

Kinetics of the Removal of Hydrogen Chloride Gas Using Hydroxysodalite at High Temperatures

Takaaki Wajima

Abstract—Hydrogen chloride (HCl) is an acidic pollutant that is present in the flue gases of most municipal and hazardous waste incinerators. It is important to treat gaseous HCl in incineration streams efficiently to avoid adverse environmental consequences. The removal of hydrogen chloride gas using hydroxysodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$) at high temperatures (600–900 °C) using a fixed-bed flow-type reactor was investigated in this study. HCl was efficiently removed from N_2 containing 1000-ppmv HCl with a reaction time of 2 h at high temperatures. The hydroxysodalite reacted efficiently with the HCl gas at temperatures between 600 and 800 °C, and was transformed into sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$). The amount of HCl fixed increased as the temperature increased to 800 °C but decreased when the temperature was increased to 900 °C because some of the hydroxysodalite and sodalite was transformed into nepheline (NaAlSiO_4). The most chlorine was fixed at 800 °C (the amount fixed was 56 mg/g). The reaction kinetics were assessed, and the pseudo-first-order and pseudo-second-order rate constants were calculated. Removal experiments showed that the removal process followed pseudo-second-order kinetics rather than pseudo-first-order kinetics. Increasing the temperature of the fixed-bed reactor to 800 °C increased the amount of HCl that was removed while keeping the removal kinetics almost the same.

Index Terms—Gaseous HCl, HCl removal, high temperature, hydroxysodalite, reaction kinetics.

I. INTRODUCTION

Incineration may be the most environmentally sound way of disposing of hazardous waste. However, certain difficulties are associated with incineration, including the need to remove air pollutants, such as hydrogen chloride (HCl), sulfur oxides, nitrogen oxides, and other contaminants, from the waste gases produced.

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. HCl gas emitted from incinerators is mainly produced through the destruction of toxic halogenated organic waste, including pesticides, chlorinated hydrocarbons (such as polyvinyl chloride in solid waste), and polychlorinated biphenyls in industrial waste [1].

In Japan, HCl gas generated when incinerating municipal

waste is treated by blowing $\text{Ca}(\text{OH})_2$ powder into the exhaust gas, converting HCl into CaCl_2 . The CaCl_2 is then collected as fly ash and disposed of in landfill sites. The currently used scrubber techniques for removing HCl at low temperatures (below 300 °C) are relatively simple, easy to operate, and have low capital costs [2]–[4]. However, CaCl_2 is very soluble, and can be leached from ash in landfill sites and released into the aquatic environment. To prevent the environmental damage this would cause, the leachate is treated with Na_2CO_3 to convert the Ca^{2+} into insoluble CaCO_3 , and the leachate is then diluted with water to decrease the Cl^- concentration. This method requires a considerable amount of water, and the lifetimes of available landfill sites are decreased because of the amount of fly ash that is disposed of. It is therefore necessary to develop new methods for treating gaseous HCl produced in incinerators.

Sodalite is a microporous crystallized aluminosilicate in zeolite group minerals, and was first synthesized by Pauling in 1930 [5]. Hydroxysodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$) is member of the sodalite mineral group, and is a major product of the hydration of calcium aluminate cement. Its structure consists of a framework of 4- and 6- membered rings of SiO_4 and AlO_4 tetrahedra, and the Si:Al ratio equals 1:1, which is the lowest possible ratio for zeolite group minerals. There are many reports for the synthesis of hydroxysodalite from various raw materials, such as coal fly ash [6]–[13], paper sludge ash [14]–[23], oil shale ash [24], [25], waste sandstone cake [26]–[29], natural kaolinite [30], metakaolin [31], expanded perlite [32], waste porcelain [33], natural clinker [34], thermally treated sediment [35] and so on.

Hydroxysodalite has recently been proposed as an adsorbent of hydrogen chloride from high-temperature incinerator exhaust gases. It has been found that hydroxysodalite can be very useful for fixing HCl gas at 150–600 °C [36]. However, little information is available on the kinetics of HCl removal by hydroxysodalite at temperatures of 600–900 °C, which are the temperatures that incinerator furnaces typically work at.

The aim of this study was to develop a new and efficient method for removing HCl gas from flue gases at high temperatures using hydroxysodalite. HCl removal from N_2 containing 1000-ppmv HCl gas was studied using a fixed-bed reactor at 600–900 °C. The experiments were mainly performed to investigate the kinetics of HCl removal using the experimental system.

II. MATERIALS AND METHODS

A. Hydroxysodalite Sample

Hydroxysodalite was synthesized in a stirred suspension, as

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described by Kato *et al.* [37]. Sodium silicate (55.6 g), sodium aluminate (54.6 g), and sodium hydroxide (253.8 g) were added to 1 L of distilled water, and the mixture was stirred with a magnetic stirrer at 90 °C for 8 h. The mixture was then filtered to separate the solid product, and the product was dried at 80 °C in an oven overnight to give the hydroxysodalite that was used in the experiments. The morphology of the hydroxysodalite sample is shown in Fig. 1.

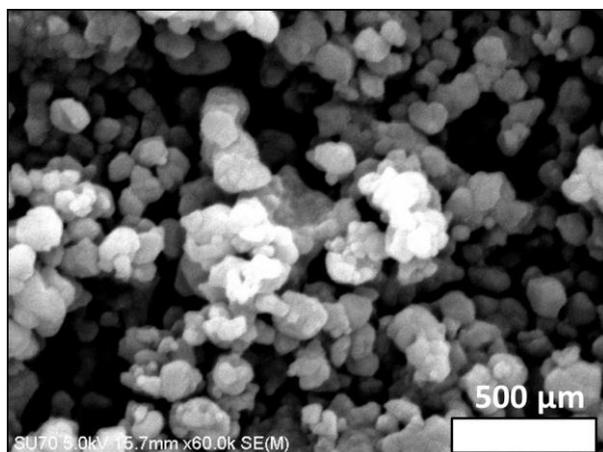


Fig. 1. Photograph of the hydroxysodalite sample.

B. Fixation of HCl Gas

The experiments in which HCl gas was fixed using hydroxysodalite at high temperatures were performed in a vertical reactor, shown schematically in Fig. 2. 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 N₂ was passed through the reactor at 1 L/min (the volume being measured at NTP) to replace the atmosphere in the reactor with N₂. The reactor was then heated to the selected temperature (between 600 and 900 °C) with N₂ flowing through it at 1 L/min. Once the required temperature was reached, the reaction gas (1000-ppmv HCl in N₂) 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 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 Cl⁻ fixed by the hydroxysodalite to be determined. The HCl feed gas was stopped at the end of the experiment, and N₂ was fed into the reactor until the reactor had cooled to room temperature. The solid sample in the reactor was then collected. The mineralogical composition of each solid sample was determined using an UltimaVI X-ray diffractometer (Rigaku, Tokyo, Japan). The Cl⁻ content of each solid sample that had been used in an HCl removal experiment was also determined. A 0.1-g aliquot of a sample was added to 10 mL of 0.1 M HNO_{3(aq)} 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 Cl⁻

concentration in the supernatant was determined to allow the Cl⁻ content of the solid sample to be calculated.

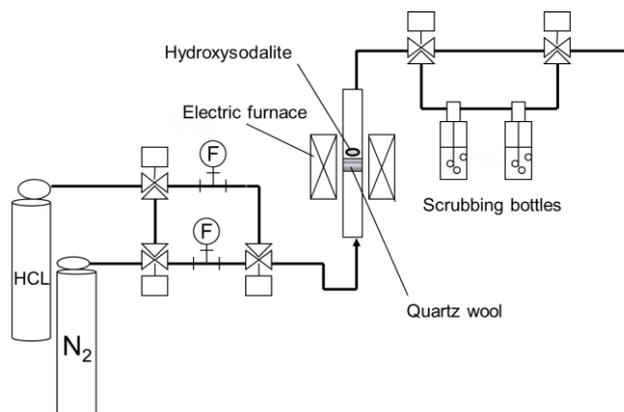


Fig. 2. Experimental apparatus used in the study.

III. RESULTS AND DISCUSSION

The removal of HCl in a hot gas stream by hydroxysodalite in a fixed-bed reactor was investigated. The amounts of Cl⁻ fixed by hydroxysodalite at different temperatures are shown in Fig. 3. Increasing the temperature from 600 to 800 °C increased the amount of Cl⁻ fixed by the hydroxysodalite from 49.3 to 56.5 mg/g, but the amount of Cl⁻ fixed decreased to 44.3 mg/g when the temperature was increased to 900 °C.

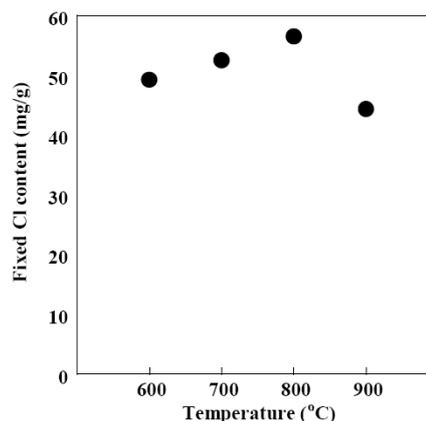
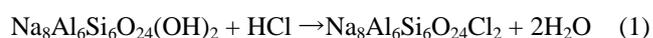


Fig. 3. Fixed Cl⁻ contents in the solid samples after experiments at different temperatures.

The X-ray diffraction patterns of the hydroxysodalite before and after reacting with HCl gas at between 600 and 900 °C are shown in Fig. 4. The hydroxysodalite (Na₈Al₆Si₆O₂₄(OH)₂) was transformed into sodalite (Na₈Al₆Si₆O₂₄Cl₂) when exposed to HCl at 600–800 °C, but nepheline (NaAlSiO₄) was produced when the hydroxysodalite was exposed to HCl at 900 °C. The HCl gas was efficiently removed to form sodalite at 600–800 °C through the reaction shown in (1).



The hydroxysodalite and sodalite were transformed into nepheline at 900 °C through the reactions shown in (2) and (3).





The nepheline did not react with HCl, so less Cl^- was fixed at 900 °C than at lower temperatures because of the formation of nepheline.

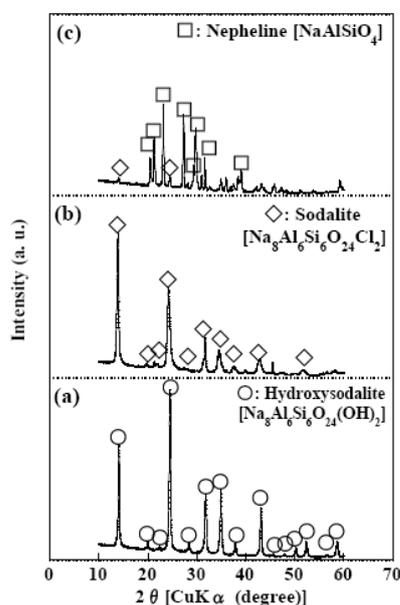


Fig. 4. X-ray diffraction patterns of (a) the raw hydroxysodalite sample, (b) the sample after an experiment at 700 °C had been performed, and (c) the sample after an experiment at 900 °C had been performed.

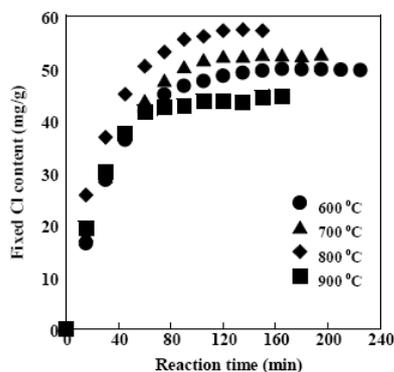


Fig. 5. Fixed Cl^- contents in the samples over time during experiments at different temperatures.

The amounts of Cl^- fixed by hydroxysodalite at temperatures between 600 and 900 °C as a function of the reaction time are shown in Fig. 5. It can be seen that the removal rate was high in the first 60 min, then lower until equilibrium was reached. Increasing the reaction temperature to 800 °C increased the amount of Cl^- that was fixed by the hydroxysodalite, but the amount of Cl^- fixed decreased when the temperature was increased to 900 °C.

The experimental kinetic data were fitted using a pseudo-first-order kinetic model [38] and a pseudo-second-order kinetic model [39], shown in (4) and (5), respectively,

$$\ln(q_e - q_t) = \ln q_e - k_1 t, \quad (4)$$

$$\frac{t}{q_t} = \frac{1}{k_2 \cdot q_e^2} + \frac{1}{q_e} t, \quad (5)$$

where k_1 (min^{-1}) and k_2 (min^{-1}) are the first order and second order rate constants, respectively. Equations (4) and (5) 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 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 I.

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.

The $q_{e,2}$ values were 56.5, 62.1, 67.1, and 49.8 mg/g at 600, 700, 800, and 900 °C, respectively. These values agreed well with experimental values obtained at t_e (49.3, 52.5, 56.5, and 44.3 mg/g at 600, 700, 800, and 900 °C, respectively). The k_2 values for between 600 and 800 °C were between 570 and 720 min^{-1} , meaning that the hydroxysodalite to sodalite reaction rates were almost the same at between 600 and 800 °C under the experimental conditions we used.

TABLE I: PARAMETERS FOR THE FIXATION OF HYDROGEN CHLORIDE GAS BY HYDROXYSODALITE

Temperature (°C)	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
600	26.1	7600	0.782	56.5	720	0.994
700	33.2	8100	0.789	62.1	570	0.991
800	37.2	10600	0.880	67.1	680	0.997
900	21.6	10200	0.781	49.8	1180	0.995

IV. CONCLUSION

Gaseous HCl was removed from a stream of gas using a fixed-bed reactor containing hydroxysodalite at high temperatures, between 600 and 900 °C, which are almost the same temperatures as those that occur in practice in incinerator furnaces. The conclusions below were drawn.

- 1) Hydroxysodalite in a fixed-bed reactor can decrease HCl gas concentrations at high temperatures.
- 2) At below 800 °C hydroxysodalite reacts with HCl to form sodalite, removing HCl gas, but above 900 °C hydroxysodalite forms nepheline, which does not remove HCl gas.
- 3) The fixation of Cl^- by hydroxysodalite follows the pseudo-second-order kinetics model rather than the pseudo-first-order kinetics model.
- 4) The amount of Cl^- fixed increases as the temperature increased to 800 °C, and the fixation reaction rate remains almost the same between 600 and 800 °C.

Our results suggest that hydroxysodalite could be used to remove HCl gas from effluent gases at high temperatures.

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