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A NEW TECHNIQUE TO CONTROL DIOXINS FORMATION ; COMBUSTION OF PRECURSOR COMPOUNDS AND REMOVAL HCl GAS USING HYDROGROSSULAR MINERALS AT HIGH TEMPERATURE

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Introduction

One method of the existing technology for the removal of dioxins is based on thermal decomposition by the high temperature gasifier melting combustors followed by adsorption using active carbon below 200°C. This technique is costly in view of plant investment and operation expenses. Dioxin compounds are formed by "de novo" from particulate organic carbon present in fly ash and inorganic chloride by a process, which is strongly activated by copper ions^{1,2}. The reaction occurs with optimum yields producing both PCDD and PCDF around 300°C. The aim of this study is to develop a new emission control technique having higher removal efficiencies of precursor of dioxins and HCl gas above 400°C using hydrogrossular. This is expected to prevent from generating dioxin obtained by HCl and precursor such as chlorobenzene with conventional waste incineration. We, at first, tested fixation of HCl and combustion of precursor compounds with experimental arrangements, and further, analyzed dioxins formation quantities and HCl concentrations generated in fluidized bed using refused derived fuel (RDF) using a pilot plant. Hydrogrossular ($\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{3-x}(\text{OH})_{4x}$, $x=0\sim 3$) is formed by hydrothermal treatment of by-products such as coal ash and molten slag at low temperature^{3,4}.

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Experimental

Sample Preparation

Hydrogrossular [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8}$] material was synthesized hydrothermally from a stoichiometric mixture of alumina-sol, amorphous silica and lime. The mixture was kept in a teflon-lined stainless steel autoclave (100mL Volume) with distilled water, then heated with rotation at 40 rpm. The water to solid ratio was 12 : 1 weight / weight. The reaction mixture was kept at 200°C for fifteen hours.

Fixation of HCl gas

Hydrogrossular pellets were prepared with 300~500 μm diameters particle size after pressing the powder sample. The length of the packed bed was 13mm for the pellets of 1g. The packed bed was placed in the center of the reactor made by quartz glass, the experiment was started by heating up the tubular furnace from 400 to 950°C under flowing N_2 gas of 500ml/min. Then the reaction gas, HCl at a concentration of 1000ppmv in dry N_2 gas, was introduced into the fixed bed reactor with flow maintained at 500ml/min. The experiment was completed when the outlet HCl concentration reached 1000ppmv. The outlet HCl level was continuously monitored by an automatic HCl analyzer.

Combustion of benzene and chlorobenzene

Catalyst testing was performed using a conventional plug flow microreactor with a quartz glass at 600°C. A stream of 1000ppmv of benzene and mono-chlorobenzene was obtained by bubbling synthetic air (N_2 :80%, O_2 :20%) through a temperature-controlled impinger. The total gas flow was 100ml/min, and the space velocity was 10000h⁻¹. Hydrogrossular was pelletized to a 300~500 μm particle size before being secured in the reactor between plugs of silica wool. Analysis of reactant and product was performed on-line using a chromatograph. Conversion data was calculated using the concentration of precursor compounds in the outlet stream. Product selectivities were expressed as percentage of the converted aromatic compounds after correction for differences in carbon number.

Analysis of dioxin and HCl with RDF combustion in fluidized bed

The analyses of the dioxin obtained by "de novo" using hydrogrossular were performed with pilot plant (Fig.1). RDF were burnt in a 0.5 × 0.5 × 9 m bubbling type fluidized bed combustor. The total gas flow was 500Nm³/h and the temperature of combustion was 850°C.

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The effluent gas (HCl, CO, SO₂, O₂ and NO₂) was continuously analyzed. The gas sampling points were placed in the outlet of combustor (① in Fig.1) and inlet side of gas cooler (② in Fig.1). Hydrogrossular powder was introduced into combustor at 6.2kg/hr.

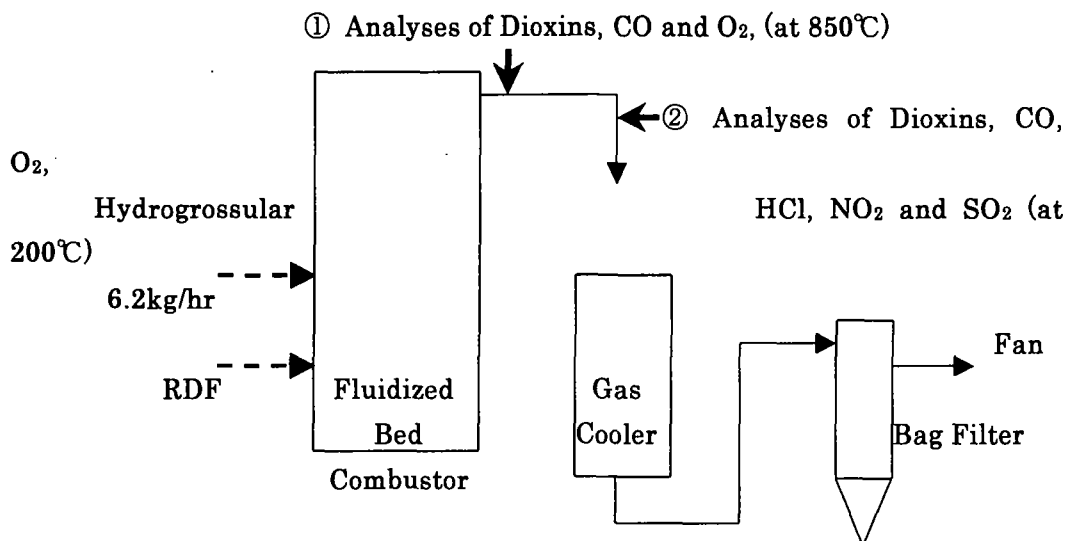
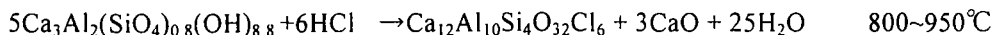
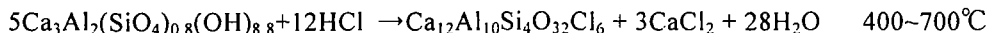


Fig. 1 RDF combustion in fluidized bed

Results and Discussion

Reaction between HCl and hydrogrossular

The HCl gas was efficiently removed from the inlet gas as Ca₁₂Al₁₀Si₄O₃₂Cl₆ (wadalite) and CaCl₂ from 400 to 700°C and as Ca₁₂Al₁₀Si₄O₃₂Cl₆ and CaO above 800°C⁵. Based on the results obtained in the present study, the reaction between hydrogrossular and HCl at high temperature can be represented by following equations.



Combustion of benzene and chlorobenzene

Hydrogrossular decomposes benzene (Bz) and chlorobenzene (CBz) at 600 °C with >97% conversion of benzene and chlorobenzene into carbon

Table 1 Catalytic activity of hydrogrossular

	Temp.(°C)	Conversion (%)	Selectivity (%)	
			CO	CO ₂
Bz	600	97.1	11	89
CBz	600	99.5	12	88

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oxides (Table 1). In the presence of chlorobenzene, hydrogrossular showed deactivation in the trial test. It is understandable that hydrogrossular reacted with chlorine ions composing of chlorobenzene and converted to wadalite and CaCl_2 .

Analysis of dioxin and HCl with RDF combustion in fluidized bed

Hydrogrossular sorbent in fluidized bed was capable of reducing HCl level to near 30ppm. The formation of dioxin at inlet side of gas cooler (Sampling ②) was depressed using hydrogrossular compared with blank test (Table 2). This is presumed to prevent from generating dioxin obtained from "de novo".

Table 2 Analysis result of effluent gas

	Sampling ①			Sampling ②				
	Dioxin	O ₂	CO	Dioxin	HCl	O ₂	CO	SO ₂
	(ng-TEQ/m ³ N)	(%)	(ppm)	(ng-TEQ/m ³ N)	(ppm)	(%)	(ppm)	(ppm)
NO ₂								
(ppm)								
Blank	0.21	2.4	687	12	174	3.2	741	0
Hy	1.2	2.3	1010	4.6	35	2.3	---	0

Hy:Hydrogrossular

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