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A new sorbent, hydrogarnet, with purging HCl gas at high temperature

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Abstract

Hydrogarnet injected in two types of reactors in a pilot plant scale was found to be capable of reducing the amount of HCl from the effluent gas at high temperatures, for which conventional sorbents such as CaO and $Ca(OH)_2$ did not. HCl gas was fixed as chlorinate mayenite [$Ca_{12}Al_{10}Si_4O_{32}Cl_6$] at >700 °C under a realistic gas composition including H_2O, CO_2 and so on. Hydrogarnet also decreased the amount of hazardous by-products such as dioxins.

Keywords: Fixation of HCl; Hydrogarnet; CaO

1. Introduction

Incineration is the environmentally soundest option for hazardous waste disposal. However, chlorine-containing wastes produce HCl gas upon incineration. HCl must be removed from flue gases before its emission into the atmosphere, because, it is one of the most troublesome substances among acidic gases. Both the combustion of refuse and the incineration of hazardous wastes are main sources for the formation of HCl. This is because HCl is mainly produced upon incineration through the oxidative destruction of toxic halogenated organic wastes such as pesticides and various chlorinated hydrocarbons like polyvinyl chloride (PVC) or polychlorinated biphenyls (PCBs) from industrial uses [1].

In recent years, much attention has focused on lowering the level of atmospheric pollution caused by HCl gas. The current scrubber technology to remove HCl using CaO or $Ca(OH)_2$ is relatively simple and easily operable and as a result, the capital cost can be reduced [2–4]. However, the scales of $CaCl_2$ are sometimes deposited on the wall of the reactor, which causes a trouble in incineration. It is, therefore, of importance to develop materials other than CaO for HCl emission control.

A component of cement minerals of hydrogarnet [$Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8}$] is a hopeful candidate to suppress the emission of acid gas from combustion processes [5,6]. It was found that hydrogarnet could capture HCl gas at above 400 °C with a fixed bed reactor resulting in its conversion to a mixture of chlorinate mayenite [$Ca_{12}Al_{10}Si_4O_{32}Cl_6$] and $CaCl_2$. The theoretical chlorine content captured with hydrogarnet is 22.1 wt.%. The activation energy of 24.2 kJ/mol was obtained for the reaction between HCl and hydrogarnet, the value of which suggested diffusion limitation for the reaction [6]. The crystalline structure of chlorinate mayenite was similar to that of zeolites in a sense of frameworks of $(Al,Si)O_4$ tetrahedra involved. Chloride ions from HCl were fixed in the micro cavity of the framework with the size of ∼4 Å and still remained in chlorinate mayenite after heating at high temperatures. The crystal structure of chlorinate mayenite was refined by the Rietveld method using the program REITAN 94 which simulate X-ray powder diffraction data of the solid [5]. Such HCl removal at high temperatures leads us to expect the suppression of the downstream formation of hazardous byproducts such as polychlorinated dibenzo-*p*-dioxins (PCDDs) or polychlorinated

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dibenzofrans (PCDFs) [7]. Therefore, hydrogarnet may be considered to be a promising material as a new sorbent of HCl applicable to an incinerator or a combustor with little modification. The objective of the present study is to examine the ability of hydrogarnet to fix HCl gas under a real gas composition in order to apply it to a conventional combustion system. The experiments were performed with two types of systems of a vertical reactor with flowing synthetic gases and a fluidized bed combustor for Refuse Derived Fuel (RDF).

Table 1
Textural properties of hydrogarnet and commercialized $Ca(OH)_2$[a]

	Hydrogarnet	$Ca(OH)_2$	$Ca(OH)_2$ with high surface area
Average particle size (μm)	15	3.5	8
Surface area (m^2/g)	43	15	45
Tapped density (g/cm^3)	0.45	0.32	0.4

[a] High quality industrial lime prescribed by the Japan Industrial Standard (JIS).

2. Experimental

2.1. Material

Hydrogarnet was synthesized by the hydrothermal reaction of a stoichiometric mixture of alumina sol, amorphous silica and CaO. The mixture was put in a teflon-lined stainless steel autoclave together with distilled water. The ratio of water to solids was 12:1 by weight. The autoclave was placed in a temperature-controlled oven, the temperature of which was controlled to increase from room temperature to 200 °C in 2 h. The mixture was then kept at 200 °C for 15 h. The solid product was separated by filtration and dried at 110 °C for 24 h. Table 1 summarizes the average particle size, the surface area and the dry density obtained by repeatedly tapping the powders in a container of hydrogarnet and commercialized HCl sorbents as references.

Table 2
Experimental conditions in vertical tube reactor

Gas phase	
HCl (ppmv)	1000
O_2 (%)	10
CO_2 (%)	10
H_2O (%)	10
N_2	Balance
Gas flow rate (L/min)	45
Superficial velocity (m/s)	15
Residence time (s)	3
Reaction temperature (°C)	700, 800
Introducing rate of hydrogarnet (g/min)	0.4, 0.8, 1.2, 1.6

2.2. Characterization

Before the reaction with HCl, the powder property was characterized with a laser diffraction particle size distribution analyzer (HORIBA, LA-700) and specific surface area was with N_2 adsorption–desorption at 77 K (Bell Japan, BELSORP 28SP). X-ray powder diffraction data of the solids were obtained with a diffractometer (Rigaku, RINT 2000) using CuKα radiation (30 kV and 30 mA). The concentration of HCl was monitored with an automatic HCl analyzer (HL-36: Kyoto Electrons Manufacturing). The analysis of the solid reaction products were determined by an atomic absorption spectrometer (Hitachi, Z-5000) for the filtrate, and titration with 0.1N silver nitrate ($AgNO_3$) solution using potassium chromate (K_2CrO_4) as an indicator to analyze chloride ion. The concentrations of CO, O_2, SO_x and NO_x in the fluidized bed combustor were recorded with a multi-gas analyzer (Shimadzu Co., NSA-307). TEQ (Toxicity Equivalent Quantity) of dioxin (PCDDs, PCDFs and PCBs) was evaluated in Shimadzu Techno Research, where the selected ion monitoring method by using GC-MS (MICROMASS) was adopted.

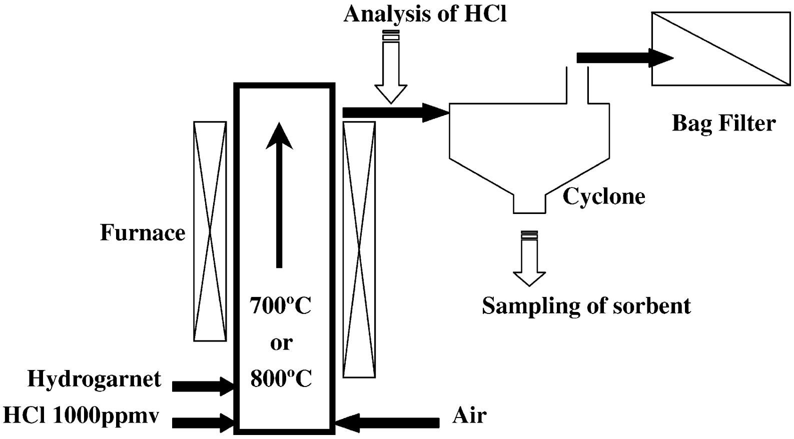

Fig. 1. Schematic drawing of the vertical reactor.

Table 3
Experimental conditions in fluidized bed combustor

Gas flow rate (Nm^3/h)	500
Superficial velocity (m/s)	1.0
Residence time (s)	6
Temperature in combustor (°C)	750 ± 50
Introducing rate of hydrogarnet (g/min)	103

2.3. Fixation of HCl at high temperatures

2.3.1. Vertical reactor with flowing synthetic gases

The experiment was started by heating the vertical tubular furnace at 700 or 800 °C in flowing air of 45 L/min (see Fig. 1). The reaction gas, 1000 ppmv HCl diluted with air, was introduced into a quartz glass reactor with the size of 0.1 m in diameter and 4.5 m in height. Table 2 summarizes the gas composition in this reactor. The rate of hygrogarnet injected into a reactor was 0.4, 0.8, 1.2, and 1.6 g/min. According to Eq. (2) described below, 0.4 g/min of hygrogarnet is necessary to remove all HCl (1000 ppmv) contained in the synthetic gas of 45 L/min, which in turn, 0.8, 1.2 and 1.6 g/min of hydrogarnet added correspond, respectively to 2, 3, and 4 times amount of HCl to be removed.

2.3.2. Fluidized bed combustor

Table 3 summarizes the experimental condition for the fluidized bed combustor. RDF composing of a mixture of polyvinyl chloride (PVC), plastics waste and paper was burnt in a 1.2 m × 1.2 m × 9 m bubbling type fluidized bed combustor. The gas flow rate was 500N m^3/h and the temperature of combustion was 750 ± 50 °C. The concentrations of exhausted gases (HCl, CO, SO_2, O_2, and NO_2) were continuously recorded. The gas sampling points were placed in the outlet of the combustor (sampling point a in Fig. 2) and the outlet side of the gas cooler (sampling point b in Fig. 2). Hydrogarnet powders were injected into the combustor at the injection rate of 103 g/min. The amount of dioxin formed by "*de-Novo synthesis*" was also determined.

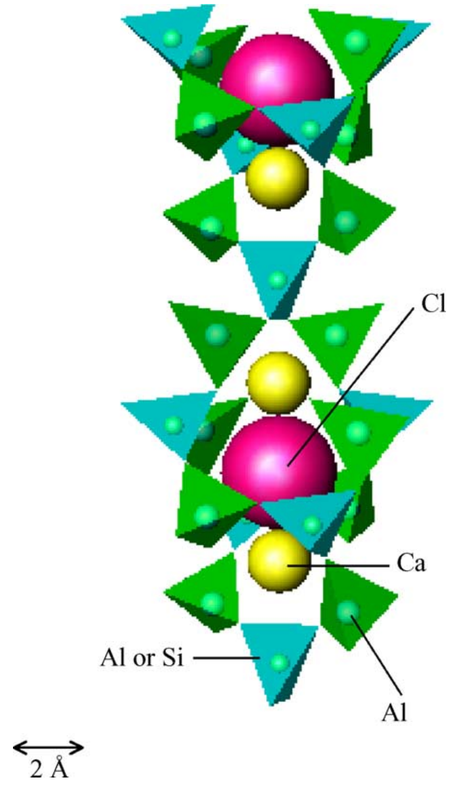

Fig. 3. Crystal structure of chlorinate mayenite [$Ca_{12}Al_{10}Si_4O_{32}Cl_6$].

3. Results and discussion

3.1. Ability of capturing HCl at high temperature in the vertical reactor

In the absence of HCl, hydrogarnet was dehydrated to mayenite [$Ca_{12}Al_{10}Si_4O_{35}$] and calcium oxide at 320 °C (Eq. (1)), while chlorinate mayenite [$Ca_{12}Al_{10}Si_4O_{32}Cl_6$]

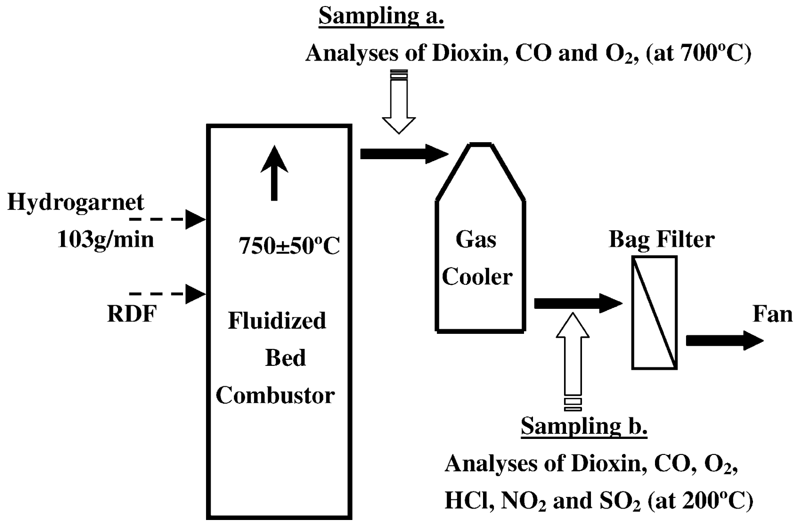

Fig. 2. Schematic drawing of the fluidized bed combustor.

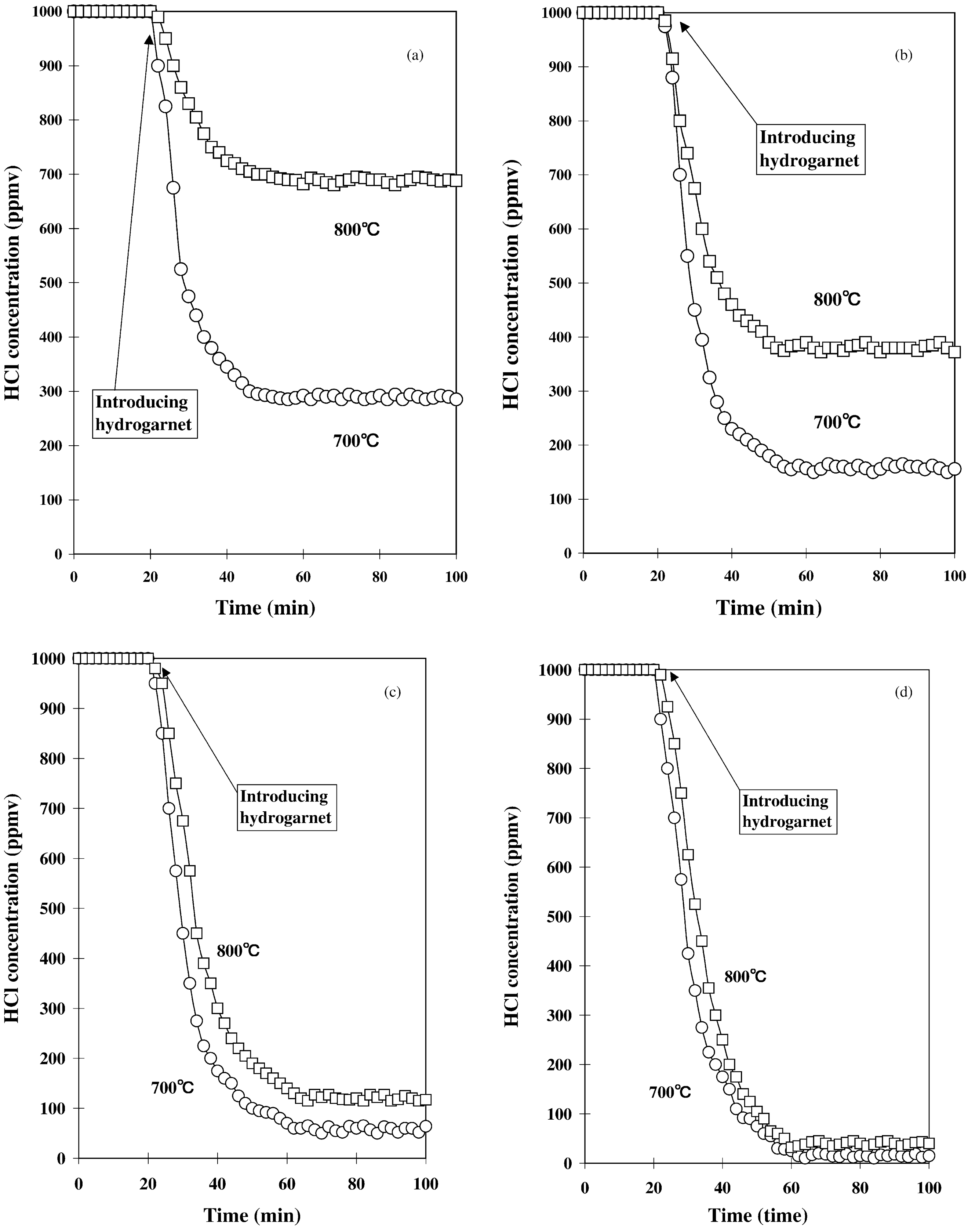

Fig. 4. The concentration of HCl in the reactor for the rate of hydrogarnet introduction of 0.4 (a), 0.8 (b), 1.2 (c), and 1.6 g/min (d).

was formed in the presence of HCl (Eq. (2)).

$$5Ca_3Al_2(SiO_4)_{0.8}(OH)_{8.8} \rightarrow Ca_{12}Al_{10}Si_4O_{35}\,[\text{or } Ca_{12}Al_{10}Si_4O_{32}\,(O_3)] + 3CaO + 22H_2O \qquad (1)$$

$$Ca_{12}Al_{10}Si_4O_{35} + 3CaO + 12HCl \rightarrow Ca_{12}Al_{10}Si_4O_{32}Cl_6 + 3CaCl_2 + 6H_2O \qquad (2)$$

Mayenite forms a zeolitic structure with the framework of the $(AlSi)O_4$ tetrahedra occluding the superoxide anion (O_2^-) and peroxide species (O_2^{2-}) in a cavity [8,9]. The anions of superoxide (O_2^-) and peroxide (O_2^{2-}), denoted in parenthesis in Eq. (1), were occluded in mayenite and those of chloride (Cl^-) were in chlorinate mayenite (see Fig. 3.) [8]. At high temperatures, O_2^- and O_2^{2-} in the micro pore of the mayenite structure were readily substituted with Cl^- resulting in the formation of chlorinate mayenite ($O_2^- \rightarrow Cl^-$, $\mathbf{O}_2^{2-} \rightarrow 2Cl^-$) [5,6]. A cavity in the framework accommodates Ca–Cl–Ca linearly coordinated atoms. The structure of chlorinate mayenite derives from mayenite structure with incorporation of excess Cl^- and substitution of Si^{4+} for Al^{3+} for charge compensation. Fig. 4 a–d illustrate the output concentrations of HCl at 700 and 800 °C for the rate of hydrogarnet introduced into the vertical reactor via flowing synthetic gases. As the introduction rate increased from 0.4 to 1.6 g/min, the HCl concentration decreased to 290, 160, 60 and 15 ppm at 700 °C and to 690, 380, 140, and 40 ppm at 800 °C. It was interesting to note that HCl was removed more effectively at 700 °C than at 800 °C. Fig. 5 displays XRD patterns for the solids after the reaction. Although, chlorinate mayenite was formed at the both reaction temperatures, the additional product was different between these reaction temperatures: $CaCl_2{\cdot}2H_2O$ at 700 °C and CaO at 800 °C. The absence of $CaCl_2{\cdot}2H_2O$ in the product at 800 °C should be responsible for the inferior effectiveness of HCl removal at 800 °C. Further study is necessary to reveal the difference in the products between 700 and 800 °C.

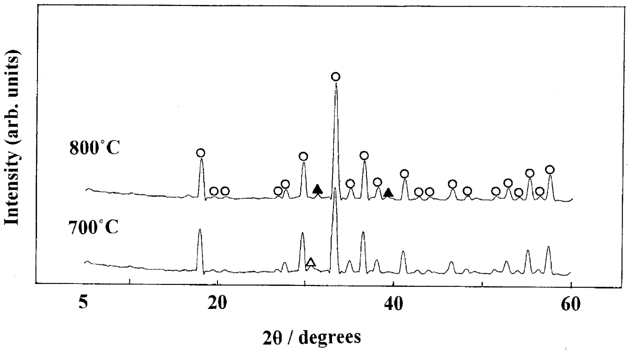

Fig. 5. XRD patterns of hydrogarnet after reaction with HCl gas. (○) chlorinate mayenite, (▲): CaO, (△): $CaCl_2{\cdot}2H_2O$.

Table 4
Composition of exhaust gas

	Blank	Hy
Sampling point a		
Dioxin (ng-TEQ/m^{3}N)	0.21	1.2
O_2 (%)	2.4	2.3
CO (ppm)	687	1010
Sampling point b		
Dioxin (ng-TEQ/m^{3}N	12	4.6
HCl	174	35
O_2 (%)	3.2	2.3
CO (ppm)	741	>1100
SO_2 (ppm)	0	0
NO_2 (ppm)	18	21

Hy means hydrogarnet.

3.2. *Suppression of dioxin formation in the fluidized bed combustor*

In the fluidized bed, Table 4 summarizes the composition of the exhaust gas from RDF in the combustor. After introducing hydrogarnet, the HCl concentration decreased from 174 ppm to near the level of 30 ppm. The dioxin concentration (0.21 ng-TEQ/m^{3}N) without the introduction of hydrogarnet (sampling point a in Table 4) was lower than that with hydrogarnet. A more oxidizing condition for combustion, as a lower CO concentration (687 ppm versus 1010 ppm) suggested, was a possible cause for the reduction of dioxin formation. It was noted that the formation of dioxin at the inlet of the gas cooler was more pronouncedly suppressed with the use of hydrogarnet than without it, although the combustion conditions were different from each other. This suppression should result from capturing Cl^- with hydrogarnet at high temperatures, by which the formation of dioxin was avoided. It is also probable that the oxidative decomposition of dioxin occurs, even if it is formed during the combustion of RDF. This is because mayenite has the ability for the oxidative decomposition of chlorinated compounds to CO_2 probably due O_2^- and O_2^{2-} present in it [8,9]. Anyway, it was confirmed that the amount of dioxin could be decreased by simply introducing hydrogarnet into a conventional combustor with no modification.

4. Conclusions

Hydrogarnet introduced into two types of reactors with a pilot plant scale was found to be capable of reducing the amount of HCl from the effluent gas at high temperatures, the conditions under which conventional sorbents such as CaO and $Ca(OH)_2$ were not used. HCl gas was fixed by hydrogarnet as chlorinate mayenite and $CaCl_2$ by which the formation of dioxins was suppressed. The ability of mayenite to combust aromatic compounds played another possible role in the decrease in the amount of dioxin emitted to the atmosphere.

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References

[1] B.K. Gullett, Reduction of Chlorinated Organics in the Incineration of Wastes, US Patent, 1991 5, 021, 229.

[2] M. Daoudi, J.K. Walters, The reaction of HCl gas with calcined commercial limestone particles: the effect of particle size, Chem. Eng. J. 47 (1991) 11–16.

[3] G. Mula, A. Lallai, On the kinetics of dry reaction between calcium oxide and gas hydrochloric acid, Chem. Eng. Sci. 47 (1992) 2407–2411.

[4] C.E. Weinell, P.I. Jensen, K. Dam-Johansen, K. Livbjerg, Hydrogen chloride reaction with lime and limestone: kinetics and sorption capacity, Ind. Eng. Chem. Res. 31 (1992) 164–171.

[5] S. Fujita, K. Suzuki, M. Ohkawa, Y. Shibasaki, T. Mori, Reaction of hydrogrossular with hydrogen chloride gas at high temperature, Chem. Mater. 13 (2001) 2523–2527.

[6] S. Fujita, K. Suzuki, T. Mori, Y. Shibasaki, A new technique to remove hydrogen chloride gas at high temperature using hydrogrossular, Ind. Eng. Chem. Res. 42 (2003) 1023–1027.

[7] L. Stieglitz, G. Zwick, J. Beck, H. Bautz, W. Roth, Carbonaceous particles in fly ash—a source for the de-novo-synthesis of organochlorocompounds, Chemosphere 19 (1989) 283–290.

[8] S. Fujita, K. Suzuki, M. Ohkawa, T. Mori, Y. Iida, Y. Miwa, H. Masuda, S. Shimada, Oxidative destruction of hydrocarbons over a new zeolite-like $Ca_{12}Al_{10}Si_4O_{35}$ crystal including O_2^- and O_2^{2-} radicals, Chem. Mater. 15 (2003) 255–263.

[9] S. Fujita, M. Ohkawa, K. Suzuki, H. Nakano, T. Mori, H. Masuda, Controlling the quantity of radical oxygen occluded in a new aluminum silicate with nanopores, Chem. Mater 15 (2003) 4879–4881.