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Solidification of coal fly ash using hydrothermal processing method

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Solidification of Coal Fly-ash (CFA) has been carried out using a hydrothermal processing method. In the hydrothermal processing, the CFA was first compacted in a mold at 20 - 50 MPa, and then hydrothermally cured in an autoclave. The hydrothermal curing was performed at 150 – 250°C for 15 – 60 h. The experimental results showed that NaOH solution, $Ca(OH)_2$ content, compaction pressure, autoclave curing temperature and time significantly affected the strength of solidified bodies. The most important strength-producing constituent in the solidified bodies produced with CFA was tobermorite, or tobermorite-like calcium silicate hydrate. When the CaO/SiO_2 ratio of the starting material was close to 0.83, tobermorite readily formed and the formed tobermorite enhanced the strength of solidified bodies. The tensile strength determined by the Brazilian test reached more than 10 MPa under the hydrothermal processing. As such, the hydrothermal processing method may provide a high potential for recycling CFA on a large scale.

1. Introduction

Coal ash is produced from thermal power plants as a by-product. More than 500 and 8.0 million tons coal ash is generated yearly in world and Japan respectively [1]. The coal ash can be separated into fly ash and bottom ash. Usually, the coal fly ash (CFA) comprises more than 80% of volumes of total coal ashes. Of the CFA produced, approximately 15% of the CFA is used as a raw material of cement and concrete in the world. Although, the CFA has also been used in various other applications, such as pavement base materials [2], and as zeolite materials [3, 4], most of it is still being disposed directly by landfilling. Hence, the urgent requirement to develop a mass-treatable and environmentally acceptable recycling/reusing technology has created worldwide concern and attention.

One of the most challenging means for treatment of CFA may be the hydrothermal processing technique which has recently been used to convert concrete wastes [5] and metals-contaminated soils [6] into construction materials. The hydrothermal technique is considered to be so attractive in that it is capable not only of producing a very tough and durable product, but also of providing an opportunity to treat or recycle wastes on a massive scale. However, to the best of our knowledge, there seems to be few published work dealing with hydrothermal solidification of CFA.

In order to treat or recycle CFA on a large scale, the hydrothermal processing technique has been used to solidify the CFA. The aim of this study is to investigate the potential of reusing or recycling the CFA by hydrothermal solidification and the effects of additive, compaction pressure and curing temperature and time on the strength development in solidified bodies. The study is expected to provide fundamental information for the assessment of

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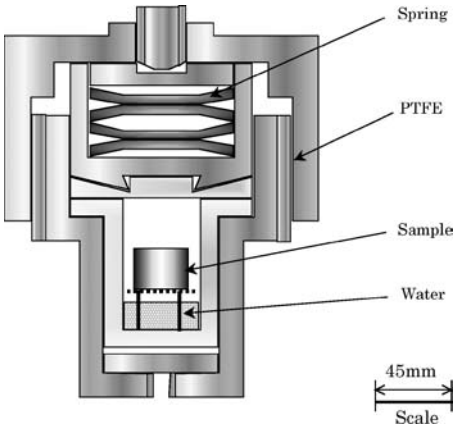

Figure 1 Hydrothermal apparatus used for curing compacted specimens.

TABLE I Composition of coal flyash used (mass%)

Component	Composition
SiO_2	53.1
Al_2O_3	24.1
Fe_2O_3	5.1
CaO	3.5
MgO	0.61
TiO_2	4.58
SO_3	0.08
Na_2O	5.09
K_2O	0.43

feasibility to reuse or recycle CFA on a large scale using the hydrothermal processing technique.

2. Experimental methods

The raw material used in this study was coal fly-ash (CFA) collected from coal-fired power station in Tokyo, Japan. The chemical composition of the CFA used is shown in Table I. Since the formation of tobermorite has capability of enhancing the strength of calcium silicate products [7], and of solidified bodies produced with municipal incineration ash [8], slaked lime ($Ca(OH)_2$) for industrial use (CaO > 72.5%) was added to the CFA to form tobermorite. The CFA powder mixed with the slaked lime was used as starting materials. The mixture was then compacted at 20 – 50 MPa by uniaxial pressing in a mold (30 mm in diameter and 120 mm in height). The compacted specimens (30 mm in diameter and 20 mm in height) were autoclaved under saturated steam pressure (0.4716 – 3.9762 MPa) at 150 – 250°C for 15 – 60 h. After autoclaving, the solidified specimens were dried and then used to measure their mechanical and chemical properties. The autoclave used for the hydrothermal treatments is shown in Fig. 1.

The disk-shaped specimens were used to determine the tensile strength employing the Brazilian testing method [9]. The Brazilian tests were conducted on an Instron universal testing machine (Model 8562, max load: 98,000 N) at a crosshead speed of 0.2 mm/min. At least three specimens were tested for each hydrothermal processing condition, and the averaged data were then used as the tensile strength in this study. After the Brazilian testing, the crushed specimens were investigated for phase analysis by an X-ray diffraction (XRD) and their microstructure was observed by a scanning electron microscope (SEM).

Usually, CFA can be considered to be non-hazardous due to the fact that it results from the burning of coal. Recently, there is growing concern that certain fly ash may be hazardous [10]. In this study, the concentration of dissolved heavy metals from the CFA has been measured by a leaching test, in accordance with the notification No. 13 & 46 of Environment Agency of Japan. The results of the leaching test showed that the dissolved heavy metals from the CFA was very low, well below the regulatory levels for the environmental quality standard of Japan. Therefore, the heavy metals dissolved from the hydrothermally-solidified bodies produced with the CFA was not carried out in this study.

3. Results and discussion

In order to hydrothermally solidify the CFA, water or other solutions must be added into starting material as a reaction solvent. Therefore, the effect of water content on strength of solidified bodies was investigated first. The processing conditions are: $Ca(OH)_2$ content 20 mass%, compaction pressure 20 MPa, curing temperature 200°C, and time 15 h. Fig. 2 shows that the solidification processing cannot be carried out without water. The tensile strength increases with increasing water content up to 15 mass%, and then decreases. NaOH solution, a substitute for water, was also added to accelerate the hydrothermal reaction, and the result (Fig. 3) showed that the strength of solidified bodies increases very quickly until the NaOH concentration researches 2M, and then

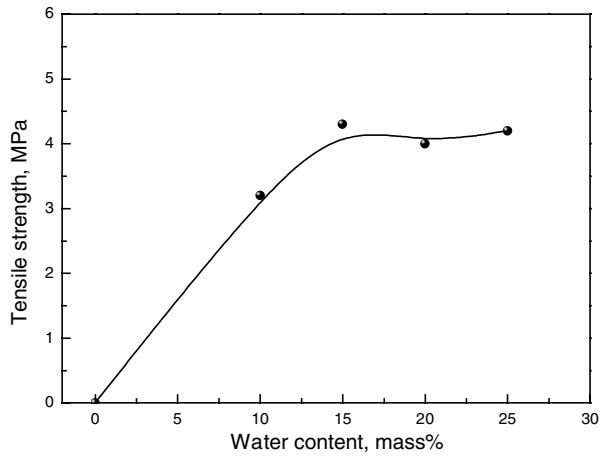

Figure 2 Effect of water content on the tensile strength of solidified bodies. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; compaction pressure: 20 MPa; curing temperature: 200°C and time: 15 h.

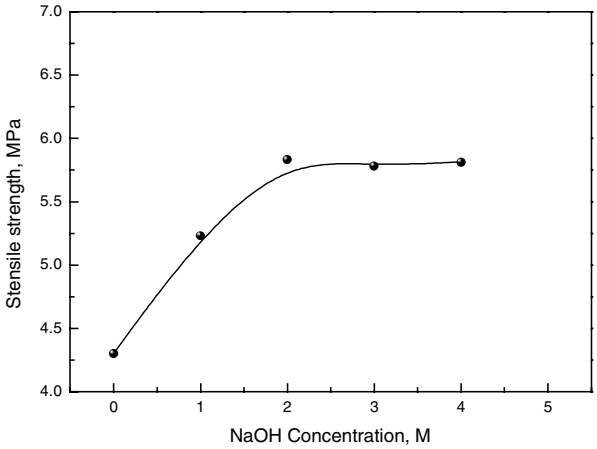

Figure 3 Effect of NaOH concentration on the tensile strength of solidified bodies. NaOH concentration significantly affects the strength of solidified bodies. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; NaOH solution content 15mss%, compaction pressure: 20 MPa; curing temperature: 200°C and time: 15 h.

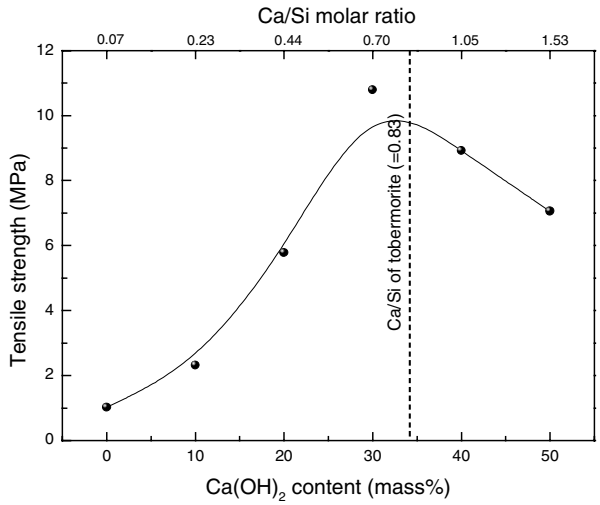

Figure 4 Effect of $Ca(OH)_2$ content on the tensile strength of solidified bodies. Hydrothermal processing conditions: compaction pressure, 20 MPa; curing temperature: 200°C; curing time: 15 h. Ca/Si ratio around 0.83 in the starting material could provide a good tensile strength for solidified bodies.

gives the almost constant value for the larger NaOH concentrations. The strength enhancement may be due to the increased solubility of silica present in CFA at higher pH levels, thus making more silica available for reaction with calcium to form cementitious hydrates. Based on those results, the 15 mass% 2M NaOH solution was selected as a reaction solvent throughout this study.

The formation of tobermorite is expected to affect the strength development of solidified bodies. The slaked lime ($Ca(OH)_2$) was added to the CFA to form tobermorite, and the effect of $Ca(OH)_2$ content on the strength of solidified bodies was investigated. The experiments were conduced under the conditions: compaction pressure 20 MPa, hydrothermal curing temperature 200°C and curing time 15 h. The experimental result is shown in Fig. 4. The molar ratio CaO/Sio_2 (Ca/Si) in the starting material is also plotted in addition to the $Ca(OH)_2$ content. The Ca/Si ratio for 1.1 nm tobermorite (=0.83) is indicated in the figure. As expected, the tensile strength increases with $Ca(OH)_2$ content up to 30 mass%, and then decreases, suggesting that an optimum $Ca(OH)_2$ content exists for the solidification of CFA under hydrothermal processing. The tensile strength at 30 mass% $Ca(OH)_2$ content is approximately 11 MPa, which is higher than ordinary concrete. It should be noted that the highest tensile strength achieved is around the Ca/Si ratio of 0.83, thus suggesting that the increase in strength may be due to the formation of tobermorite.

Fig. 5 indicates XRD patterns for the solidified bodies with different $Ca(OH)_2$ contents. The processing conditions are the same as those shown in Fig. 4. Fig. 5 shows that only calcite ($CaCO_3$), mullite ($Al_6Si_2O_{13}$) and quartz (SiO_2) exist in the initial specimen. However, a new phase of 1.1 nm tobermorite is observed with the addition of $Ca(OH)_2$, showing that the added $Ca(OH)_2$ has reacted

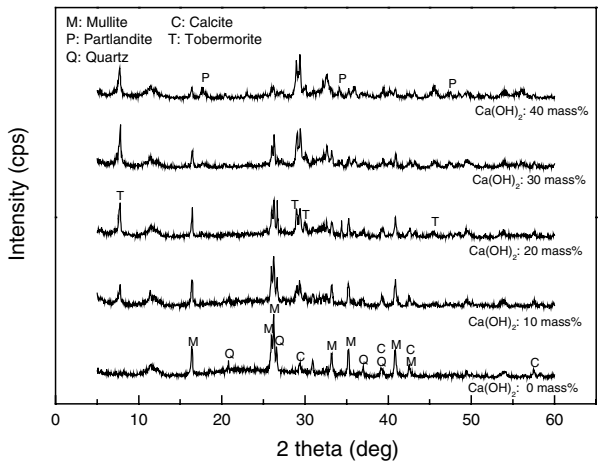

Figure 5 XRD patterns of solidified bodies with different content of $Ca(OH)_2$. Hydrothermal processing conditions: compaction pressure, 20 MPa; curing temperature: 200°C; curing time: 15 h. With addition of $Ca(OH)_2$, tobermorite forms.

with Sio_2 in the starting material to form 1.1 nm tobermorite, i.e., $5Ca(OH)_2 + 6SiO_2$ $5CaO$ $6SiO_2$ $5H_2O$. The peak intensity of tobermorite appears to increase with the $Ca(OH)_2$ content up to 30 mass%. It is worthy of note that almost no trace of $Ca(OH)_2$ is observed, suggesting that the added $Ca(OH)_2$ has been consumed thoroughly to form tobermorite for curing time of 15 h. In contrast, above the $Ca(OH)_2$ content of 40 mass%, a trace of partlandite phase ($Ca(OH)_2$) starts to appear and the peak intensity of tobermorite decreases. Compared with the results shown in Fig. 4, this suggests that excessive addition of $Ca(OH)_2$ causes the reduction in tobermorite formation and then results in decrease in the strength.

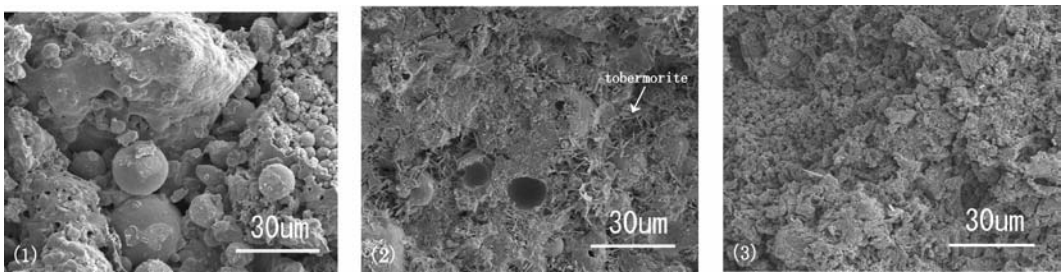

Figure 6 SEM photographs of solidified bodies compacted by 20 MPa, and cured at curing temperature of 200°C for 15 h. (1). $Ca(OH)_2$ content of 0 mass%; (2). $Ca(OH)_2$ content of 30 mass%; (3). $Ca(OH)_2$ content of 40 mass%. Different $Ca(OH)_2$ content leads to different morphologic crystals formed.

SEM was also used to investigate the effect of the $Ca(OH)_2$ content on the tobermorite formation. SEM photographs of the fracture surfaces of solidified bodies for the $Ca(OH)_2$ content of 0, 30 and 40 mass% is shown in Fig. 6. As shown in Fig. 6(1), without the addition of $Ca(OH)_2$, few crystals form in the solidified body; in contrast, with the $Ca(OH)_2$ addition of 30 mass%, an overgrowth of cardhouse-like tobermorite (Fig. 6(2)) forms, and the formation of tobermorite binds ash particles together and fills the space between ash particles. However, for the $Ca(OH)_2$ content of 40 mass% (Fig. 6(3)), many small granular crystals form, accompanying reduction in the tobermorite formation, suggesting that the excessive addition of $Ca(OH)_2$ seems to have retarded the tobermorite formation. The origin of this may be similar to the one occurred in cement compounds. Brunauer *et al*. [11] pointed out that $Ca(OH)_2$ retards the hydration of cement compounds by forming a protective coating on the surfaces of unhydrated compounds, and slowing down the hydration.

The strength of solidified body is usually correlated with degree of hydrothermal reaction and total porosity. The relationships between the compaction pressure, apparent density and tensile strength were investigated. For the experiments under conditions of $Ca(OH)_2$ content 20 mass%, curing temperature 200°C and curing time of 15 h, the results (not shown) showed that a higher compaction pressure results in a denser and stronger solidified bodies. This behavior shows the effect of pre-compression on the strength of hydrothermally solidified bodies.

Figs. 7 and 8 show the effects of the autoclave curing temperature and time on the strength of solidified bodies processed with $Ca(OH)_2$ content 20 mass%, compaction pressure of 20 MPa. The data of both the room temperature and zero curing time show the results for as-compacted specimens (without hydrothermal processing). As expected, the tensile strength increases rapidly after the hydrothermal treatment. The curing temperature (Fig. 7) affects significantly the strength of solidified bodies, i.e. the higher the curing temperature, the higher the strength. Fig. 8 shows that the tensile strength increases

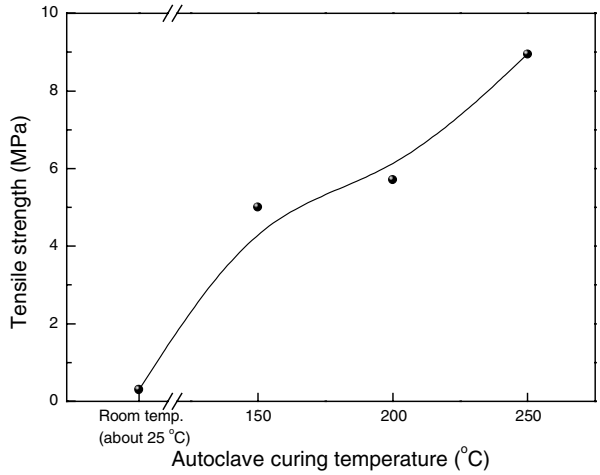

Figure 7 Effect of curing temperature on the tensile strength of solidified bodies. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; compaction pressure: 20 MPa; curing time: 15 h. The higher the curing temperature, the higher the tensile strength.

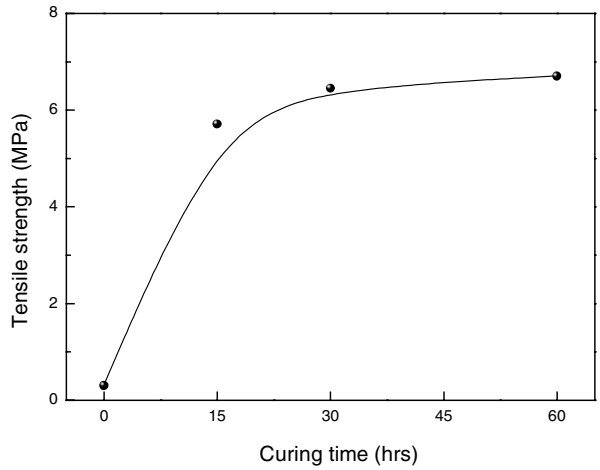

Figure 8 Effect of curing time on the tensile strength of solidified bodies. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; compaction pressure: 20 MPa; curing temperature: 200°C. Excessive curing time has little influence on the tensile strength of solidified bodies.

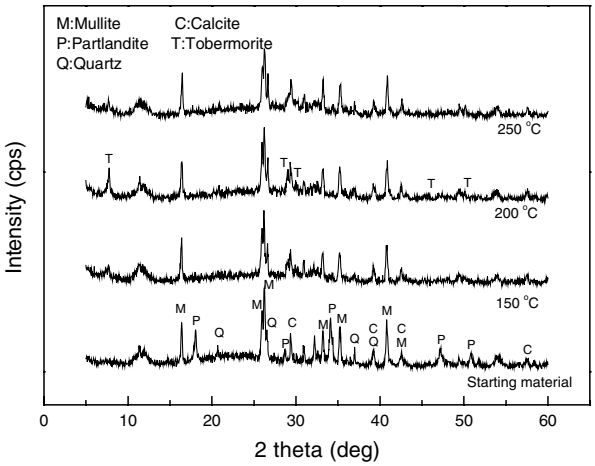

Figure 9 XRD patterns of starting material and solidified bodies cured by different temperatures. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; compaction pressure: 20 MPa; curing time: 15 h. The curing temperature affects the formation of tobermorite.

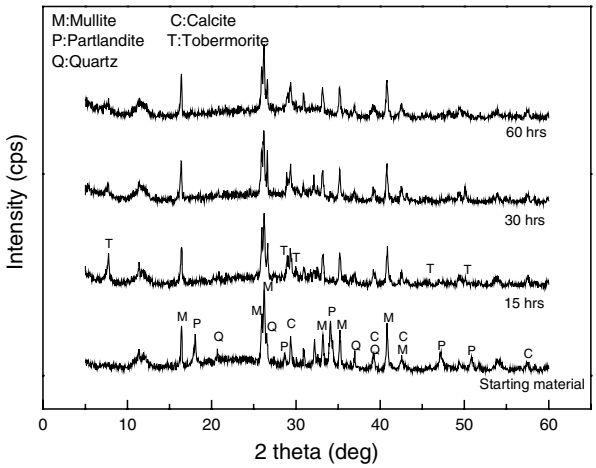

Figure 10 XRD patterns of starting material and solidified bodies cured by different times. Hydrothermal processing conditions: $Ca(OH)_2$ content: 20 mass%; compaction pressure: 20 MPa; curing time: 15 h. The longer the curing time, the lower the peak intensity of tobermorite.

drastically after autoclave curing time of 15 h, and then tends to level off, thus suggesting that the excessive curing time (>30 h) appears to exert little influence on the strength development.

Figs. 9 and 10 depict XRD patterns of the starting material and the solidified bodies discussed in Figs. 7 and 8, respectively. Fig. 9 confirms calcite, mullite, quartz and partlandite in the starting material. After hydrothermal processing at 150°C for 15 h, a trace of 1.1 nm tobermorite starts to be observed. The peak intensity of tobermorite increases until curing temperature reaches 200°C, and then decreases. Compared the peak intensity (from 150 to 200°C's) with the strength of solidified bodies mentioned in Fig. 7, it is clear that the higher curing temperature (200°C) accelerates the tobermorite formation, and the formation of tobermorite, in turn, results in the better mechanical property of solidified bodies. However, it should be noted that for curing temperature of 250°C, the lower peak intensity leads to the higher tensile strength. The similar trend can be seen in Fig. 10 for the curing time influence, i.e., when the curing time becomes longer, the peak intensity tends to decrease.

Fig. 11 shows SEM photographs of solidified bodies cured at 250°C for 15 h (Fig. 11(1)) and at 200°C for 60 h (Fig. 11(2)) respectively. The processing conditions are the same as the one shown in Figs7,8, 9 and 10.

At the curing temperature of 200°C for curing time of 15 h, an overgrowth of tobermorite can be observed, similar to the Fig. 6(2). The formation of tobermorite enhances the strength of the solidified bodies. When the curing temperature reaches 250°C, however, the dissolution in the solidified body is observed in Fig. 11(1). The dissolution of crystals glues ash particles together, and fills the space between ash particles. Compared with the strength development shown in Fig. 7, it is clear that the dissolution of crystals results in the further enhancement in strength.

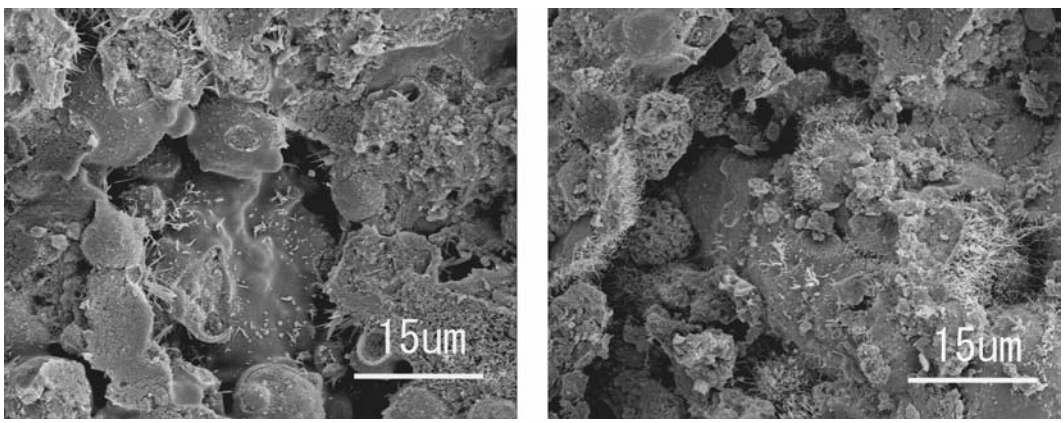

Figure 11 SEM photographs of solidified bodies compacted by 20 MPa, and (1) cured at curing temperatures of 250°C, for 15 h; (2) cured at curing temperature of 200°C for 60 h. At 250°C, the dissolution of crystals in solidified body occurred; for 60 h, the crumpled fibrous and radiating fibrous crystals can be observed.

When the autoclave curing time changes from 15 to 60 h, the cardhouse-like tobermorite appears to decrease, while crumpled fibrous and radiating fibers crystals start to be observed in Fig. 11 (2). These crumpled fibrous and radiating fibrous crystals belong to calcium silicate hydrate (CSH). This suggests that prolonged curing time leads to the transformation of tobermorite to CHS. Both morphologic crystals failed to be identified by XRD due perhaps to their poor crystallinity or few quantities of crystals formed. Relating with the strength result shown in Fig. 8, it suggests that the development of strength of solidified bodies may be dependent on the formation of not only tobermorite but also calcium silicate hydrate, similar to the one reported by Crennan *et al*. [12] who pointed out that the strength development of concrete is due to the sum of tobermorite and CSH contents.

4. Conclusions

In order to recycle of reuse CFA on a lager scale, a hydrothermal processing method has been developed for solidification of the CHA. The experimental results of this study can be summarized as follows. CHA could be hydrothermally solidified by autoclave curing at 150 - 250°C for 15 h. The tensile strength determined by the Brazilian test reached more than 10 MPa under the conditions: $Ca(OH)_2$ 30 mass%, compaction pressure 20 MPa, curing temperature 200°C and curing time 15 h. The most impotent strength-producing constituent in the solidified bodies produced with CFA was proved to be or tobermorite-like calcium silicate hydrate. Experimental results showed that at Ca/Si ratio around 0.83 in the starting material, tobermorite formed readily, and tobermorite formation could provide a good tensile strength for solidified bodies. The autoclave curing temperature and time also affected significantly the formation of tobermorite and the strength. Although higher curing temperature (250°C) and longer curing time (60 h) appeared to exert a negative influence on the formation of tobermorite, the dissolution of crystals and the formation of tobermorite-like CSH instead seem to enhance or support the strength development. The experimental results also showed that the excessive $Ca(OH)_2$ added appeared to exert a retardant influence on hydrothermal reaction, thus leading to the decrease in strength.

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