl sodalite into a conventional combustor without any modification.

4 CONCLUSIONS

New ecofunctional ceramics, namely hydroxyl sodalite and hydrogrossular have been investigated in the present study for the abatement of HCl and dioxins from waste combustion gas. As a result of a plant scale test in the incinerator, it has been demonstrated that these new ecofunctional ceramics could decrease the concentrations of HCl at high temperatures and dioxins contained in waste combustion gas. In addition, it has been found that hydroxyl sodalite fixed copper in vapor phase at high temperatures. The above results confirm that the new ecofunctional ceramics are effective for the purification of waste combustion gas in the high temperature region without recovery of the waste incinerator. Generally, the recovery of the waste incinerator is very expensive and the presence of the ecofunctional ceramics would make the recovery unnecessary.

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