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Paper

Hydrothermally Solidified Water Purification Sludge with High Specific Surface Area

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Hydrothermal reaction was investigated for a recycling technology of sludge from water purification plant. The calcined sludge at 600°C for the removal of organic compound was mixed with $Ca(OH)_2$ so that the Ca/(Al+Si) atomic ratio was in the range from 0.02 to 0.25. Specimens were formed by uniaxial pressing at 30 MPa and hydrothermal treatment under saturated steam pressure at 220°C for 6 to 10 h. The Ca/(Al+Si) ratio of the mixture had influence on the strength development. Hydrothermal reaction at 220°C for 10 h with Ca/(Al+Si) =0.07 yielded the maximum flexural strength of 13 MPa with a bulk density of 1090 $kg \cdot m^{-3}$, resulting from the formation of about a few 10 nm size hydrate. The high specific surface area (157 $m^2 \cdot g$) of the sample suggests an application as a humidity conditioning material. [Received August 6, 2003; Accepted December 22, 2003]

Key-words : *Inorganic waste, Sludge, Ca/(Al+Si), Hydrothermal treatment, Flexural strength, BET, Mercury intrusion porosimetry, Self humidity control*

1. Introduction

We are faced with serious global environmental issues of the shortage of natural resources and the increase in waste disposal. For establishing the sustainable society, it is urgently necessary to develop innovative re-circulation technology reducing the impacts on the Earth. One of the serious problems in Japan is the disposition of the garbage and wastes because of the shortage of waste disposal sites. In the fiscal 2000, the amount of discharged industrial waste was 406 million tons in Japan.[1] Among the nineteen categories of industrial wastes, sludge accounted for the largest ratio of 47% (189 million tons). Furthermore, the recycle ratio of sludge was the lowest value of 8%. Therefore, novel recirculation technology using sludge comes to play an important role for the sustainable society.

The hydrothermal reaction as one of the effective low energy consumption wastes conversion methods have been investigated using low-SiO_2 and high-Al_2O_3 starting materials with lime.[2)-5)] Although many works have been published for the hydrothermal reaction in the $CaO-SiO_2$ system, little has been reported on the influence of high Al_2O_3 content in the starting waste on the strength development during hydrothermal solidification. It has been commonly stated that the formation of hydrogarnet ($Ca_3Al_2(SiO_4)(OH)_8$) leads to lowering strength.[6)] It is suggested that the problem is avoided by the controlling the crystal size of hydrothermally formed aluminous phases such as hydrogarnet and zeolite.[5)] The sludge, containing very fine particles of quartz and clay minerals, is usually treated with coagulant agent of poly aluminum chloride (PAC) for the disposition, resulting in the higher content of reactive amorphous $Al(OH)_3$ in the sludge. Thus, the hydrothermal reaction is possibly applied to the re-circulation technology for sludge waste.

The objective of the present work was to investigate the influence of Ca/(Al+Si) ratio on the strength development and its relation to the microstructure in the hydrothermal reaction system of water purification sludge-calcium hydroxide.

2. Experimental

2.1 Sample preparation

The sludge from a water purification plant in central Japan and calcium hydroxide ($Ca(OH)_2$, UBE Industries, Ltd., Japan) were used as starting materials. **Table 1** shows the chemical composition of the sludge. The SiO_2 and Al_2O_3 content were 33 and 15%, respectively. The Al/(Al+Si) atomic ratio was 0.47. X-ray diffraction pattern (XRD) of the sludge indicated that quartz, muscovite, albite, clinochlore, and kaolinite were the main constituent minerals (**Fig. 1**). Aluminum hydroxide derived from PAC seemed to be amorphous. The sludge was calcined at 600°C for 5 h to remove organic compounds, followed by wet-ball milling.

The calcined sludge and calcium hydroxide were weighed to obtain mixtures with calcium hydroxide/(calcium hydroxide + calcined sludge) mass ratios of 0, 0.02, 0.05, 0.1, 0.15, and 0.2, which were equivalent to the bulk Ca/(Al+Si) atomic ratio of 0.02, 0.04, 0.07, 0.12, 0.18, and 0.25, respectively. After weighing, an additional amount of distilled water was added for mixing and forming (30 mass% of the powder mix). Rectangular test specimens with the size of 15(W)×10(H)×40(D) mm were formed by uniaxial pressing (30 MPa) and hydrothermal treatment under saturated steam pressure at 220 °C for 10 h. The bulk density of the green body was about 1100 $kg \cdot m^{-3}$.

2.2 Analytical methods

After hydrothermal treatment, the test specimens were dried at 80°C for 2 days. The dried specimens were tested for three point flexural strength (Tensilon RTM-500, A & D, Japan;

Table 1. Chemical Composition of Sludge from Water Purification Plant (mass%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	MnO	F	Cl	SO_3	P_2O_5	L.O.I.
33	25	6.3	1.1	1.2	1.1	0.5	0.6	0.6	0.2	0.3	1.3	1.7	26.5

L.O.I means loss on ignition.

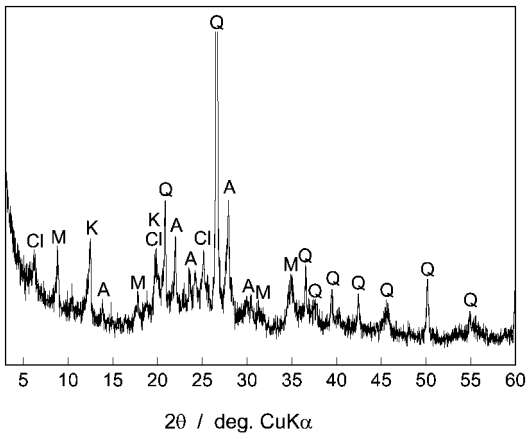

Fig. 1. XRD pattern of the sludge from a water purification plant. Q; quartz (SiO_2), M;muscovite ($KAl_2(Si_3Al)O_{10}(OH, F)_2$), A; albite ($NaAlSi_3O_8$), Cl; clinochlore ($(Mg, Al)_6(Si, Al)_4O_{10}(OH)_8$), K; kaolinite ($Al_2Si_2O_5(OH)_4$).

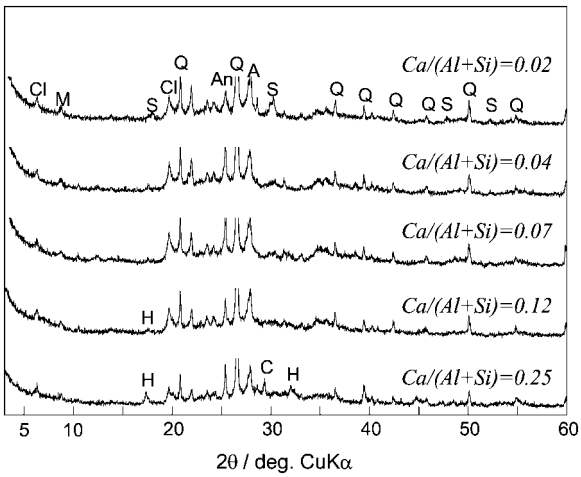

Fig. 2. XRD patterns of specimens with various bulk Ca/(Al+Si) autoclaved at 220°C for 10 h.
Q; quartz (SiO_2), M; muscovite ($KAl_2(Si_3Al)O_{10}(OH, F)_2$), A; albite ($NaAlSi_3O_8$), Cl; clinochlore ($(Mg, Al)_6(Si, Al)_4O_{10}(OH)_8$), S; $3Al_2O_3 \cdot 4SO_3 \cdot 8H_2O$, An; anhydrite ($CaSO_4$), H; hydrogarnet ($Ca_3Al_2(SiO_4)(OH)_8$), C; calcite ($CaCO_3$).

support distance 30 mm, cross head speed 0.5 mm/min) and their bulk density was calculated from the mass and dimensions. The phases that constitute the specimens were identified by XRD analysis (RAD-B, Rigaku, Japan). The microstructures observation of the specimens was carried out using FE-SEM (JSNM-5400, JEOL, Japan). The atomic ratio of formed phases was determined with analytical TEM (JEM-2010F, JEOL, Japan). The specific surface area and pore distribution were measured by the N_2 gas adsorption BET and BJH method (Macsorb HM, model-1201, Mountech, Japan), and mercury intrusion pore distribution was determined by mercury intrusion porosimetry (PoreMaster-33P, Quantachrome, USA). The self humidity controlling property was evaluated by the released moisture amount from specimens (55 mm in width, 5 mm in height, 55 mm in depth) between 90%RH and 50%RH at 25°C in the chamber (PR-3KP, Espec Co., Japan).

3. Results and discussion

3.1 Reaction products

(1) XRD results

Figure 2 shows XRD patterns of the samples with various bulk Ca/(Al+Si) ratio autoclaved at 220°C for 10 h. The XRD patterns after the autoclaving were similar in spite of various bulk Ca/(Al+Si) ratio. The typical binding compound such as tobermorite or calcium aluminate silicate hydrates could not be observed, suggesting that the reaction products had near amorphous nature. Anhydrite ($CaSO_4$) was observed for all the specimens. The sample using only sludge (Ca/(Al+Si)=0.02) gave $3Al_2O_3 \cdot 4SO_3 \cdot 8H_2O$. The hydrogarnet was formed for the sample with the bulk Ca/(Al+Si) ratio of 0.12 and higher. As for the starting material, quartz, muscovite, albite, clinochlore were remained.

(2) SEM observation and chemical composition of reaction products

Figure 3 shows SEM photographs of samples with various Ca/(Al+Si) ratio autoclaved at 220°C for 10 h. Except for the specimen with the bulk Ca/(Al+Si)=0.07, the hydrothermally formed platy phase were observed. With the increase of the bulk Ca/(Al+Si) ratio, the thickness of the platy phase increased. For the specimens with the bulk Ca/(Al+Si)=0.07, the granular particles in a few tens nm size were mainly observed as the hydrothermally formed phase.

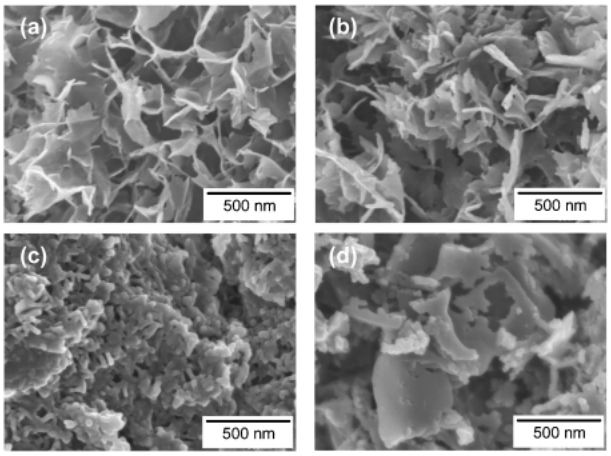

Fig. 3. SEM photographs of the specimens with the bulk Ca/(Al+Si) ratio (a) 0.02, (b) 0.04, (c) 0.07 and (d) 0.25 after autoclaved at 220°C for 10 h.

Table 2 shows the major element ratios of the granular phase using the starting mix of Ca/(Al+Si)=0.07 obtained by analytical TEM. The major elements in formed phase were Al, Si, and Ca, having the average Ca/(Al+Si) ratio of 0.02 and Al/(Al+Si) ratio of 0.61. However, it was not possible to identify the formed phase.

3.2 Flexural strength

The bulk density of the specimens remained almost constant at around 1100 $kg \cdot m^{-3}$ during hydrothermal treatment. **Figure 4** shows the flexural strength of hydrothermally treated body at 220°C for 10 h as a function of the bulk Ca/(Al+Si) atomic ratio of starting mixture. Noteworthy is that no addition of $Ca(OH)_2$ in the starting mix (Ca/(Al+Si)=0.02) yielded the flexural strength of 8.5 MPa, which was about 8 times higher than that of green body. This suggests that the calcined sludge is very suitable waste for the hydrothermal solidification. The flexural strength gave maximum strength of 13 MPa at Ca/(Al+Si) ratio of 0.07. With the increase in

Table 2. Analytical TEM Results of Hydrothermally Formed Phase Using Starting Mix of Ca/(Al+Si) = 0.07 Treated at 220°C for 10 h (Atomic Ratio)

	Ca/(Al+Si)	Al/(Al+Si)	Al/Si
	0.020	0.371	0.590
	0.015	0.431	0.757
	0.019	0.490	0.960
	0.034	0.603	1.520
	0.028	0.608	1.551
	0.019	0.653	1.882
	0.015	0.705	2.386
	0.015	0.731	2.719
Average	0.021	0.607	1.546
Std. div.	0.007	0.130	0.763

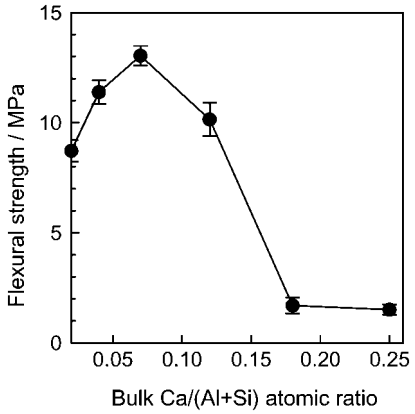

Fig. 4. Variation of flexural strength with bulk Ca/(Al+Si). The specimens were autoclaved at 220°C for 10 h.

Ca/(Al+Si), the strength decreased to 1 MPa at Ca/(Al+Si) = 0.18, which is comparable with that of green body.

Although the binding materials was not clear, XRD results and analytical TEM results show the possibility of the near amorphous calcium aluminate hydrate having Ca/(Al+Si) ratio of 0.02 and Al/(Al+Si) ratio of 0.57. As anhydrite was formed even in the lowest strength specimen, it could not be the binding material.

3.3 Microstructure

(1) Mercury intrusion porosimetry

Figure 5 shows micropore distribution measured by mercury intrusion porosimetry. The hydrothermal treatment yielded the modal peak diameter shift from 1 μm to 0.01–0.02 μm. With the increase of the bulk Ca/(Al+Si) ratio, the modal peak diameter after autoclaving increased: 0.08 μm in the case of Ca/(Al+Si) = 0.02 and 0.04, 0.1 μm (Ca/(Al+Si) = 0.07), 0.2 μm (Ca/(Al+Si) = 0.12) and 0.05 μm (Ca/(Al+Si) = 0.25).

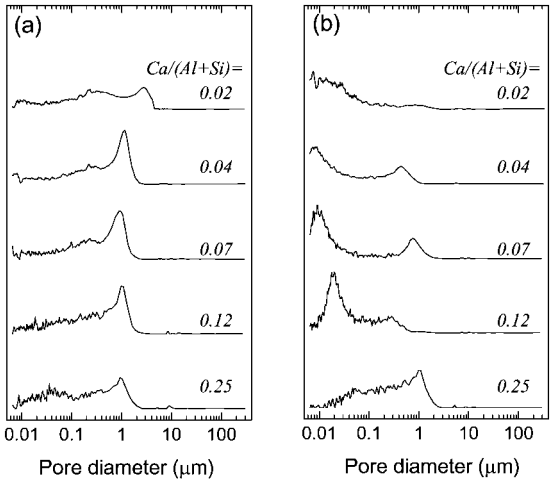

Fig. 5. Mercury intrusion pore size distribution of the specimens. (a) before autoclaving, and (b) after autoclaved at 220°C for 10 h.

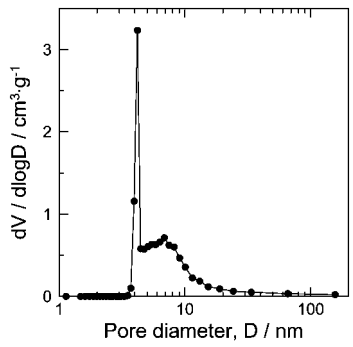

Fig. 6. N_2 absorption pore size distribution of the specimens with the bulk Ca/(Al+Si) = 0.07 autoclaved at 220°C for 10 h.

(2) N_2 adsorption porosimetry

The specific surface area of the specimen was increased by the hydrothermal treatment. For the specimen with the bulk Ca/(Al+Si) of 0.07, the specific surface area increased from 30.2 $m^2 \cdot g^{-1}$ to 157.6 $m^2 \cdot g^{-1}$ by the hydrothermal treatment. This is attributed to the formation of nano sized reaction product (Fig. 3(c)). The specific surface area was 5 times higher than that of autoclaved aerated concrete, hydrothermally solidified porous material.[7),8)]

Figure 6 shows the pore distribution of the sample with the bulk Ca/(Al+Si) = 0.07 after autoclaving. The sharp peak at 4 nm and broad peak at around 7 nm were observed. The high specific surface area and the pore distribution are suited for self humidity controlling material. The mesoporous materials with a 3 to 7 nm pore diameter are able to keep humidity in the range of 40 to 70% according to Kelvin's equation.[9),10)] The specimen with the bulk Ca/(Al+Si) of 0.07 had higher humidity controlling property (460 $g \cdot m^{-2}$) than that of cedar (65 $g \cdot m^{-2}$) and hydrothermally solidified waste soil (76 $g \cdot m^{-2}$).[11)]

4. Conclusions

The recycling technology of sludge from water purification plant was investigated using hydrothermal reaction. The solidified specimen using the mixture of the sludge and calcium hydroxide with the bulk Ca/(Al+Si) atomic ratio of 0.07

yielded the highest flexural strength of 13 MPa with a bulk density of 1090 $kg \cdot m^{-3}$, resulting from the formation of about few 10 nm size hydrate. The high specific surface area of 157 $m^2 \cdot g$ and the higher amount of released moisture suggests an application as a humidity conditioning material.

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