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Reaction of Hydrogrossular with Hydrogen Chloride Gas at High Temperature

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The reaction between hydrogrossular and hydrogen chloride (HCl) gas was performed in a fixed bed reactor above 400 °C. The hydrogrossular was efficiently reacted with HCl gas in the temperature range of 400 to 950 °C and transformed into $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ (calcium aluminum chlorosilicate). The crystal structure of the product phase $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ was cubic, space group $I\bar{4}3d$, with unit cell $a = 12.0173(1)$ Å, and was similar to that of wadalite. The structure consists of a framework of $(Al,Si)O_4$ tetrahedra. A large cavity in the framework accommodates Ca−Cl−Ca linearly coordinated atoms.

Introduction

Incineration may be the most environmentally sound option for hazardous waste disposal, provided the problems associated with incineration are assessed and dealt with. Among these problems is the removal of air pollutants such as hydrogen chloride (HCl), sulfur oxides (SO_x), nitrogen oxides (NO_x), and other contaminants. In recent years, a great deal of attention has been paid to the problem of reducing the level of atmospheric pollution caused by HCl derived from incineration of poly(vinyl chloride) plastics. The present scrubber technologies for removing HCl, which use calcium hydroxide [$Ca(OH)_2$] or calcium carbonate ($CaCO_3$) sorbents at low temperature (below 300 °C), are relatively simple, easy to operate, and have low capital costs.[1−3] However, this technology may cause a side reaction by which polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) can form by de novo synthesis in the municipal waste incineration process[4] and can cause hot corrosion of the body of incinerator.

Hydrogrossular is one of the possible hydration products in solidified cement pastes (from both portland and alumina cements).[5] Hydrogrossular is also formed by hydrothermal treatment of byproducts such as coal ash at low temperature. The general molecular formula of hydrogrossular is given as $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$, where x is in the range between 0 and 3. The minerals with $0 < x \leq 1.5$ and $1.5 < x \leq 3$ are referred to as hibschite [$Ca_3Al_2(SiO_4)_3 \sim Ca_3Al_2(SiO_4)_{1.5}(OH)_6$] and katoite [$Ca_3Al_2(SiO_4)_{1.5}(OH)_6 \sim Ca_3Al_2(OH)_{12}$], respectively. The hydrogrossular end members are known as grossular ($Ca_3Al_2Si_3O_{12}$) and katoite [$Ca_3Al_2(OH)_{12}$]. These phases are all cubic and members of the garnet groups of minerals. Structurally, the $(SiO_4)^{4-}$ tetrahedra in the grossular structure are replaced by $(O_4H_4)^{4-}$. Such an extensive solid solution involving the $(O_4H_4)^{4-}$ group is not found in the other common garnets and is highly unusual for silicate groups in general.[6−11]

The aim of this study is to develop new emission control techniques having higher removal efficiencies of HCl gas in the temperature range 300−950 °C using hydrogrossular with a fixed bed reactor, to clarify the reaction that occurs between hydrogrossular and HCl gas and further to refine the crystal structure of the product obtained from the reaction between hydrogrossular and HCl gas.

Experimental Section

Sample Preparation. The hydrogrossular [$Ca_3Al_2(SiO_4)(OH)_8$] sorbent material was synthesized hydrothermally from a stoichiometric mixture of alumina-sol (alumina-sol 520; Nissan Chemical Industries, Ltd.),

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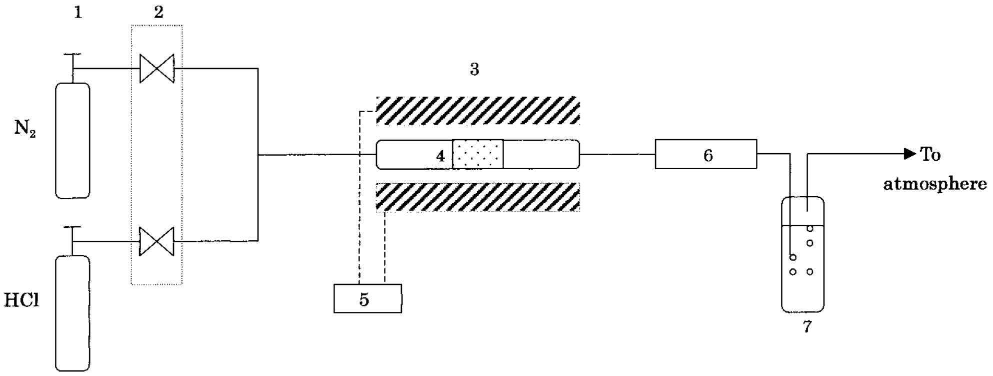

Figure 1. Schematic representation of fixed bed reactor used in the present study: 1, reagent gases; 2, mass flow controllers; 3, furnace; 4, hydrogrossular; 5, temperature controller; 6, automatic HCl gas analyzer; 7, NaOH absorber.

amorphous silica (synthetic silica powder; Hakusui Tech. Co., Ltd.), and lime (reagent grade, calcium oxide; Kanto Chemical Co., Ins.). The mixture was put in a Teflon-lined stainless steel autoclave (25 mL volume) with distilled water and then heated with rotation at 50 rpm. The water-to-solid ratio was 12:1 weight/weight. The autoclave was placed in the temperature-controlled oven where the heating rate was controlled so that it increased from room temperature to 200 °C in 2 h. The reaction mixture was kept at 200 °C for 15 h. The solid products were separated by filtration and dried at 110 °C for 24 h.

Fixation of HCl Gas by Hydrogrossular in a Fixed Bed Reactor. Hydrogrossular pellets were prepared with 300−500 μm diameter particle size after pressing of the powder sample. The length of the packed bed was 13 mm for the pellets of 1 g. The packed bed was placed in the center of the reactor made by quartz glass, and the experiment was started by heating the tubular furnace from 300 to 950 °C under flowing nitrogen (N_2) gas of 500 mL/min (see Figure 1). Then the reaction gas, HCl at a concentration of 1000 ppmv in dry N_2 gas, was introduced into the fixed bed reactor with flow maintained at 500 mL/min. The concentration of HCl 1000 ppmv is similar to that of average composition including exhaust gas of incinerators in Japan. The experiment was completed when the outlet HCl concentration reached 1000 ppmv. The residual HCl level was continuously monitored by an automatic HCl analysis instrument which permitted the breakthrough behavior of the fixed bed to be measured.

Measurements. The powder properties of the starting materials were characterized with a laser diffraction particle size distribution analyzer (HORIBA, LA-700) and N_2 adsorption−desorption at 77 K using a BET method (Bell Japan, BELSORP 28SP). The HCl concentration from the outlet of the fixed bed reactor was measured by HCl analysis instrument (Thermo Electron Co., model 15C). The chemical compositions of hydrogrossular and the solid reaction products were determined by XRF spectroscopy (Shimadzu Co., Lab center, XRF-1700WS sequential X-ray fluorescence spectrometer) for the solid sample, an atomic absorption spectrometer (Hitachi, model Z-5000) for the filtrate, and titration with 0.1 N silver nitrate ($AgNO_3$) solution using potassium chromate (K_2CrO_4) as an indicator to analyze chloride ion.

Table 1. Textural Properties of Hydrogrossular

chemical formula	$Ca_{2.98}Al_{1.98}(Si_{0.81}O_{3.23})(OH)_{8.77}$
average particle size (μm)	15
surface area (m^2/g)	43
tapped density (g/mL)	0.45

X-ray powder diffraction data of the solids were obtained with a M18XHF diffractometer (MAC Science Ltd.) using Cu Kα radiation (40 kV, 100 mA) and a diffracted beam monochromator (graphite). The diffraction pattern was collected at room temperature from 15 to 100° in 2θ using 0.01° 2θ step increments and a 1.2 s counting time/step.

The crystal structure refinement was carried out by the Rietveld method using the program REITAN 94.[12] The lattice constant and some instrumental parameters were determined with mixture of silicon (National Bureau of Standards, 640) and solid product after washing which react with HCl at 700 °C. After that, the Rietveld analysis was made on the diffraction pattern collected on the solid sample. The parameters determined prior to the analysis were used as initial values and were also varied in the least-squares. The refinement was initiated with the positional parameters of wadalite, $Ca_6Al_3(Al_2Si_2)O_{16}Cl_3$.[13] In the final refinement cycle, the occupancy parameters were fixed by assuming that the Ca, T(1), and T(2) sites were occupied by Ca, Al, and $Al_{1/3}Si_{2/3}$, respectively, and the Cl site was fully occupied by Cl.

Results and Discussion

Physicochemical Properties of the Hydrogrossular Powder. The empirical formula calculated from the chemical compositions corresponds to $Ca_{2.98}Al_{1.98}(Si_{0.81}O_{3.23})(OH)_{8.77}$. The hydrothermal treatment method produced very fine particles. The average particle size, surface area, and dry density obtained by repeatedly tapping the powder in a container of hydrogrossular powder are shown in Table 1.

Reaction of HCl Gas with Hydrogrossular in the Fixed Bed Reactor. The removal of HCl from the input stream with hydrogrossular was investigated in the fixed bed reactor. Figure 2 shows breakthrough curves for the reaction at various temperatures. Figure

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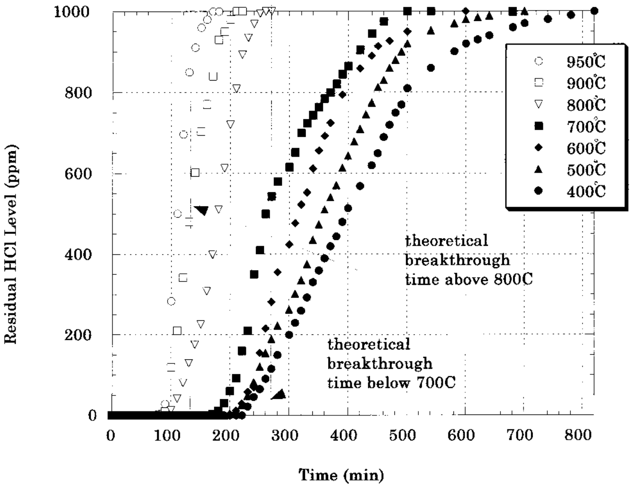

Figure 2. HCl breakthrough curves for hydrogrossular sorbent in a fixed-bed reactor at various temperatures.

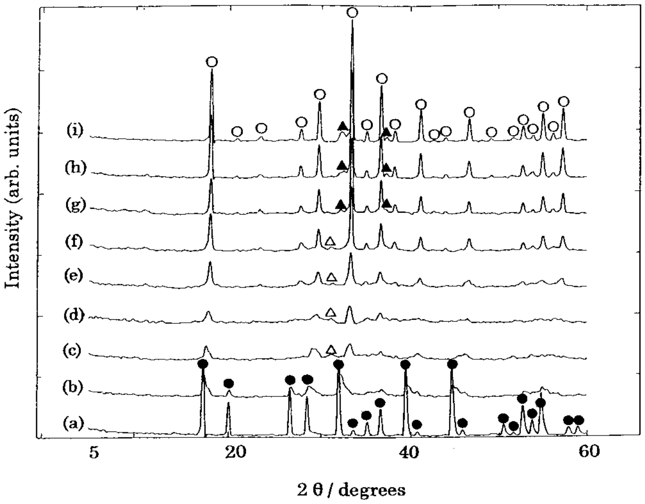

Figure 3. XRD patterns for hydrogrossular after reacting with HCl gas at various temperatures: (a) hydrogrossular; (b) 300 °C; (c) 400 °C; (d) 500 °C; (e) 600 °C; (f) 700 °C; (g) 800 °C; (h) 900 °C; (i) 950 °C. Key: ●, $Ca_{2.98}Al_{1.98}(Si_{0.81}O_{3.23})(OH)_{8.77}$ (hydrogrossular); △, $CaCl_2{\cdot}2H_2O$; ○, $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ (calcium aluminum chlorosilicate); ▲, CaO.

3 contains XRD patterns of hydrogrossular before and after reaction with HCl gas at 300−950 °C. The XRD patterns of solid products reacting with HCl were measured at the ambient conditions after cooling from each reaction temperature to room temperature. Hydrogrossular remained without unreacted with HCl at 300 °C. At the reaction temperatures of 400−700 °C, a second phase corresponding to $CaCl_2{\cdot}2H_2O$ was observed. Since $CaCl_2$ is highly hygroscopic, it may take up moisture and form $CaCl_2{\cdot}2H_2O$. Above 800 °C, the second phase was CaO. The chemical composition of the solid sample, after removing the second phase ($CaCl_2{\cdot}2H_2O$) by washing in distilled water, was $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$, which has a chlorine content of 13.2 wt %. Chloride ion analyzed in the filtrate was absent in the products from the above 800 °C reactions. $CaCl_2$ has a melting point of 772 °C, and the lowest liquidus temperature in the CaO−$CaCl_2$ system is 750 °C. Above 772 °C CaO is stable and does not react with HCl from the standpoint of thermodynamics. The HCl gas is efficiently removed from the inlet gas as $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ and $CaCl_2$ from 400 to 700 °C and as $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ above 800 °C. On the basis of the results obtained in the present study, the reaction between hydrogrossular and HCl at high temperature can be represented by eqs 1 and 2.

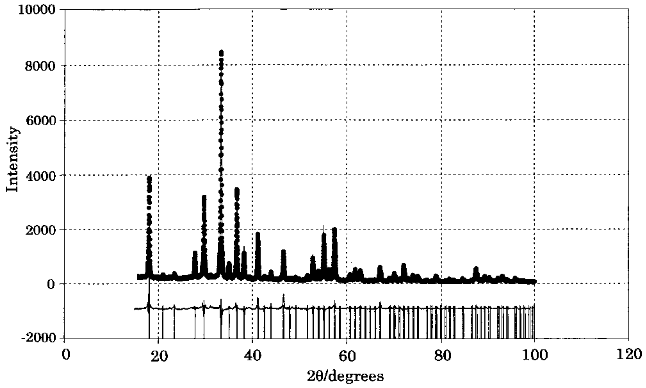

Figure 4. Rietveld refinement pattern of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$. Filled circles (●) represent the observed data, and the solid line indicates the calculated pattern. A difference (obsd − calcd) plot is shown beneath.

$$5Ca_{2.98}Al_{1.98}(Si_{0.81}O_{3.23})(OH)_{8.77} + 12HCl \rightarrow Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9} + 2.9CaCl_2 + 28H_2O \qquad 400{-}700\ ^\circ C \quad (1)$$

$$5Ca_{2.98}Al_{1.98}(Si_{0.81}O_{3.23})(OH)_{8.77} + 6HCl \rightarrow Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9} + 2.9CaO + 25H_2O \qquad 800{-}950\ ^\circ C \quad (2)$$

Our results also indicated that the pelletized sorbents in the fixed bed reactor are capable of reducing the HCl level to near zero levels at high temperatures. The theoretical breakthrough times computed from eqs 1 and 2, the flow rate, and gas composition are 270 and 135 min, respectively (Figure 2). The breakthrough times of reaction from 400 to 700 °C and from 800 to 950 °C are around 200 and 100 min, respectively, which are close to the theoretical breakthrough times as computed by assuming that, at the end, all the hydrogrossular has been converted to $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ and $CaCl_2$ below 700 °C and $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ above 800 °C. This reaction is especially likely to be controlled by reactant diffusion through the product layer at lower temperature. Wadalite containing chloride ion can be very well regenerated into hydrogrossular by treating wadalite with CaO/H_2O under steam pressure at 200 °C. The details regarding recycle process will be reported separately.

Crystal Structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$. The X-ray diffraction pattern of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is shown in Figure 4. The lattice parameter is a = 12.0173(1) Å (Table 2). Table 3 and Figure 5 show the positional parameters and crystal structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$, while Table 4 collects the interatomic distance and angles. The present $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ has a structure similar to that of wadalite ($Ca_{12}Al_{10}Si_4O_{32}Cl_6$), which belongs to the mayenite-type ($Ca_{12}Al_{14}O_{33}$) family. Mayenite has an oxygen ion that is readily replaced with 2(OH^-, F^-, Cl^-) giving a composition of $Ca_{12}Al_{14}O_{32}[O,(OH)_2,F_2,Cl_2]$.[14−17] Naturally occurring mayenite has a composition close to $Ca_{12}Al_{14}O_{32}$-

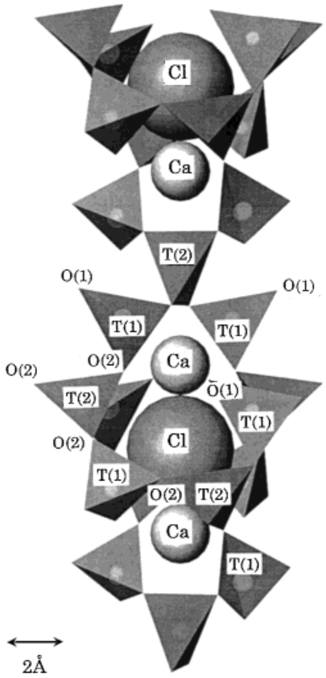

Figure 5. Crystal structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$, showing the links of tetrahedra. The large and small spheres represent chloride and calcium ions, respectively.

Table 2. Crystallographic Data for $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$

Results of Rietveld Refinement	
cryst system	
a (Å)	12.0173(1)
V (Å^3)	1735.48
space group	$I\bar{4}3d$
thermal param ($B_{overall}$, Å^2)	1.5(3)
Reliability Factors	
R_{wp}[a] (%)	15.73
R_p[b]	12.00
R_{expt}[c]	6.15
R_I[d]	12.69
R_F[e]	7.42
s[f]	2.55

[a] Weighted pattern R-factor. [b] Pattern R-factor. [c] Expected R-factor. [d] Integrated intensity R-factor. [e] Structure factor R-factor. [f] Goodness of fit indicator (R_{wp}/R_{expt}).

Table 3. Atomic Positions for $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$

atom	site	x	y	z
Ca	24d	0.1075(11)	0	1/4
T(Al)	16c	−0.0192(11)	−0.0192	−0.0192
T(Al,Si)	12a	3/8	0	1/4
O(1)	16c	0.069(2)	0.069	0.069
O(2)	48e	0.022(2)	0.056(2)	0.660(2)
Cl	12b	1/8	1/2	1/4

$(OH)_2$. The structure of wadalite is a derivation of the mayenite structure, with incorporation of excess Cl^- and substitution of Si^{4+} for Al^{3+} for charge compensation. The cell volume of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is comparable to wadalite and is more expanded than that of $Ca_{12}Al_{10.6}Si_{3.4}O_{32}Cl_{5.4}$[18] because of greater occupation of chloride ions (Table 5).

Table 4. Interatomic Distances (Å) and Angles (deg) for $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$[a]

	Ca Decahedron	
Ca−O(1)	2.37(3) × 2	
Ca−O(2)	2.35(3) × 2	
Ca−O(2^i)	2.34(2) × 2	
Ca−Cl	2.79(1)	
mean	2.41	
		O−Ca−O(Cl)
O(1)−O(2)	3.68(4)	75.0(10)
O(1)−O(2^{ii})	3.19(4)	74.8(10)
O(1)−O(2^{iii})	3.19(4)	97.6(9)
O(1)−Cl	3.29(3)	78.8(8)
O(2)−O(2^i)	2.70(5)	63.0(3)
O(2)−O(2^{ii})	4.06(2)	116.0(5)
O(2^i)−O(2^{ii})	2.55(5)	71.9(4)
O(2^i)−Cl	3.44(2)	79.8(4)
	T(Al) Tetahedron	
T(Al)−O(1)	1.84(3)	
T(Al)−O(2)	1.82(3) × 3	
mean	1.825	
		O−T(Al)−O
O(1)−O(2)	2.87(4)	110.6(12)
O(2)−O(2)	2.70(5)	108.3(5)
	T(Al,Si) Tetrahedron	
T(Al,Si)−O(2)	1.77(2) × 4	
mean	1.77	
		O−T(Al,Si)−O
O(2^i)−O(2^{ii})	2.55(5)	92.0(18)
O(2^i)−O(2^{iv})	2.70(5)	108.9(7)

[a] Symmetry code: (i) ∫ − z, −x, ∫ + y; (ii) ∫ − z, x, −y; (iii) x, −y, ∫ − z; (iv) π + z, π + y, π + x.

The crystal structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ has been classified as a framework silicate. Framework density[19] can be calculated using the equation $d_f = 1000n_T/V_{cell}$, where V_{cell} is the volume of the unit cell and n_T ($=n_{Al} + n_{Si}$) is the number of T atoms in the unit cell. The framework of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ ($d_f = 18.4$) is relatively open compared with those of common framework silicates such as feldspar $NaAlSi_3O_8$ ($d_f = 29.9$)[20] and coesite (high-pressure type) SiO_2 ($d_f = 29.3$).[21] A low framework density indicates the existence of large voids and channels in the structures. For example, framework densities of zeolites which can accommodate certain cations and water molecules include 12.7 for faujasite, $(NaCa_{0.5})[Al_2Si_5O_{14}]\cdot 10H_2O$,[19] and 18.1 for scapolite, $(Na_{2.9}Ca_{0.8}K_{0.2})Al_{3.7}Si_{8.3}O_{24.2}Cl_{0.7}(CO_3)_{0.2}$,[22] where anions ($Cl^-$, CO_3^{2-}) are surrounded by the framework. The framework density of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is similar to framework densities of these zeolites, and the crystal structure has enough space to accommodate large anions such as the chloride.

Two tetrahedra, T(1) and T(2), link together to form the framework structure. The T(1) cation is bonded to one O(1) and three O(2) anions while the T(2) cation is bonded to four O(2) anions. The O(1) oxygen is a nonbridge oxygen and interrupts the linkage of tetrahedra. The T(2)−O mean distance (1.77 Å) is shorter than T(1)−O (1.83 Å) because of the substitution of Si

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Table 5. Crystal Data for $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$, Wadalite, and Mayenite Groups

	sample				
	this study	wadalite[23]	wadalite[13]	calcium aluminum chlorosilicate[18]	mayenite[16]
chem formula	$Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$	$Ca_{12}(Al_{6.8}Si_{5.4}Mg_{1.2}Fe_{0.6})_{14}O_{32}Cl_{5.8}$	$(Ca_{12}Mg_{0.4})_{12.4}(Al_{8.8}Si_{4.0}Fe_{1.0})_{13.8}O_{32}Cl_{5.4}$	$Ca_{12}Al_{10.6}Si_{3.4}O_{32}Cl_{5.4}$	$Ca_{12}Al_{14}O_{33}$
cryst system	cubic $I\bar{4}3d$	cubic $I\bar{4}3d$	cubic $I\bar{4}3d$	cubic $I\bar{4}3d$	cubic $I\bar{4}3d$
cell dimensions: a:, Å, ; V:, Å^3	$a = 12.0173(1)$ $V = 1735$	$a = 12.014(1)$ $V = 1734$	$a = 12.001(2)$ $V = 1729$	$a = 11.981(6)$ $V = 1719$	$a = 11.989(1)$ $V = 1723$

in the T(2) site. The Ca polyhedron consists of two O(1), four O(2), and one Cl^- anions. The Cl^- ion bonds to two Ca^{2+} ions, linearly, and Ca−Cl−Ca ions lie on the 2-fold axes parallel to the unit-cell edges.

Crystallographic Relationship and Observation between Hydrogrossular and HCl Gas. Hydrogrossular reacts with HCl gas at high temperature and transforms to wadalite structure $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ plus either $CaCl_2$ or CaO as a second solid phase, depending on temperature (see eqs 1 and 2). The crystal structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is cubic with a space group of $I\bar{4}3d$ and the unit cell dimension $a = 12.0173$ Å. $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is noncentrosymmetric while hydrogrossular is centrosymmetric; the space group of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ ($I\bar{4}3d$) is a subgroup of that of hydrogrossular ($Ia3d$). The atomic positions of hydrogrossular and $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ are closely related. The structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ can be described as a derivative of that of the hydrogrossuar structure.[23,24]

In nature as well as in the laboratory, hydrogrossular can be easily transformed into $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ by reacting with HCl. As noted above, the same phenomenon is observed in nature. Wadalite was first described in a skarn xenolith of tertiary volcanics at Koriyama, Fukushima Prefecture, in Japan and La Negra mine, Queretaro, in Mexico and found to be associated with hydrogrossular. Most grains of wadalite are rimmed by hydrogrossular and are replaced secondarily by hydrogrossular.[22] Optical properties of wadalite are so similar to those of hydrogrossular that it is difficult to distinguish the former from the latter. It has been assumed that wadalite is formed by metamorphism of hydrogrossular under acidic conditions that included HCl.

Conclusions

The following conclusions can be made: (1) Hydrogrossular sorbents in a fixed bed reactor are capable of reducing HCl level to near zero levels in the temperature range 400−950 °C.

(2) Hydrogrossular reacts with HCl gas to form $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ and $CaCl_2$ below 700 °C or $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ and CaO above 800 °C.

(3) The crystal structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ is the same as that of the mineral wadalite and derives from mayenite structure with incorporation of excess Cl^- and substitution of Si^{4+} for Al^{3+} for charge compensation.

(4) The structure of $Ca_{12}Al_{9.9}Si_{4.05}O_{32}Cl_{5.9}$ consists of framework $(Al,Si)O_4$ tetrahedra. A large cavity in the framework accommodates Ca−Cl−Ca linearly coordinated atoms.

(5) Although the method for HCl removal reported in this paper is costlier than the existing method, there are several advantages. For instance, there is no possibility for the formation of hazardous byproducts such as PCDDs and PCDFs, which are usually generated in the existing technology. Further studies are necessary under more realistic conditions to establish the feasibility and viability for the commercial application of our methodology, and they are currently in progress.

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