

Reproduction of a new high temperature HCl sorbent, Sodalite ($\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$) and chlorinate mayenite ($\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$) — The removal of Cl ion occluded in nano space of zeolite structure —

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Hydroxyl sodalite [$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$] and hydrogamet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8}$] reacted with high-temperature HCl to the respective chlorine containing compounds, sodalite [$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$] and chlorinate mayenite [$\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6$] and as a result, their absorption ability was lost. The hydrothermal reaction of nepheline [NaAlSiO_4], which was formed by heating the sodalite at 1000 °C, with NaOH was found to reproduce hydroxyl sodalite. Hydrogamet was also reproduced by the hydrothermal reaction of the chlorinate mayenite with CaO and H₂O. The products thus reproduced exhibited the same absorbing performance as that of the respective virgin materials.

Key-words: Hydroxyl sodalite, Hydrogamet, Fixation of Cl⁻ ion, High temperature, Reproduction of the reactant

1. INTRODUCTION

In the 21st century, it is not too much to say that the important problems in the world are environment and energy problems. Especially, in Japan where resources are scarce, these problems are serious. The waste management problem exists in one of the environment problems in Japan. In the past, the waste management was done by the burning-up using an incinerator. The main purpose of the burning-up is a loss in weight and quantity and the prevention of the growth of a plague. Because the toxic gases such as HCl, dioxins and the others occur when burning up the waste, they pollute environment often. Under such a situation, the researches to reduce and/or remove them and to prevent their occurrence are developing before anything happened.

It is well known that a great deal of thermal energy generates when burning waste. The electric power generates electricity reusing the thermal energy. Because the thermal energy is gotten through the heat exchanger, the acid gas such as HCl contained in exhaust gas corrodes the heat exchanger. The more the corrosion of the heat exchanger is hot, the more intensely it occurs. Therefore, it is necessary to reduce HCl gas at high temperature. If HCl contained in exhaust gas can be reduced at high temperature, the thermal collection efficiency improves

and the efficiency of the generation of electricity, too, improves more. As a result, it is possible for the environmental pollution by HCl to solve and to contribute for the energy problem to be solved, too. Realizing this point early, the authors commenced a study of this subject and recently successful results have been obtained.

The authors found hydroxyl sodalite [$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}(\text{OH})_2$] and hydrogamet [$\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8}$] already as materials, which can fix Cl⁻ ion at high temperature [1-6]. However, these materials lose the Cl⁻ ion fixation performance after reaction with HCl. Because, the development of the reproduction method for the reactants is desired.

In this paper, the authors introduce in detail about hydroxyl sodalite and hydrogamet as new high temperature HCl recovery materials. In addition, the reproduction method of the materials after HCl recovery to hydroxyl sodalite and hydrogamet was studied.

2. EXPERIMENTAL

2.1 Sample preparation

Preparation of hydroxyl sodalite was as follows. The kaolinite [$\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$] was used as Al and Si source, and NaOH was used in the Na source. A mixed paste of kaolinite

and NaOH was prepared in the mole ratio of 3:10. The ratio of NaOH added was in considerable excess of that theoretically required. The hydroxyl sodalite was synthesized by heat treatment (100°C , 24h) of the mixed paste in an oven. After the hydroxyl sodalite was synthesized, and further, sufficiently washed in the distilled water to remove an excess of NaOH.

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 with distilled water. The water to solid ratio was 12:1 weight/weight. The autoclave was placed in the temperature-controlled oven, the temperature of which was controlled to increase from room temperature to 200°C in 2 hours. The mixture was then kept at 200°C for 15hours. The solid product was separated by filtration and dried at 110°C for 24hours.

2.2 Reaction with HCl gas at high temperature

A small-sized fixed bed reactor was used to examine the reaction between HCl gas without the moisture and hydroxyl sodalite and hydrogarnet in the temperature range from 400 to 900°C . Rough drawing of the reactor is shown in Fig.1. The HCl reaction test was done as follows: A quartz glass tube packed by a sample of 0.5g was placed in the tubular electric furnace, then the sample was heated up to desired temperature in flowing dry N_2 . After the sample temperature reached to desired temperature, HCl of 1000ppm was flowed for 3hours at 200ml/min flow rate.

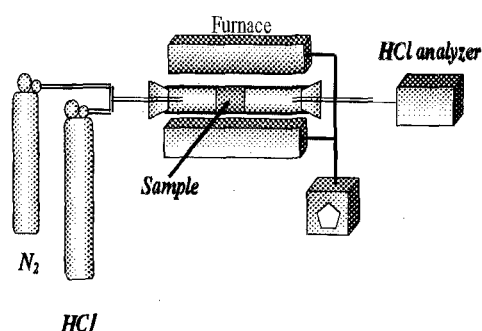


Fig.1 Rough drawing of the small-sized fixed bed reactor

2.3 Measurement

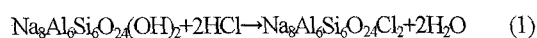
Thermal decomposition behavior, crystal structure and chemical composition of samples before and after reaction with HCl gas were examined by TG-DTA, XRD and XRF, respectively.

3. RESULTS AND DISCUSSIONS

3.1 Fixation of Cl^- ion

3.1.1 Hydroxyl sodalite

When hydroxyl sodalite reacts with HCl gas, OH^- ions are replaced with Cl^- ions in the β cage of sodalite structure and it becomes sodalite [$\text{Na}_8\text{Al}_6\text{Si}_6\text{O}_{24}\text{Cl}_2$] (Equation 1). [2] The lattice constant (a_0) of sodalite structure became large from 8.86 to 9.04\AA according to substitution between OH^- (ionic radius: 1.32\AA) and Cl^- ion (1.81\AA).



The relationship between the amount of Cl^- fixed in sodalite structure and the reaction temperature in Fig.2. The weight ratio of Cl^- ion was measured by XRF, and the weight ratio to the sodalite (wt%) was regarded as the amount of Cl^- fixed. The amount of Cl^- fixed increased with increasing the reaction temperature, however it was drastically decreased after the highest value was shown at 800°C . The amount of Cl^- fixed at 900°C was zero. The amount of Cl^- fixed at 800°C was $7.3\text{wt}\%$, this value was correspondent to the Cl^- weight ratio in sodalite.

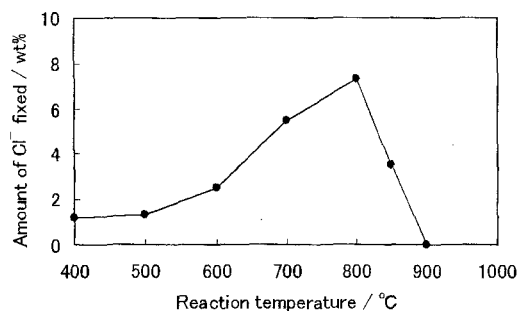


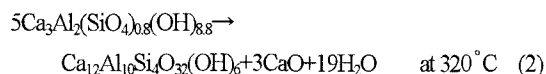
Fig.2 The relationship between the amount of Cl^- fixed in sodalite structure and the reaction temperature

According to the measurement result of TG-DTA of hydroxyl sodalite, the dehydration reaction which originated for OH^- occurred at 260°C , and hydroxyl sodalite made phase change in carnegieite [NaAlSiO_4] at 877°C . As a result of examining the reaction of carnegieite and HCl, the carnegieite already did not react with HCl in the temperature range from 400 to 900°C .

3.1.2 Hydrogarnet

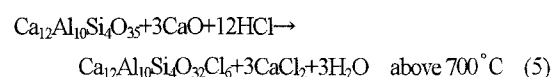
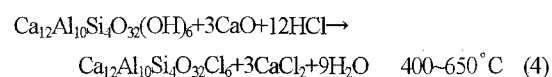
There was next fact from the TG-DTA measurement of hydrogarnet. The endothermic peaks at 320 and 680°C

recorded in DTA can be attributed to the release of OH radical. Hydrogamet was transformed into anhydrous mayenite $[\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{35}]$ through hydrous mayenite $[\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}(\text{OH})_6]$ phase. The ideal phase transition of hydrogamet with increasing temperature can be given by equation 2 and 3, respectively.



The XRD patterns of hydrogamet reacting with HCl were measured at the ambient conditions after cooling from each reaction temperature to room temperature. At the reaction temperature above 400°C , the main phase was wadalite $[\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_6]$, and the second phase corresponding to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ was observed. Since CaCl_2 is highly hygroscopic, it may take up moisture and form $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. The chemical composition of the sample, after removing the second phase $[\text{CaCl}_2 \cdot 2\text{H}_2\text{O}]$ by washing in distilled water, was $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_{5.9}$ (Wadalite), which has chlorine content of 13.2wt%. The HCl gas is efficiently removed from the inlet gas as $\text{Ca}_{12}\text{Al}_{10}\text{Si}_4\text{O}_{32}\text{Cl}_{5.9}$ and CaCl_2 above 400°C .

On the basis of the results obtained, the reaction formula of hydrogamet and HCl is shown in equation 4 and 5.



3.2 Reproduction of the reactants

3.2.1 Sodalite

It was tried that it removed Cl^- ions fixed in the β cage of sodalite in NaOH solution and reproduced in hydroxyl sodalite. A mixed paste of sodalite and NaOH was prepared in the weight ratio of 1:4. NaOH existed sufficiently in excess. The mixture was hydrothermally treated at 150°C for 10 hours. As a result of examining the amount of Cl^- ion included in the product, the amount was almost equal to the amount of Cl^- ion included in sodalite. In addition, the result was same, even if the temperature rose at 200°C . From the above result, it became clear that this method could not use for the reproduction of sodalite to hydroxyl sodalite.

Sodalite was decomposed by heating at 1000°C in nepheline $[\text{NaAlSiO}_4]$, and NaCl was formed as a by-product. By utilizing this reaction, the removal of Cl^- ions included in sodalite becomes possible. At the beginning, NaCl was removed in the washing. Then, the reproduction of sodalite to hydroxyl sodalite was confirmed, when it carried out the hydrothermal treatment at 200°C by adding NaOH to nepheline. The mixture ratio of nepheline and NaOH was 1:2 in mole ratio. The XRD patterns of reproduced sodalite are shown with it of the virgin material (0) in Fig. 3. Though the diffraction intensity from the reproduction material was weaker than it of virgin material, those profiles were almost same to it of the virgin material, hydroxyl sodalite. Therefore, it was concluded that the material after the reproduction treatment was hydroxyl sodalite.

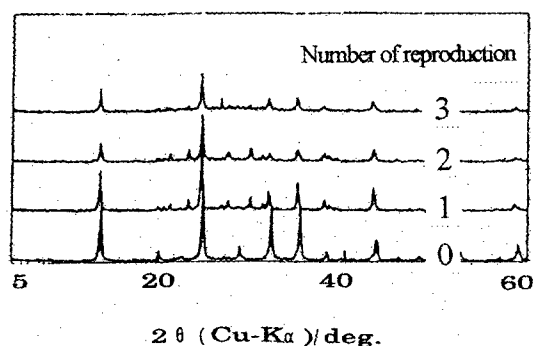


Fig.3 The XRD patterns of reproduced sodalite

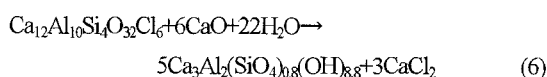
The reaction of reproduced hydroxyl sodalite and HCl gas is carried out at 700°C , and the result is shown in table 1. The amount of Cl^- ion fixed in the virgin material was 5.5wt%, and it of reproduced hydroxyl sodalite was decreased to 4.4wt%. The amount was almost same by decreasing about 1wt%, even if the reproduction treatment was repeated. The reproduction treatment was repeated to 7 times, and the fixation performance of the reproduced hydroxyl sodalite for Cl^- ion was almost same.

Table 1 The amount of Cl^- ion fixed in the reproduced hydroxyl sodalite

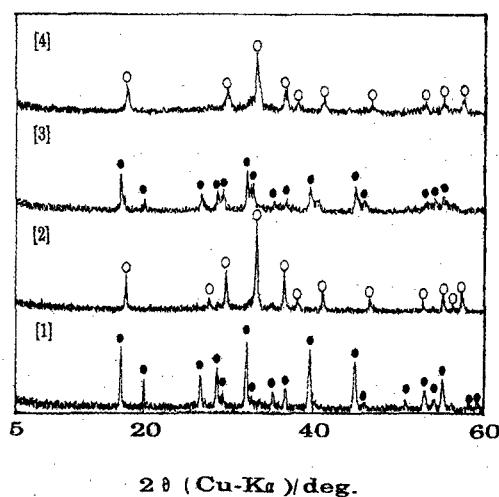
Number of reproduction	Amount of Cl^- ion fixed wt%
0 (Virgin material)	5.5
1	4.4
2	4.8
3	4.6

3.2.2 Chlorinate mayenite

It is difficult to decompose thermally, because the thermal stability for wadalite is higher than it of hydroxyl sodalite. Wadalite was thermally stable in the heating at 1000 °C. Therefore, it was impossible to remove the Cl^- ions in wadalite by the thermal decomposition. The mixture which consisted of wadalite, CaO and water was prepared, and then it was treated hydrothermally (200 °C, 15hours) in an autoclave. The generation of hydrogarnet was confirmed, when the product material after the treatment was examined by XRD. It is possible to show the reproduction from wadalite to hydrogarnet by equation 6.



The amount of Cl^- ion fixed in the reproduced hydrogarnet was examined at 700 °C. The measurement result is shown in table II. In addition, XRD profiles before and after reaction of reproduced hydrogarnet and HCl is shown in Fig.4. From the experiment described above, we conclude that the reproduction to hydrogarnet from wadalite was possible, and that Cl^- fixation performance of the reproduced hydrogarnet was almost same to that of the virgin material.



●: hydrogarnet, ○: wadalite

Before [1] and after [2] reaction for virgin material

Before [3] and after [4] reaction for reproduced material

Fig.4 XRD profiles before and after reaction of reproduced hydrogarnet and HCl.

Table II The amount of Cl^- ion fixed in the reproduced hydrogarnet at 700 °C

Sample	Amount of Cl^- ion fixed / wt%
Virgin material	22
Reproduced material	19

4. SUMMARY

- 1) Hydroxyl sodalite and hydrogarnet are the materials which react with HCl gas at high temperature above 400 °C.
- 2) Hydroxyl sodalite changes to sodalite after reaction with HCl gas.
- 3) Hydrogarnet changes to chlorinate mayenite after the reaction with HCl gas.
- 4) It is possible to remove HCl gas in exhaust gas at high temperatures by hydroxyl sodalite and/or hydrogarnet.
- 5) Since sodalite and chlorinate mayenite are stable materials, they do not react with HCl gas.
- 6) The reproduction to hydroxyl sodalite and hydrogarnet from sodalite and chlorinate mayenite is possible by heating and hydrothermal treatment.
- 7) Reproduced hydroxyl sodalite and hydrogarnet recover the reaction performance with HCl gas.

Acknowledgments

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