

# Preparation of HCl Gas Sorbent from Paper Sludge

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## Abstract

Paper sludge (PS) is generated as an industrial waste during the manufacture of recycled paper products, and amounts discharged globally are increasing annually. On the other hands, hydrogen chloride (HCl) is an acidic pollutant that is present in the flue gases of most municipal and hazardous waste incinerators. In this study, the removal of hydrogen chloride gas using the product from paper sludge at high temperatures (700°C) using a fixed-bed flow-type reactor was investigated. PS can be granulated with distilled water using granulators, and the particle shapes can be kept after calcination and alkali reaction. Calcined PS and the product after alkali reaction of calcined PS have amorphous phases and katoite ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ) phase, respectively, and both of these indicate HCl removal ability at high temperature (700°C). The product from calcined PS via alkali reaction has higher HCl fixation ability (78 mg/g) than calcined PS. Removal experiments for HCl gas showed that the removal process followed pseudo-second-order kinetics rather than pseudo-first-order kinetics. These results suggested that the product particles with HCl gas removal ability at high temperature can be prepared from PS using calcination and alkali reaction.

## Keywords

Paper Sludge, Hydrogen Chloride Gas, Granulation, Katoite, High Temperature

## 1. Introduction

During the manufacture of recycled paper, paper sludge is discharged as an industrial waste. Over 3 million tonnes of sludge are discharged per year in Japan, and approximately 8 and 2 million tonnes are discharged in the United States and the United Kingdom, respectively [1] [2] [3]. These amounts are increasing annually. The paper industry is of great environmental importance due to the quantity of paper sludge generated, and its disposal. Although a small part of

paper sludge is used as a soil improver and fertilizer in agriculture [4] [5] [6] [7] [8], most of paper sludge is usually disposed of in open dumps or in landfills after incineration. Recently, reduction of available landfill space increasing costs of land disposal of waste in industrial countries necessitates other means for the disposal of waste paper sludge. An economically valuable solution to this problem should include utilization of the waste materials as new products for other applications rather than disposal in a landfill.

Combustion processes, especially municipal waste combustion and hazardous waste incineration, require in most cases the removal of air pollutants, especially hydrogen chloride (HCl) gas [9] [10]. The high solubility and corrosive nature of HCl gas make it one of the most troublesome acidic gases even though it is not emitted into the environment in particularly large quantities. HCl must be removed from flue gases before the flue gases are emitted to the atmosphere. The combustion of municipal and hazardous waste is a major source of HCl to the environment. In recent years, a great deal of attention has been paid to the problem of reducing the level of atmospheric pollution caused by HCl gas. The present techniques for removing HCl gas use calcium hydroxide ( $\text{Ca(OH)}_2$ ) and calcium carbonate ( $\text{CaCO}_3$ ) at low temperatures (below  $300^\circ\text{C}$ ) because they are relatively simple, easy to operate, and have low capital costs [11] [12] [13]. However, these techniques may evolve polychlorinated dibenzo-p-dioxins (PCDDs) and dibenzo-furans (PCDFs) by de novo synthesis in the municipal waste incineration process [14], and cause hot corrosion of the body of the incinerator.

In this study, we attempted to prepare the materials with HCl removal ability at high temperature from paper sludge. In our previous study, katoite, one of the hydrogarnet group mineral, was synthesized from paper sludge ash using alkali reaction with NaOH [15]. Hydrogarnet ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ) is known as a major product of the hydration of calcium aluminate cements, and could be very useful for the fixation of hydrogen chloride gas at high temperatures [16] [17]. The aim of this study was to develop a new method for the removal of the HCl gas present in the gas burning at high temperatures using the particle including hydrogarnet synthesized from paper sludge as a starting material.

## 2. Experimental

### 2.1. Sample

Paper sludge (PS) from a paper company in Japan was used as the starting material. The PS was dried at  $80^\circ\text{C}$  overnight, and sieved for particle size less than  $250\ \mu\text{m}$ . The chemical composition of the PS is listed in **Table 1**. The PS contained 4.3% moisture, organic components such as cellulose fibers (29.0%), and inorganic components (66.7%), predominantly CaO (29.7%),  $\text{SiO}_2$  (15.5%), and  $\text{Al}_2\text{O}_3$  (15.6%). The moisture and organic contents in the PS were determined by differential thermal analysis (DTA)/thermogravimetry (TG) (TG8120, Rigaku, Japan) in the temperature range  $20^\circ\text{C}$  -  $1000^\circ\text{C}$  at a heating rate of  $10^\circ\text{C}/\text{min}$  in flowing air. The inorganic elements in the PS were determined by X-ray fluorescence (XRF) (Primini, Rigaku, Japan).

**Table 1.** Chemical composition of paper sludge (wt.%).

Moisture	Organic Content	Inorganic Content							
		CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	Fe <sub>2</sub> O <sub>3</sub>	Cl	SO <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
4.3	29.0	29.7	15.5	15.6	4.1	0.7	0.1	0.4	0.2

## 2.2. Granulation and Calcination

In this study, two types of granule particles were prepared from paper sludge using a pan granular (DPZ-01R, as one, Japan) and granule maker (KAR-75, Tsutsui Rigaku kikai, Japan), respectively.

A pan granular with a diameter of 300 mm and depth of 120 mm was used for granulation of paper sludge. The pan speed was fixed at 50 rpm and pan angle at 45°. Initially, distilled water was sprayed using a hand held sprayer on the granulator surface and powder PS were added to form a wet bed. 10 grams of powder PS was used, and addition of distilled water to rotation pan granulator was used as they helped in formation of granules. After the granulation process, the samples were first dried in a drying oven overnight, and then the granulated particles within the range between 2 mm and 4 mm were selected by the sieving process.

A granule maker has the cylindrical basket with the diameter of 75 mm and its cylindrical inner wall has the 1 mm holes on the surface. The PS powder was mixed with distilled water in the basket by three blade impeller, and then the mixture was squeezed out of the basket to form the cylindrical PS. These cylindrical PS was dried in a drying oven overnight to prepare the cylindrical particles.

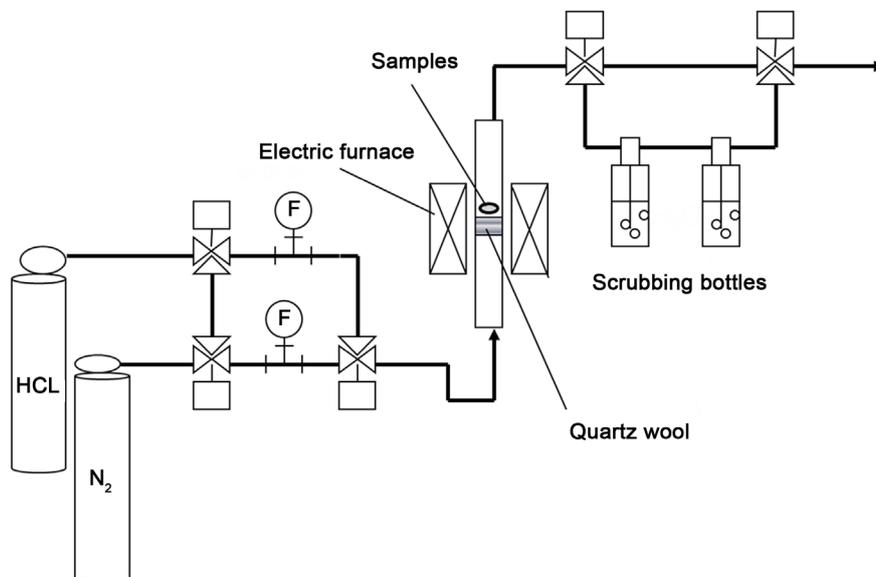
The obtained PS particles were calcined at 800°C for 1 h in an electric furnace under air atmosphere, and then cooled to room temperature to obtain the calcined sample.

## 2.3. Synthesis

Alkali conversion was performed in 50 mL Teflon-lined autoclave. One gram of the PS granules were added into 10 mL of 3 M NaOH solution in autoclave, and then heated at 100°C for 8 h in an electric furnace. After reaction, the solid product was separated from the solution by filtration, washed with distilled water and dried at 60°C overnight in a drying oven. The crystalline phases in each sample were identified by powder X-ray diffraction using monochromated CuK $\alpha$  radiation (XRD) (Ultima IV, Rigaku, Japan).

## 2.4. HCl Gas Removal

The experiments in which HCl gas was fixed using the samples at high temperatures were performed in a vertical reactor, shown schematically in **Figure 1**. The reactor was a fused silica tube (17 mm i.d., 1 m long). The reactor was surrounded by an electric furnace to control its temperature. The sample was placed in the reactor, then N<sub>2</sub> was passed through the reactor at 1 L/min (the volume



**Figure 1.** Experimental apparatus used in this study.

being measured at NTP) to replace the atmosphere in the reactor with  $N_2$ . The reactor was then heated to  $700^\circ\text{C}$  with  $N_2$  flowing through it at 1 L/min. Once the required temperature was reached, the reaction gas (1000-ppmv HCl in  $N_2$ ) was fed at 500 mL/min into the fixed-bed reactor. An HCl concentration of 1000 ppmv is similar to the average concentration in incinerator exhaust gas in Japan. Each experiment was ended when the outlet HCl concentration reached 1000 ppmv. The gas exiting the reactor was periodically passed through distilled water in scrubbing bottles for 5 min, which was enough time for all of the HCl in the gas to be dissolved. The  $\text{Cl}^-$  concentrations in the solution from the scrubbing bottle samples were determined using an ion meter (TiN-5102; Toko Instruments, Tokyo, Japan) to allow the amount of  $\text{Cl}^-$  fixed by the samples to be determined. The HCl feed gas was stopped at the end of the experiment, and  $N_2$  was fed into the reactor until the reactor had cooled to room temperature. The solid sample in the reactor was then collected. The  $\text{Cl}^-$  content of each solid sample that had been used in an HCl removal experiment was determined. A 0.1-g aliquot of a sample was added to 10 mL of 0.1 M  $\text{HNO}_3$  solution in a 50-mL centrifuge tube, then the tube was shaken using a reciprocal shaker for 6 h. The tube was then centrifuged for 10 min, and the  $\text{Cl}^-$  concentration in the supernatant was determined to allow the  $\text{Cl}^-$  fixed content of the solid sample to be calculated.

### 3. Results and Discussion

**Figure 2** shows the photos of (a) raw PS, (b) granulated PS, and (c) cylindrical PS. Two types of granules, granulated PS ( $\phi 2 - 4$  mm) (**Figure 2(b)**) and cylindrical PS ( $\phi 1$  mm) (**Figure 2(c)**) can be prepared from fine powdered PS (**Figure 2(a)**) using distilled water, which means that the granulation of PS is possible without chemical binders.



**Figure 2.** Photos of (a) raw paper sludge; (b) granuled PS and (c) cylindrical PS.

**Figure 3** shows the photos of (a) calcined granuled PS, (b) calcined cylindrical PS, (c) the product from calcined granuled PS, and (d) the product from calcined cylindrical PS. Calcined samples keep the granulation forms with white color and their weight decrease due to the burning the organic content in PS. Furthermore, the products after alkali reaction keep the granulation forms with white color and become hard.

**Figure 4** shows the X-ray diffraction patterns of (a) raw PS, (b) calcined PS, and (c) the product from calcined PS. It is noted that the XRD patterns for granule PS and cylindrical PS indicate almost same. Raw PS mainly composed of organic cellulose (with relatively broad peaks owing to the low crystallinity of the fibers around  $2\theta = 20^\circ$ ) and inorganic minerals, calcite ( $\text{CaCO}_3$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) and talc ( $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) (the filler and/or coating components of paper) (**Figure 4(a)**). After calcination, the peaks of talc remained, those of kaolinite and calcite disappeared and those of lime appeared due to the decarbonation of calcite and the formation of amorphous  $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$  (CAS) [18] [19] (**Figure 4(b)**). Finally, the product mainly composed of katoite ( $\text{Ca}_3\text{Al}_2(\text{SiO}_4)(\text{OH})_8$ ), which belongs to hydrogarnet group known as the materials with HCl removal ability (**Figure 4(c)**).

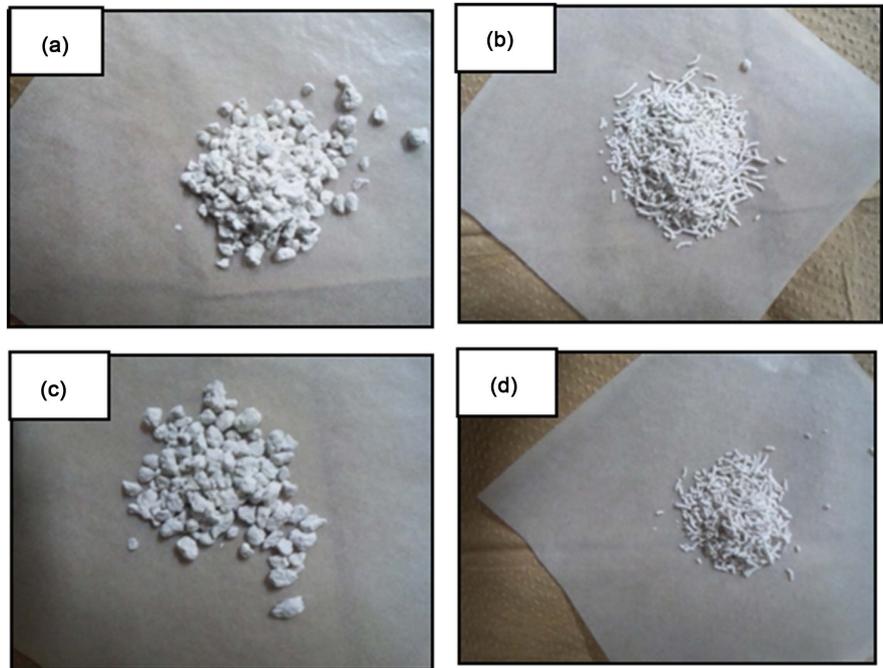
The HCl removal tests using calcined granule PS and the product were carried out. The amounts of  $\text{Cl}^-$  fixed by calcined PS and the product at  $700^\circ\text{C}$  as a function of the reaction time are shown in **Figure 5**. Both calcined PS and the product have the HCl removal ability. The HCl removal rate of the product was high in the first 60 min, then lower until equilibrium was reached, while that of calcined PS was in the first 40 min, then be almost constant. The total amount of fixed  $\text{Cl}^-$  content in the product is 78 mg/g, which is higher than that in calcined PS.

The experimental kinetic data were fitted using a pseudo-first-order kinetic model [20] and a pseudo-second-order kinetic model [21], shown in (1) and (2), respectively,

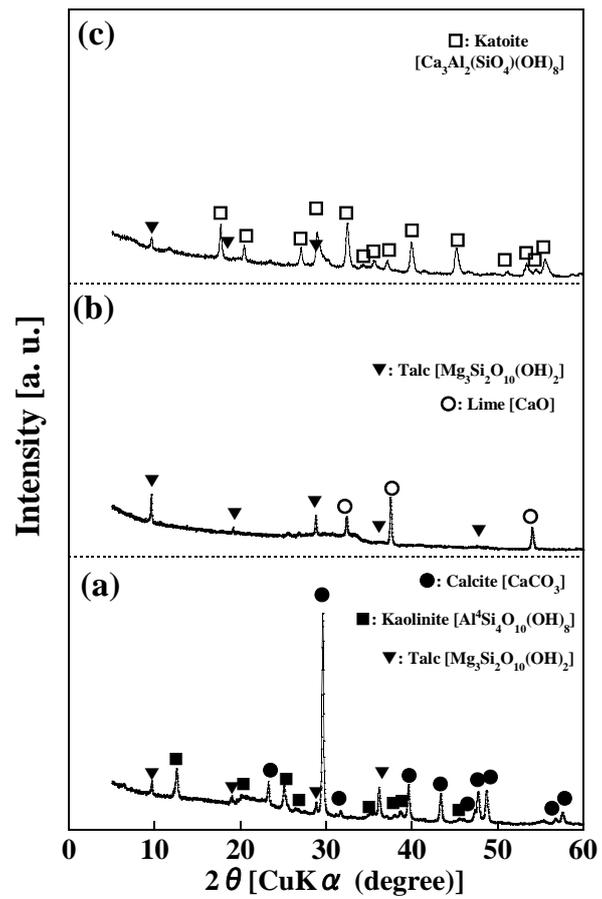
$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{k_2 n q_e^2} + \frac{1}{q_e} t \quad (2)$$

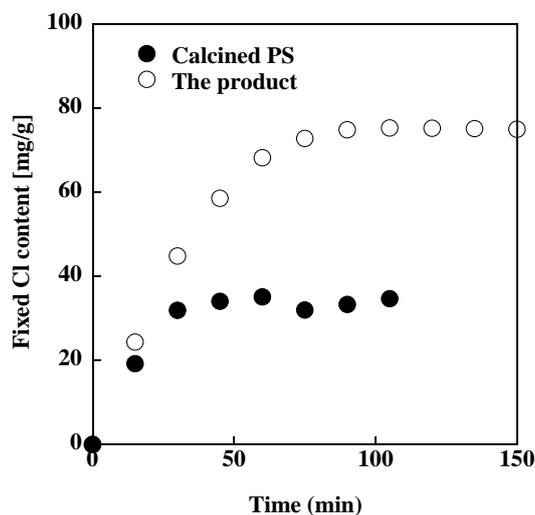
where  $k_1$  ( $\text{min}^{-1}$ ) and  $k_2$  ( $\text{min}^{-1}$ ) are the first order and second order rate constants, respectively. Equations (1) and (2) were applied for times between  $t = 0$  and  $t = t_e$  (the equilibration time, which was usually different for the different systems).  $q_e$  (mg/g) is the amount of  $\text{Cl}^-$  fixed at  $t_e$ . The values of  $k_1$ ,  $k_2$ ,  $R^2$  (the linear correlation coefficient), and  $q_e$  (*i.e.*,  $q_{e,1}$  and  $q_{e,2}$ ) are shown in **Table 2**.



**Figure 3.** Photos of (a) calcined granuled PS; (b) calcined cylindrical PS; (c) the product from calcined granuled PS; and (d) the product from calcined cylindrical PS.



**Figure 4.** X-ray diffraction patterns of (a) raw PS; (b) calcined PS; and (c) the product from calcined PS.



**Figure 5.** Fixed Cl contents in the samples during the HCl removal test.

**Table 2.** Parameters for the fixation of HCl gas by calcined PS and the product.

Sample	Pseudo-first-order kinetics model			Pseudo-second-order kinetics model		
	$q_{e,1}$ (mg/g)	$k_1$ (1/min)	$R^2$	$q_{e,2}$ (mg/g)	$k_2$ (1/min)	$R^2$
Calcined PS	10.5	0.014	0.425	37.3	3.3	0.984
The product	60.7	0.0079	0.759	99.0	0.3	0.973

The  $R^2$  values showed that, regardless of the temperature, the experimental data fitted the pseudo-second-order model much better than the pseudo-first-order model, indicating that the fixation process was second order.

#### 4. Conclusion

We attempted to prepare the particles with HCl removal ability from PS. PS can be granulated with distilled water using a pan granular and granule maker, and the shapes of particles were unchanged by calcination and alkali reaction. Calcined PS and the product from calcined PS via alkali reaction have amorphous phases and katoite, respectively, and indicate the removal ability for HCl gas at 700°C. The product has higher removal ability for HCl gas than calcined PS. The removal reaction kinetics is found to fit the pseudo-second-order kinetics model better than the pseudo-first-kinetics model. Therefore, PS can be granulated simply using only water, and the product particles with HCl gas removal ability at high temperature can be prepared from PS by calcination and alkali reaction.

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