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Hydrothermal solidification of blast furnace slag by formation of tobermorite

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Abstract Blast furnace water-cooled slag (BFWS) has been solidified using a hydrothermal processing method, in which the BFWS could be solidified in an autoclave under saturated steam pressure (1.56 MPa) at 200 °C for 12 h by the additions of quartz or coal flyash. The tensile strength development was shown to depend on the formation of tobermorite and the packing state of the formed tobermorite in the solidified bodies. The additions of quartz or fly ash were proved to be favorable not only to the formation of tobermorite but also to the transformation of hibschite, the former improving the strength, and the latter deteriorating the strength. The excessive addition of quartz appeared to cause strength deterioration due to the fact that the residual quartz affected the formation of tobermorite in the solidified bodies.

Introduction

There has been currently an increasing trend for the use of industrial waste or by-products as supplementary materials or admixtures in the manufacture of building materials due to environmental and economic reasons. Blast furnace slag (BFS), for example, is one of these industrial wastes used in Portland cement manufacture [1]. More than 24 million tons BFS is being generated yearly in Japan, and around 65% of it has been utilized for the manufacture of Portland slag cement [2] which is being widely used to produce building materials.

BFS, of higher lime content, is well known to have a hydraulic activity when mixed with water. Therefore, the BFS may have a potential as a useful material for producing building materials directly like Portland slag cement, which will, in turn, offer both energy saving and cost reductions.

In hydration of Portland cement, tobermorite has been shown to be the most important strength-producing constituent of hydrated cement [3–5]. In the hydrothermal processes of calcium silicate products and insulating materials, the strength development has been proven to be due to the formation of tobermorite and calcium silicate hydrate (CSH)[6–7]. In our previous studies, municipal incineration ash [8] and coal fly ash [9] have also been solidified hydrothermally with the formation of tobermorite. Therefore, the hydrothermal solidification technology may have such a potential for producing building materials from BFS directly. The hydrothermal solidification technology is considered to save energy due to a lower hydrothermal autoclaving temperature (<200 °C). Ishida [10] reported that the energy required for the hydrothermal solidification (at 150 °C) of earth ceramics is only 1/6th that of energy needed for fired ceramic tiles.

However, very little has been reported regarding the hydrothermal solidification of BFS. The objective of the present work is to investigate how to solidify BFS hydrothermally with tobermorite formation, and to evaluate the effect of tobermorite formation, and the packing state of the tobermorite formed in solidified bodies on the strength development. The results are expected to provide useful

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information on the manufacture of building from BFS by hydrothermal solidification technology.

Experimental procedure

The blast furnace water-cooled slag (BFWS) used throughout in this research was obtained from Sumitomo Metals Ltd. in Japan. The BFWS was ground with a ball mill to obtain a BET specific surface area of 370 m^2/kg. According to our previous investigations [8–9], additions of Portland cement and slaked lime into municipal incineration ash and coal flyash were favorable to the formation of tobermorite, therefore, fresh Portland cement powder and slaked lime were used as the additives here. Compositions of the BFWS, Portland cement, coal fly ash and quartz as determined by x-ray fluorescence (XRF; RIX3100, Rigaku) are shown in Table 1. The BFWS powder mixed with these additives at different mixing ratio was used as starting materials. The starting material (20 g) was first mixed with 5 mass% distilled water (1 mL) in a mortar manually, and then the mixture was compacted by compaction pressure of 30 MPa in a disc-shaped mould (φ 30 mm × H120 mm). The demoulded specimens were subsequently autoclaved under saturated steam pressure (1.56 MPa) at 200 °C for 12 h. The hydrothermal apparatus for curing the demoulded specimens is shown in Fig. 1. After autoclaving, all the solidified specimens were dried at 80 °C for 24 h before testing.

The solidified disc-shaped specimens (φ 30 mm × H20 mm) were used to measured the tensile strength by Brazilian testing [11]. The Brazilian tests were conducted in an instron universal testing machine (M1185) at a crosshead speed of 0.2 mm/min. The measured rupture load (maximum load) was substituted into the following equation to calculate tensile strength, σ_t

$$\sigma_t = 2P_{max}/\pi dt$$

where P_{max} is the max load, d (=30 mm) specimen diameter, and t (=20 mm) specimen thickness. Three specimens were tested for each hydrothermal processing condition, and the average values of the strength results are presented in this paper. After the Brazilian test, the crushed specimens were investigated for phase analysis by X-ray diffraction (XRD, MiniFlex, Rigaku), for microstructure by a scanning electron microscope (SEM S-4100, Hitachi), and for pore diameter distribution by the mercury intrusion method (Poremaster 33P, Quantachrome).

Table 1 Compositions of the BFWS, cement, quartz, flyash and slaked lime used (mass%)

	BFWS	Cement	Quartz	Flyash	Slaked lime
SiO_2	32.6	21.8	89.7	53.1	
CaO	44.7	61.7	0.91	3.5	>75
Al_2O_3	15.8	6.5	7.02	24.0	
MgO	3.5	1.4		0.61	
SO_3	1.2			0.08	
Mn_2O_3	0.3				
TiO_2	1.1		0.25	4.58	
Fe_2O_3			0.62	5.1	

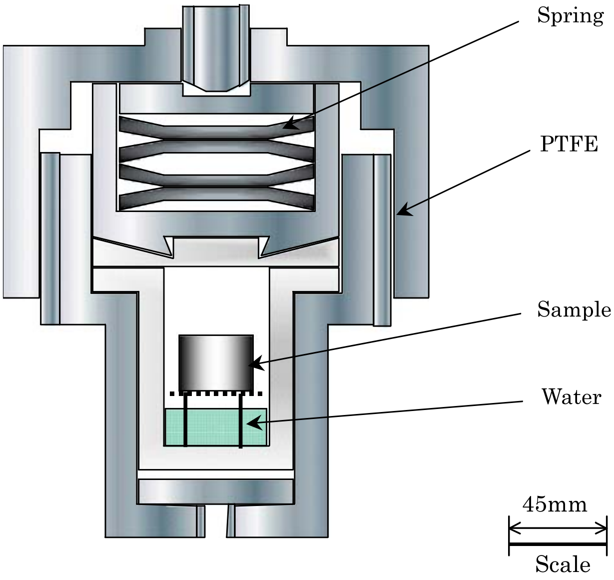

Fig. 1 Hydrothermal apparatus used for curing compacted specimens

Results and discussion

Additions of Portland cement and slaked lime were expected to improve the strength of hydrothermally-solidified bodies. Thus, the effects of the contents of Portland cement and slaked lime on the tensile strength were investigated first. The results (Fig. 2) show that the additions of cement and slaked lime do not exert a significant influence on the development of strength until the contents reach 30 mass%.

The effects of the additions of cement and slaked lime were also investigated by XRD analysis. Figure 3 indicates the XRD patterns for the solidified specimens synthesized with the slaked lime at 20 mass%, with the cement at 20 mass%, and without the slaked lime and cement (only BFWS) respectively. The BFWS is X-ray amorphous, displaying a typical background feature, and after autoclaving, however, a new phase corresponding to hibschite $\left(Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x\ (x=0.2to1.5)}\right)$, which belongs to hydrogarnet group, is superimposed on the broad amorphous background feature. With the additions of Portland cement and slaked lime, main phases of calcium silicate (Ca_3SiO_5) and portlandite ($Ca(OH)_2$) are distinct, but few tobermorite phases are found, which possibly explains the

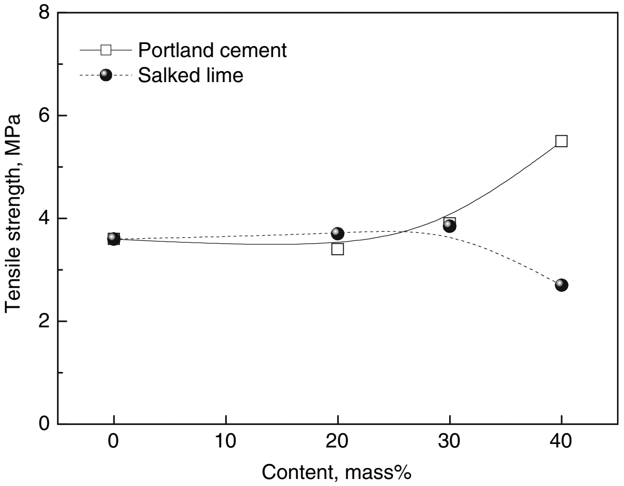

Fig. 2 Effects of Portland cement and slaked lime contents on the tensile strength of solidified bodies

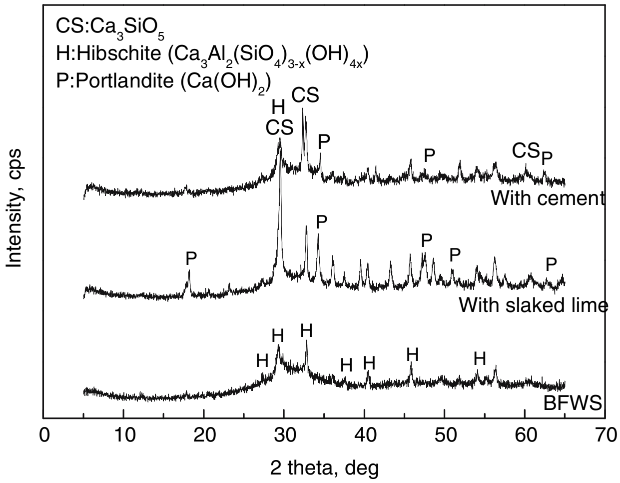

Fig. 3 XRD patterns for the solidified specimens synthesized with slaked lime 20 mass%, cement 20 mass%, and without slaked lime and cement (only BFWS) respectively

small influence on the strength shown in Fig. 2. SEM photograph (Fig. 4) of the fracture surface of solidified specimen produced only with BFWS shows the octahedral morphology of hibschite, which is very similar to that of hydrogarnet. It was reported that formation of hydrogarnet causes strength deterioration in calcium silicate materials [10]. From Fig. 3, the hibschite peaks remain discernible after additions of cement and slaked lime, and the existence of hibschite in solidified specimens perhaps is another reason that the additions of cement and slaked lime did not improve the strength.

Tobermorite is a calcium silicate hydrate mineral of ideal composition $5CaO \cdot 6SiO_2 \cdot 5H_2O$, and it can be formed by the reaction of $5Ca(OH)_2 + 6SiO_2 \rightarrow 5CaO \cdot 6SiO_2 \cdot 5H_2O$.

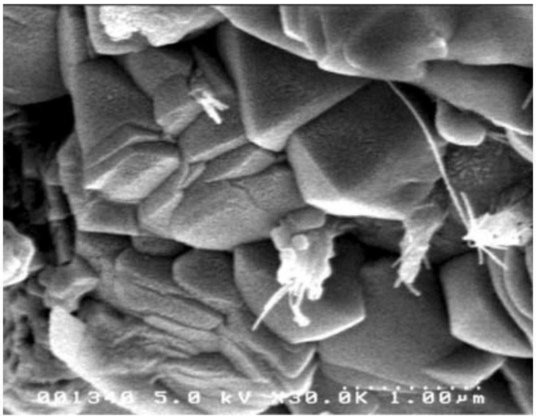

Fig. 4 SEM photograph of the fracture surfaces of solidified specimen produced with only BFWS

As shown in Table 1, because the CaO content in the BFWS composition is higher than the SiO_2 content, clearly the addition of either cement or slaked lime, which also has higher content of CaO, will be unfavorable to tobermorite formation. In contrast, addition of SiO_2 should improve the tobermorite formation.

Figure 5 shows the influence of quartz content on the tensile strength of solidified specimens. The tensile strength, as expected, increases with increasing the quartz content up to 20 mass%, and then decreases.

The development in strength was also examined by XRD analysis (Fig. 6). With the addition of quartz, the hibschite peaks tend to be much less distinct, while, at the same time, peaks of 1.1 nm tobermorite and quartz are observed. This shows that the added quartz has made the hibschite transform, at least in part, to 1.1 nm tobermorite. Klimesch and Ray [12] reported that hydrogarnet decreased and finally disappeared while 1.1 nm

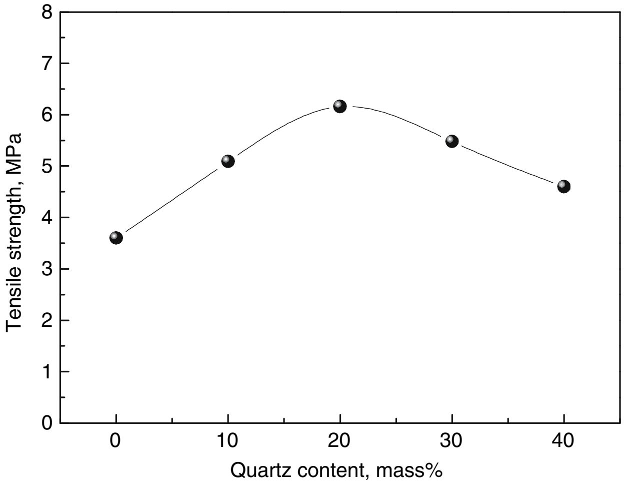

Fig. 5 Influence of quartz contents on the tensile strength of solidified specimens

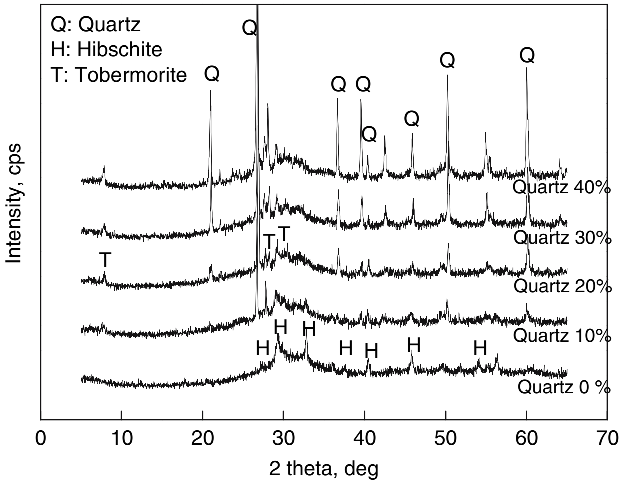

Fig. 6 XRD patterns for the solidified specimens with different quartz contents

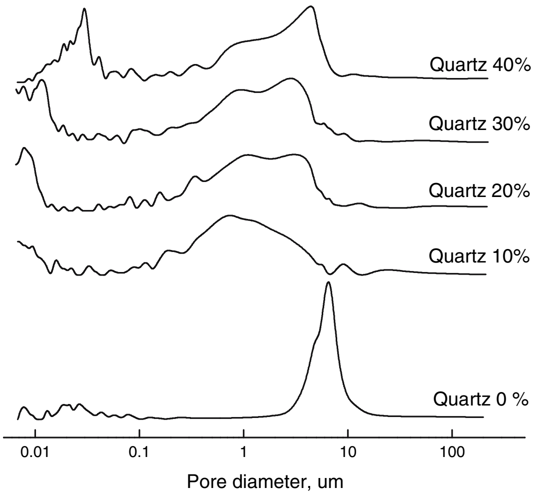

Fig. 8 Pore size distributions of the solidified specimens with different quartz contents

tobermorite increased concurrently for the hydrothermal solidification of CaO, metakaolin and ground quartz. Based on the results, the strength development may be attributed to both the formation of tobermorite and the disappearance of hibschite, the former improving the strength, and the latter deteriorating the strength. From Fig. 6, with the addition of quartz, the quartz peak intensities became stronger, reflecting more residual quartz left in the solidified body. This suggests that even if tobermorite exists in solidified bodies, the residual quartz could cause a reduction in strength.

Figure 7 shows SEM photograph of solidified specimen with the quartz content of 20 mass%. An overgrowth of fibrous tobermorite bonds slag particles together and fills the space between these slag particles. The formed tobermorite is believed to enhance the strength of the solidified body.

Figure 8 shows the pore diameter distribution of the solidified specimens with different quartz contents. In the solidified specimen without the addition of quartz, the highest frequency was of 7 μm in diameter, similar to that of the green block sample of autoclaved aerated concrete (AAC) reported by Mitsuda et al. [13]. With the addition of quartz, however, the main pore diameter distribution peaks (macropore diameter >0.1 μm) shifted to a smaller pore diameter and became wider, and new micropore distributions (pore diameter < 0.1 μm) formed. These peaks correspond to the spaces between the particles (macropore), or the space of intercrystalline (micropore) within specimen at the time of its formation. The peak shift and formation suggest some crystals form, which have resulted in a change in macropore diameter. According to the XRD (Fig. 6) and SEM (Fig. 7) results, the peak shift and formation is due mainly to the formation of 1.1 nm tobermorite. It is notable that both of the macropore and micropore distribution peaks with the quartz contents of 20–40 mass% shifted to a larger pore diameter (the micropore distribution peak is small for the quartz content of 10 mass%). This suggests with the addition of quartz, the tobermorite formed in the macropore of the specimens has become fewer (it has led to a larger macropore), and at the same time the intercrystalline space of formed tobermorite has also become larger (the tobermorite formed becomes sparser). This larger macropore and the sparser formed tobermorite may result in the reduction in strength for the excessive addition of quartz mentioned above.

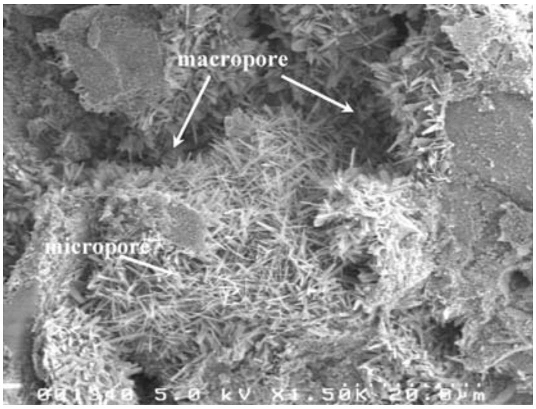

Fig. 7 SEM photograph of the solidified specimen with addition of quartz 20 mass%

For practical application, if waste, of higher SiO_2 content, could be used as additive instead of quartz, it will reduce the cost of hydrothermal solidification of BFWS. Coal flyash, collected from coal-fired power station in Tokyo, Japan, was used as one of the additives. The composition of the flyash used is shown in Table 1.

Figure 9 shows the influence of the coal flyash content on the tensile strength of solidified specimens. As

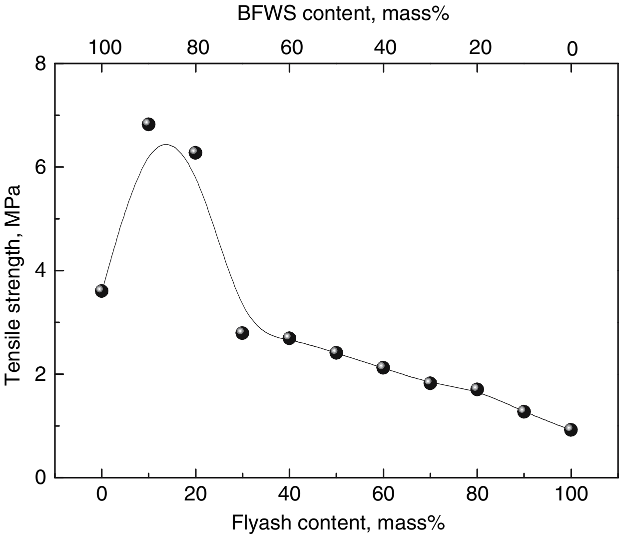

Fig. 9 Influence of coal flyash contents on the tensile strength of solidified specimens

expected, the tensile strength increases with the flyash content of up to 10 mass%; above 20 mass% it decreases drastically, suggesting that an optimum flyash content exists for the solidification of BFWS under hydrothermal processing.

XRD results for the solidified specimens with the different flyash contents are shown in Fig. 10. The results confirm main phases corresponding to mullite ($3Al_2O_3 \cdot 2SiO_2$), calcite ($CaCO_3$), and quartz (SiO_2) in the fly ash solidified specimen (fly ash 100%), and to hibschite $\left(Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}\ _{(x=0.2to1.5)}\right)$ in the BFWS solidified specimen (flyash 0%), respectively. However, a phase of 1.1 nm tobermorite becomes discernible with flyash at 20 mass%. This shows that the strength increase shown in Fig. 9 is due possibly to the formation of tobermorite. At the same time, with the addition of flyash, the peaks of hibschite, which is speculated to lead to strength deterioration, become much less distinct. This may also exert a positive effect on the strength increase.

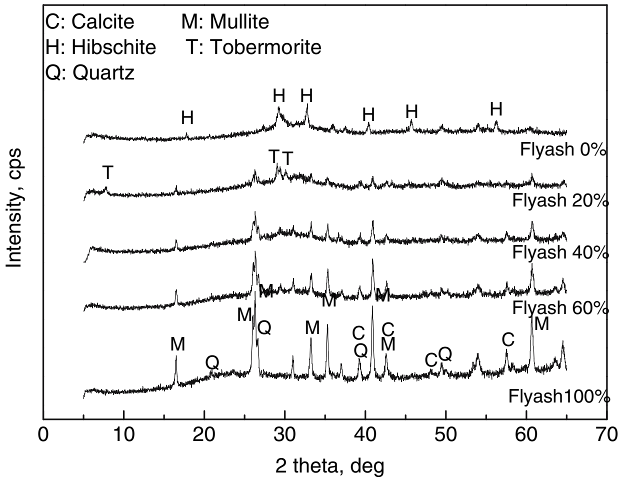

Fig. 10 XRD patterns for the additions of flyash content of 0, 20, 40, 60 100 mass%

SEM photographs of the solidified specimens with flyash contents of 20 and 40 mass% are shown in Fig. 11. At the flyash content of 20 mass% (Fig. 11(1)), an overgrowth of fibrous tobermorite forms, while for the flyash content of 40 mass% (Fig. 11(2)), only few fibrous crystals can be observed. The SEM photographs clearly show why the strength at the flyash content of 20 mass% is much higher than that at 40 mass%, and how the formation of crystals affects the strength development.

The pore distributions of solidified specimens with different flyash contents were also investigated. Figure 12 shows the pore diameter distributions with the addition of 0–60 mass% of coal flyash. With the addition of 10–20 mass% of flyash, the pore diameter distributions have changed thoroughly, while the others remains almost unchanged. As shown in Fig. 11(1), overgrowth tobermorites form in macropore of the solidified specimen, thus leading to the macropore distribution shift to a smaller pore diameter and the micropore distribution formation for the addition of 10–20 mass% of flyash; in contrast, few

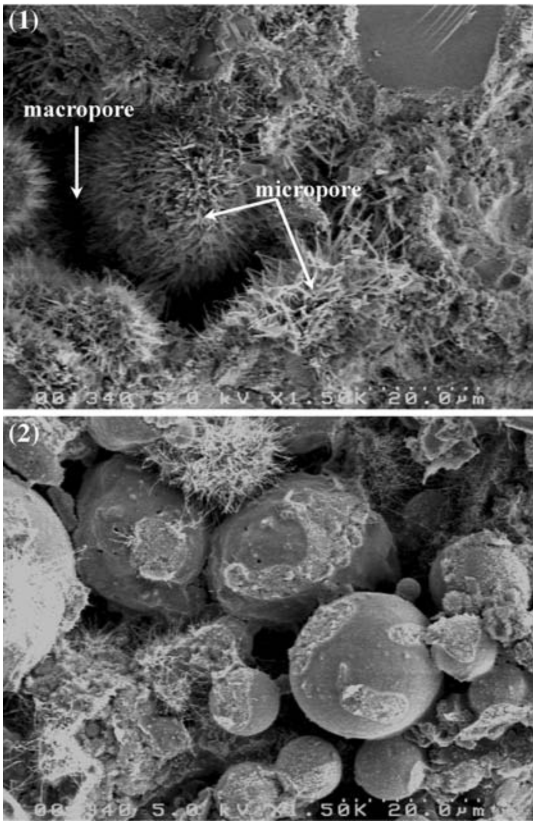

Fig. 11 SEM photographs of solidified specimens with the additions of the flyash (1) 20 mass%, and (2) 40 mass%

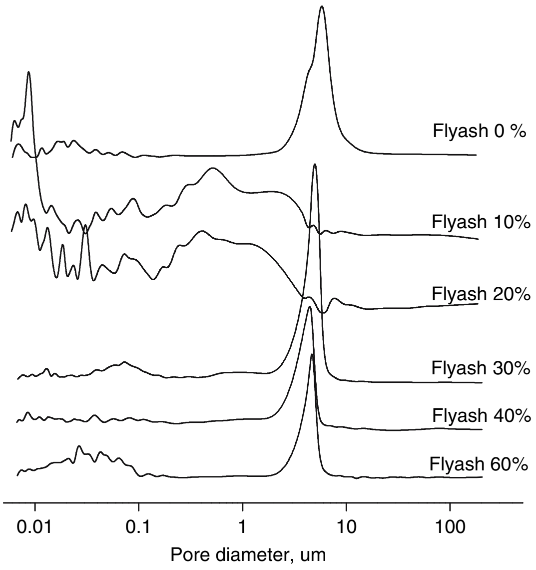

Fig. 12 Pore size distributions of solidified specimens with different flyash contents

crystals formed in the solidified specimens (Fig. 11(2)) with the addition of 30–60 mass% of flyash causes few changes in pore diameter distributions for the others. The formed tobermorite, clearly, did enhance the strength of the solidified bodies.

Conclusions

(1) BFWS could be hydrothermally solidified at 200 °C for 12 h by the additions of quartz or coal fly ash. With the additions of 20 mass% of quartz, or 10–20 mass% of coal flyash, the tensile strengths of the solidified specimens researched more than 6 MPa, which is higher than that of ordinary concrete.

(2) The development in tensile strength depended on both tobermorite formation and the packing state of the tobermorite formed in the solidified blocks.

(3) With formation of crystals in solidified body, the macropore diameter distribution peak will shift and the micropore will form. The macro and micro pore distribution shift, reflecting a change in packing state of formed crystal, will have a significant influence on the strength development.

(4) With excessive quartz addition (>20 mass%), the residual quartz left in the specimen appeared to cause strength deterioration due to the fact that the residual quartz affected the tobermorite formation in the solidified bodies.

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