Solidification of Al-Rich Inorganic Waste Materials Using Hydrothermal Technology

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Increasing environmental concerns highlight the need to build up a sustainable society based on recirculation of our limited natural resources. The authors have been studying the application of hydrothermal solidification for the recirculation of inorganic waste materials with lesser energy at the waste heat level. The wastes generally contain higher amount of Al2O3, yielding the formation of large hydrogarnet crystals as the prevention factor of the strength development of hydrothermal solidification. It was found that the formation of nano-size hydrogarnet crystals by the controlling of reaction condition enables the strength development on the hydrothermal solidification of wastes. Similarly, the formation of nano-size zeolite crystals gives high strength. It was expected that these solidified waste materials show the self-humidity controlling property and the fixation of heavy metals through ion exchange.

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1. Introduction

Increased environmental concerns, such as shortage of the natural resources, environmental pollution, global warming and waste disposal, highlight the need to build up a recirculation-based society, which reduces much of the input from nature (e.g. raw materials, fossil fuels) as well as its output into nature (e.g. waste materials, exhaust gases, exhaust heat) and makes efforts to recirculate and regenerate the input from nature within the human society. Especially, the waste disposal is one of the serious problems. In Japan, about 80% of the final disposal waste is inorganic waste and reaches about 70 million tons per year (Table 1). Therefore, a technology which reproduces the inorganic waste into the useful materials becomes very important. It is necessary to choose...
the waste conversion technology with low energy consumption, because a large quantity of energy consumption will lead a new problem as the increase of CO₂ emission.

The hydrothermal solidification technology appears promising as one of the waste conversion technologies because of its low energy consumption at the waste heat level. Since the hydrothermal solidification technology has been used for the building materials such as autoclaved aerated concrete, sand lime brick and autoclaved fiber-reinforced calcium silicate board at 150–200°C, the manufacturing energy consumption for unit volume of the hydrothermal products is estimated approximately 1/6 compared with the ceramic manufacturing using the firing process.\(^1\)

However, there is a problem in applying the waste for the hydrothermal solidification technology. Since the calcium silicate hydrate formed through the hydrothermal dissolution and precipitation process yields the strength development, the raw materials with 90 mass% or higher purity of SiO₂ have been generally used for the hydrothermal solidification.\(^4\) On the other hand, the waste materials usually contain much amount of aluminum element which is next Clarke number of silicon element. Because the aluminum element in the waste materials yields the formation of large hydrogarnet crystals as the prevention factor of the strength development of hydrothermal solidification,\(^5\) the waste materials could not use as the raw material in the over 100 years history of the hydrothermal solidification technology. If this problem is resolved, it is expected that the choice of raw materials drastically expands for the hydrothermal solidification technology.

The authors have tried that the formed phases such as hydrogarnet act as a binding material in the hydrothermal solidification for the waste materials containing much amount of Al₂O₃. Since it is expected that the nano-order crystals formed through hydrothermal reaction yields the strength development, we have investigated that the dry press forming process to the hydrothermal solidification technology in order to form fine crystals by decreasing the void among the each particle of raw materials, and by higher supersaturation of Ca, Al and Si in the reaction condition, resulting in dominating the nuclear formation rather than crystal growth. In this paper, the results of the basic experiments and the application regarding the hydrothermal solidification by the formation of hydrogarnet\(^6\) or zeolite\(^7\) will be discussed.

2. Solidification by hydrogarnet formation

Waste soil usually contains kaolinite \((\text{Al}_2\text{Si}_2\text{O}_5\cdot\text{OH})_x\) as the Al source. In order to recirculate the Al rich waste soil from the mine and construction site, the possibility of the hydrothermal solidification by the hydrogarnet formation using dry press forming process in kaolinite-quartz \((\text{SiO}_2)\)--lime \((\text{CaO})\) mixtures (Table 2) was investigated.

After weighing, distilled water was added and mixed in sufficient quantity for slaking the lime, followed by an additional amount of water for forming (10 mass% of the powder mix). 10 mm × 15 mm × 40 mm rectangular test specimens were formed by uniaxial pressing at 30 MPa and hydrothermally treated under saturated steam pressure at 200°C for 2–20 h.

The flexural strength and phases formed in the hydrothermally treated samples are shown in Fig. 1 as a function of treatment time. Formation of hydrogarnet \((\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}·x\text{H}_2\text{O})\) \((\text{OH})_{2x}, x = 2.7\) was observed over the entire range of kaolinite-containing compositions, i.e. those with \(\text{Al}/(\text{Al} + \text{Si})\ = 0.05\) to 0.50. In particular, only hydrogarnet was formed without the formation of calcium silicate hydrates in the specimens with \(\text{Al}/(\text{Al} + \text{Si})\ ≥ 0.24. On the other hand, for \(\text{Al}/(\text{Al} + \text{Si}) ≤ 0.05, \) calcium silicate hydrate gel \((\text{C}–\text{S}–\text{H})\), gyrolite \((\text{Ca}_6\text{Si}_4\text{O}_{16}\cdot7\text{H}_2\text{O})\) and tobermorite \((\text{Ca}_3\text{Si}_2\text{O}_7\cdot4\text{H}_2\text{O})\) were formed as main phases. These relationships between \(\text{Al}/(\text{Al} + \text{Si})\) ratio and phases formed by hydrothermal treatment are in good agreement with the previously reported results.\(^8,9\)

For all compositions, it was clear that hydrothermal treatment led to an increase in strength. Even those compositions with \(\text{Al}/(\text{Al} + \text{Si}) = 0.24\) to 0.50, where only hydrogarnet was formed, could be solidified by hydrothermal treatment. In the case of specimens with \(\text{Al}/(\text{Al} + \text{Si}) = 0\) and 0.05, where calcium silicate hydrates were the main phase, the maximum flexural strength of about 30 MPa was reached for treatment times of 2 to 5 h. On the other hand, the flexural strengths of the kaolinite rich specimens with \(\text{Al}/(\text{Al} + \text{Si}) = 0.24–0.50\) ranged from 15 to 20 MPa after 2 h treatment, tending to

![Fig. 1. Variation of flexural strength and phases formed with treatment time.](image)

<table>
<thead>
<tr>
<th>K/(Q+K)</th>
<th>Al/(Al+Si)</th>
<th>Ca/Si</th>
<th>Ca/(Al+Si)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
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</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.00</td>
<td>0.23</td>
<td>0.23</td>
<td>82.6</td>
<td>0.0</td>
<td>17.4</td>
</tr>
<tr>
<td>0.1</td>
<td>0.05</td>
<td>0.24</td>
<td>0.23</td>
<td>79.1</td>
<td>3.3</td>
<td>17.6</td>
</tr>
<tr>
<td>0.5</td>
<td>0.24</td>
<td>0.51</td>
<td>0.24</td>
<td>64.2</td>
<td>17.2</td>
<td>18.6</td>
</tr>
<tr>
<td>0.9</td>
<td>0.45</td>
<td>0.45</td>
<td>0.24</td>
<td>47.4</td>
<td>32.9</td>
<td>19.7</td>
</tr>
<tr>
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<td>0.50</td>
<td>0.50</td>
<td>0.25</td>
<td>42.9</td>
<td>37.1</td>
<td>20.0</td>
</tr>
</tbody>
</table>

K/(Q+K); kaolinite/(quartz + kaolinite) mass ratio
increase very slightly for longer treatment times. The maximum flexural strength was obtained for Al/(Al+Si) = 0.05. For the Al/(Al+Si) values higher than 0.05, the maximum strength tended to decrease with increasing Al/(Al+Si) ratio. However, it can be seen that, although the maximum strength decreases by about 30% (from 29.7 MPa to 20.9 MPa) when the Al/(Al+Si) ratio is increased from 0.05 to 0.24, the strength decrease is only about 17% (from 20.9 MPa to 17.4 MPa) when the Al/(Al+Si) ratio is increased from 0.24 to 0.50. This shows that the ratio of decrease in the maximum strength is relatively low for Al/(Al+Si) ratios of 0.24 and higher. In other words, it can be said that, compared to the compositions with Al/(Al+Si) < 0.24, the variation of maximum flexural strength is relatively low in the Al/(Al+Si) range of 0.24 to 0.50. This tendency indicates that the variation in chemical composition of waste soil does not significantly affect the strength of the hydrothermally solidified body and the wide range of waste soils can be converted into the solidified material with uniform strength. 

The relation between strength development and the microstructure of the solidified bodies was investigated by mercury intrusion porosimetry (Fig. 2). For the specimens with Al/(Al+Si) = 0.05, the peak which corresponds to the spaces existing between the raw material particles at the time of forming the bodies, shift towards finer diameters up to about 0.01 μm with increasing treatment time. The reason for the observed strength development in the specimens with Al/(Al+Si) = 0.05 is the formation of fine pores 0.01 μm in size accompanying the precipitation of tobermorite.10-13 In contrast, the peak shifts toward finer diameters with hydrothermal treatment was not recognized in the specimens with Al/(Al+Si) = 0.50. The peak height at 0.1 μm decreased to about 1/2-2/3 of their original values after 2 h of treatment, after which the decrease was slight. This peak remained even after 20 h of treatment. Fresh peak at about 0.04 μm was observed to form as the treatment time increased. Since hydrogarnet is the only phase formed by hydrothermal treatment, the pore formation behavior is thought to result from the precipitation of hydrogarnet.

In the results of FE-SEM, the platy-crystals of kaolinite were covered with hydrogarnet formed after hydrothermal treatment and bonded among each kaolinite crystals (Fig. 3). The thickness of hydrogarnet crystals were at least 50 nm or less, since the thickness of platy-crystals of kaolinite was about 50 nm. It has been reported that the hydrogarnet cubic crystals in sizes ranging from a few μm to some tens of μm
were observed in the case of hydrothermally treated specimens made with slag as the starting material\textsuperscript{14} and under slurry conditions.\textsuperscript{15-17} In this study, however, such hydrogarnet crystals in the micron-size could not be observed. This suggests that the nano-size hydrogarnet formed through the hydrothermal reaction resulting from the decreasing of interparticle space among the raw materials and the supersaturation of concentration of Ca, Al and Si in the reaction condition to dominate the nucleation formation rather than crystal growth, because of the introducing the dry press forming process. It is clarified that the formation of nano-size hydrogarnet crystals by the controlling of reaction condition enables the strength development on the hydrothermal solidification of wastes.

3. Application for Earth Ceramics and its self-humidity controlling properties

As the application of technology described at section 2, the application of the hydrothermally solidified waste soil to the building material was investigated using actual waste soil as a raw material.

The waste soil from a smashed rock plant at Tochigi in Japan (SiO\textsubscript{2} 81.1 mass\%, Al\textsubscript{2}O\textsubscript{3} 8.5 mass\%, mean particle size 32.6 \( \mu \)m) and slaked lime (Ca(OH)\textsubscript{2}) were used as the starting material and mixed at the mass ratio of waste soil : slaked lime = 80 : 20 with water for forming (10 mass\% of the powder mix). The specimens having 200 mm \( \times \) 200 mm \( \times \) 20 mm were formed by uniaxial pressing at 30 MPa and hydrothermally treated under saturated steam pressure at 180°C for 6 h. The flexural strength of hydrothermally solidified waste soil was about 8 MPa and greater than that required for the building materials such as tile or brick. This hydrothermally solidified waste soil has been manufactured and sold as “Earth Ceramics” since 1996 (Fig. 4).

The comparison of the self-humidity controlling property among Earth Ceramics, wood and wallpaper was shown in Fig. 5. The amount of moisture adsorption and desorption of Earth Ceramics indicated almost similar value with wood which was a natural humidity control material. It is known that the self humidity controlling property is strongly affected by the mesopores in the diameter range of 4-20 nm estimated by the Kelvin’s equation represented the condensation phenomena of moisture in the capillary pore.\textsuperscript{18,19} It is considered that the superior self-humidity controlling property of Earth Ceramics is caused by the nano-size pores from the remaining of the pores originated in the starting soil and from the formation of the pores caused by the hydrogarnet and tobermorite formation.

Earth Ceramics were used as the flooring material for the living room (35 m\textsuperscript{2} area) in an apartment and the changes in temperature and humidity were measured under normal living conditions over a one year period.\textsuperscript{20,21} Compared with other reference apartment, the variation of temperature and humidity was smaller in Earth Ceramics floored apartment (Fig. 6). Earth Ceramics are considered to be a human friendly material which can supply us comfortable and healthy environment and also to be an energy-saving material which can control humidity without consuming energy instead of air-conditioner.

4. Solidification by zeolite formation

When the public wastes, such as fly ash, cinder of sewage sludge and cinder of municipal waste, containing higher amount of harmful sub-components compared with waste soil are used as raw material in the hydrothermal solidification technology, it is also concerned that the sub-components will dissolve from the solidified materials. Therefore, the authors have investigated the possibility of the hydrothermal solidification by the zeolite formation which works to fix many ions, e.g. alkaline ions, alkaline earth ions and heavy metallic ions, and also to develop the strength of the treated body.
After weighing to obtain mixtures with the molar ratios shown in Table 3, distilled water was added and mixed in sufficient quantity for slaking the lime, followed by an additional amount of water for forming (10 mass% of the powder mix). 10 mm × 15 mm × 40 mm rectangular test specimens were formed by uniaxial pressing at 30 MPa and hydrothermally treated under saturated steam pressure at 200°C for 24 h. In the case of cinder of municipal waste, the specimens were treated at 150°C.

The variation of flexural strength and phases formed with Na₂O/SiO₂ molar ratio is shown in Fig. 7. The formation of various kinds of zeolite was observed above Na₂O/SiO₂ molar ratio of 0.1. The specimens with Na₂O/SiO₂ = 0.1 showed flexural strengths of more than 5 MPa which is high enough for application as building materials, and the strength of specimen using the fly ash or cinder of sewage sludge developed through the formation of zeolite alone. In the case of fly ash system, the flexural strength of the specimens decreased drastically with the increase of Na₂O/SiO₂ ratio from 0.1 to 0.5. This may be due to the fact that the main phase changed from Linde B₂ zeolite to cancrinite with increasing Na₂O/SiO₂.

The SEM and mercury intrusion porosimetry were carried out in order to discuss about the decreasing of strength from the microstructural change. In the case of Na₂O/SiO₂ = 0.1, the dense matrix structure was observed just around the spherical particles of fly ash (Fig. 8(a)). From the fractured surface of the fly ash particle, it appears that the hydrothermally formed phase around the fly ash led to higher strength. By contrast, in the case of Na₂O/SiO₂ = 0.5, the hexagonal columnar crystals, cancrinite\textsuperscript{22-24}, several microns in size were formed around the fly ash particles (Fig. 8(b)). The formation of obvious void was also observed between fly ash particles and the matrix. These voids led the decreasing of strength of the specimen with Na₂O/SiO₂ = 0.5. In the case of Na₂O/SiO₂ = 0.1, the modal pore diameter shifted towards smaller values (0.01–0.1 μm) through the zeolite formation (Fig. 9(a)). This means that with the progress of hydrothermal reaction, large pores (approximately 1–2 μm) existing prior to the reaction were filled with the newly formed phases which is observed by SEM as the dense matrix structure (Fig. 8(a)) and which consists of nano-size particle. By contrast, in the case of Na₂O/SiO₂ = 0.5, these conspicuous changes of pore size through the hydrothermal treatment was not observed and the width of modal pore diameter extended (Fig. 9(b)). It is believed that this behavior is caused by the formation of columnar crystals of cancrinite and voids around

| Table 3. Molar Ratios of Public Wastes–CaO–Na₂CO₃ Mixtures |
|------------------|------------------|------------------|------------------|------------------|
| Waste            | CaO/SiO₂ / molar ratio | Na₂O/SiO₂ / molar ratio | Raw material / mass% |
|                  |                  |                  | Waste | CaO | Na₂CO₃ |
| Fly ash          | 0.3              |                  | 0     | 89.3 | 10.7  |
|                  | 0.1              |                  | 82.4  | 9.9  | 7.7   |
|                  | 0.5              |                  | 63.0  | 7.5  | 29.5  |
|                  | 1.0              |                  | 48.6  | 5.8  | 45.6  |
| Cinder of sewage sludge | 0.5             |                  | 0     | 87.0 | 13.0  |
|                  | 0.1              |                  | 82.9  | 12.4 | 4.7   |
|                  | 0.5              |                  | 69.9  | 10.4 | 19.7  |
|                  | 1.0              |                  | 58.4  | 8.7  | 32.9  |
| Cinder of municipal waste | 0.3             |                  | 0     | 95.2 | 4.8   |
|                  | 0.1              |                  | 92.4  | 4.7  | 2.9   |
|                  | 0.5              |                  | 82.7  | 4.2  | 13.1  |
|                  | 1.0              |                  | 73.1  | 3.7  | 23.2  |

Fig. 7. Variation of flexural strength and phases formed with Na₂O/SiO₂ molar ratio.
the fly ash particles. These variations of pore size distribution also indicate that the kinds of zeolite and treatment condition affect the microstructure of the solidified bodies resulting in drastic variation of flexural strength.

Table 4 shows the amounts of dissolved heavy metals from the specimen using cinder of municipal waste including heavy metals. The dissolution of Cr(III) from the cinder of municipal waste was observed. However, after the hydrothermal treatment, the dissolution of heavy metals was scarcely observed. Although a further investigation is necessary to know the minute mechanism, there are some possibilities that the prevention of heavy metal dissolution is achieved by the formation of zeolite. It can be expected the possibility to create the new function into the hydrothermally solidified wastes, since zeolite has the superior property in the adsorption of various materials, the ion exchange and so on.

5. Conclusions

In the hydrothermal solidification technology, the calcium silicate hydrates have been generally used as the main binding material. In this paper, although it is believed that the hydrogarnet formation is a prevention factor of the strength development of hydrothermal solidification, it is clarified that hydrogarnet can work as a new binding material when the size of hydrogarnet is controlled to nano-size by the introducing of the dry press forming process into the hydrothermal solidification technology. Similarly, the formation of nano-size zeolite crystals gives high strength of the hydrothermally solidified wastes. In addition, the authors have been investigating the possibility of the hydrothermal solidification by the controlling of the size and morphology of hydroxyl apatite,\textsuperscript{25} aluminum hydroxide\textsuperscript{26} and compound of SiO\textsubscript{2}–Al\textsubscript{2}O\textsubscript{3}\textsuperscript{27} formed by the hydrothermal reaction. Since some new binding materials are added in the hydrothermal solidification technology generally having calcium silicate hydrate as the main binding

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**Fig. 8.** SEM photographs of the fracture surface of the hydrothermally treated specimen in the fly ash system at CaO/SiO\textsubscript{2} of 0.3 with Na\textsubscript{2}O/SiO\textsubscript{2} of (a) 0.1 and (b) 0.5.

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**Fig. 9.** Pore size distribution of the specimen in the fly ash system at CaO/SiO\textsubscript{2} of 0.3 with Na\textsubscript{2}O/SiO\textsubscript{2} of (a) 0.1 and (b) 0.5.
material, it is expected that the range of usable raw materials drastically expands, resulting in drastic improvement of the waste recirculation. In addition, because of nano-size phases formed by the hydrothermal solidification, it is expected that the hydrothermally solidified wastes can be applied to the self-humidity controllable material, the adsorbent and the catalyst carrier and that one of the new material invention technologies is developed by these studies.

References