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Controlling ettringite formation in FBC fly ash geopolymer concrete

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ABSTRACT

Fluidized bed coal combstion (FBC) is extensively used in small self-generation power plants. The fly ash obtained from this FBC process contains high quantity of calcium and sulfate compounds which hinders its use in the construction industry. In addition, its reactivity is low and additional source material or additive is, therefore, needed to increase the reaction. This research studied the use of $Al(OH)_3$ and high concentrations of NaOH to control ettringite formation in the FBC fly ash geopolymer. Two replacement levels of 2.5 wt.% and 5.0 wt.% of $Al(OH)_3$ and three NaOH concentrations of 10, 12 and 15 M were used in the study. Results indicated that the NaOH concentration affected the ettringite formation and strength of the FBC geopolymer. No ettringite was formed at high NaOH concentration of 15 M which helped the dissolution of calcium sulfate and formed the additional calcium hydroxide. The subsequent pozzolanic reaction led to strength gain of the geopolymer. For 15 M NaOH, the addition of 2.5 wt.% $Al(OH)_3$ promoted the reaction and formed a dense matrix of alumino silicate compound. Relatively high 7-day compressive strength of 30 MPa was obtained.

1. Introduction

Fluidized bed combustion (FBC) is an efficient and environmentally-friendly technique for coal combustion process. This FBC technology is growing particularly in small enterprises due to the reduction of SO_2 and NO_x gasses released in flue gas [1]. Generally, the bed is operated at 800–900 °C, the low temperature prohibited the formation of nitrogen oxides (NOx) from the combustion air. The FBC system also permits the removal of sulfur dioxide (SO_2) from the combustion of high-sulfur fuels by the addition of sulfur absorbents such as limestone in the bed. A wide range of fuels including high-ash or high-moisture content fuels could be handled and efficiently burnt using the FBC process. The fly ash from fluidized bed combustion (FBC) contains high amount of $CaSO_4$ and CaO due to the use of lime for the SO_2 capture. These compounds hindered the use of FBC fly ash in construction since concrete with high $CaSO_4$ is prone to unsoundness [2]. Substantial amount of FBC fly ash is, therefore, disposed at landfill sites and thus needed to be utilized.

Ettringite formation, after the concrete had hardened, can promote concrete deterioration [3]. Ettringite is basically a hydrated sulfate of calcium and aluminum ($Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$) and exists in various forms, particularly as parallel needles of differing sizes in pores [4]. Ettringite is formed from the reaction between the anhydrite ($CaSO_4$) and residual dehydroxylated mineral (alumino-silicate) found in coal. This growth can lead to a deleterious effect on the mechanical properties of the material. For the FCB fly ash where sufficient $CaSO_4$ and alumino-silicate are present, its utilization as binder can lead to the formation of ettringite within the solidified matrix resulting in a significant structural problem. The needle-like crystals of ettringite growth exerts substantial internal stresses resulting in microcracking, swelling, and eventual failure [5]. However, in environments of high alkali hydroxide concentration, the formation of ettringite can be deterred [6].

Many researches indicate that the FBC-fly ash can be used as a source material for making geopolymer [7–9]. The geopolymer is an alumino-silicate compound prepared by incorporating high alkaline and sodium silicate solutions under low heat curing. This alumino-silicate cementitious compound possesses good mechanical properties viz., high compressive strength and stability at temperature up to 1400 °C [10].

Addition of alumina in geopolymer system resulted in increased aluminate ($Al(OH)_4^-$) species leading to a faster rate of condensation [11]. In the presence of sufficient quantity of calcium, calcium alumino-silicate hydrate (C–A–S–H) is formed [12,13]. FBC fly ash contains significant amount of calcium and sulfate, it is expected that addition of the alumina results in the formation of both C–A–S–H and ettringite. Formation of ettringite plays an important role in the FBC fly ash geopolymer system.

Since the calcium compounds ($CaSO_4$ and CaO) in FBC fly ash could result in the formation of ettringite in the geopolymer, this research attempted to control the formation of the ettringite by

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preparing the FBC-fly ash geopolymer with various NaOH concentrations and addition of $Al(OH)_3$. $Al(OH)_3$ is commercially available and when dissolved it produces strong alkali solution forming aluminate ion, $Al(OH)_4^-$. This ion can react with silica to form additional alumino-silicate compound, and it reacts with calcium compounds present in FBC fly ash to form calcium aluminate hydrate (C–A–H). This would result in the geopolymer formation with strength gain and good physical properties.

2. Experimental procedure

2.1. Materials

FBC-fly ash obtained from a small power plant in Thailand was used as a source material for geopolymer synthesis. Typical chemical composition of this FBC fly ash determined by X-ray fluorescence (XRF) is shown in Table 1. The major compounds were lime (CaO), quartz (SiO_2), alumina (Al_2O_3) and anhydrite ($CaSO_4$). The FBC-fly ash contained high CaO content of 42.2% due to the addition of lime to extract sulfate oxides. This fly ash had the particle size (D_{50}) of 24 μm with a specific gravity of 2.34. The FBC-fly ash reactivity was low and the glassy phase content was also low owing to the low burning temperature of 900 °C. Aluminum hydroxide ($Al(OH)_3$) was also used as the additional source of aluminum compound for making geopolymer. Sodium hydroxide (NaOH) pellets were dissolved with distilled water to provide the NaOH solutions of 10, 12 and 15 M concentrations. The sodium silicate solution (Na_2SiO_3) with 9% Na_2O and 30% SiO_2 by weight was used as the external source of SiO_2. River sand with specific gravity of 2.65 and fineness modulus of 2.8 was employed to prepare the mortar for strength test in accordance with ASTM C109.

2.2. Geopolymer preparation

The effect of NaOH concentration on the ettringite formation was studied by varying the NaOH concentration. For preliminary study, 15 M NaOH was selected to prepare the $Al(OH)_3$-FBC fly ash blend geopolymer as it was reported that there was no ettringite formation [5]. 2.5 wt.% and 5.0 wt.% $Al(OH)_3$ were incorporated to make the FBC fly ash geopolymer [14]. The Na_2SiO_3-to-NaOH mass ratio of 2 was used for the study. The NaOH and Na_2SiO_3 were thoroughly mixed together and then added to the powdery raw material. Owing to the high water absorption of the sample, the high powder-to-liquid mass ratio of 1.5 was used. The mix proportion is tabulated in Table 2. The mixture was continuously mixed in a pan mixer for 2 min before casting in 5-cm cubic acrylic mold and vibrated for 10 s to remove the air bubbles. The specimens were then covered with clingfilm and cured at 60 °C for 24 h.

For the geopolymer mortar strength test, sand was added to the paste mixture with the sand to powder ratio of 2:1 (by weight) and mixed for another 2 min. Casting and curing condition were similar to the paste preparation. Compressive strength test was performed at the ages of 7, 30 and 90 days. The results were reported as the average of three samples.

Table 1
Chemical composition and LOI of FBC fly ash.

Chemical composition	(wt.%)
SiO_2	21.0
Al_2O_3	8.1
Fe_2O_3	6.9
CaO	42.2
SiO_3	14.8
Other oxides	6.0
Loss on ignition (LOI)	1.0

2.3. Geopolymer testing

The geopolymer pastes were prepared for the XRD, TGA and SEM analyses. In addition, the degree of reaction was determined both on geopolymer and starting materials. This method was based on the dissolution of the powdery sample in 2 M HCl and 3 wt.% Na_2CO_3 [14–16]. 2 M HCl was used to dissolve CaO and MgO from the hydrated product, and 3 wt.% Na_2CO_3 was then employed to dissolve SiO_2, Al_2O_3, and Fe_2O_3. The remaining portion was the unreacted fly ash residue. The degree of reaction was calculated from the following equation:

$$\text{Degree of reaction} = \frac{m_{\text{sample}} - m_{\text{residue}}}{m_{\text{sample}}} \times 100 \quad (1)$$

where m_{sample} is the weight of powdery sample (g); m_{residue} the weight of dried residue (g).

The degree of reaction of the "blank" (raw materials before mixing with alkali solutions) was also determined. The degree of reaction of blank was then subtracted from those of geopolymers to obtain the corrected degree of reaction. The results were reported as an average of three samples.

3. Results and discussion

3.1. Morphological study of geopolymer pastes

The effect of NaOH concentration on ettringite formation was presented in XRD pattern as shown in Fig. 1. The XRD of FBC fly ash showed numerous sharp peaks of crystalline phases. Calcium and silica were the main compounds detected in the ash. Low reactive FBC fly ash could be converted to a more amorphous material by the geopolymerization process. The broad peaks and peak shift were found with the geopolymer pastes at 24–38° 2θ, indicating that the geopolymerization reaction resulted in the highly disorder material in the form of amorphous gel with some crystalline products [7,8]. This corresponded to the detection of aluminosilicate in the geopolymer matrix. New compounds of ettringite, calcium-silicate, and calcium-alumino-silicate were also formed. Ettringite was found quite readily in the sample with NaOH concentration of 10 M at 41° and 43° 2θ. Less ettringite was formed for the concentration of 12 M NaOH with the presence of peak at only 43° 2θ. For the highest concentration of 15 M NaOH, ettringite could not be detected and the peaks at 41° and 43° 2θ disappeared. It was previously reported that difficulty of ettringite formation was found in the presence of high alkali hydroxide concentration [6]. The high NaOH concentration could reduce the amount of gypsum in the FBC fly ash system resulting in the gypsum dissolution via the double decomposition reaction as shown in Eq. (2)[17].

$$CaSO_4 \cdot 2H_2O(s) + NaOH(aq) \rightarrow 4Ca(OH)_2(s) + Na_2SO_4(aq) \quad (2)$$

Sodium hydroxide, thus, promoted gypsum dissolution and the formation of calcium hydroxide. As gypsum dissolved in the NaOH solution, the concentration of both calcium and sulfate ions increased leading to the precipitation of calcium hydroxide ($Ksp = 7.9 \times 10^{-6}$). Therefore the amount of calcium hydroxide formed could limit the ettringite formations and thus allowing the formation of other phases [17].

From the result, 15 M NaOH was selected as the alkali solution to prepare the $Al(OH)_3$-FBC fly ash blend geopolymer. $Al(OH)_3$ was then incorporated to the FBC fly ash geopolymer. Two dosages of 2.5% and 5.0% of $Al(OH)_3$ by weight were blended with FBC fly ash and used as the source materials for making geopolymer. The results of XRD pattern of blend geopolymer pastes are shown in Fig. 1. The incorporation of $Al(OH)_3$ resulted in the formation of the alumino-silicate compound at 34° 2θ. At high $Al(OH)_3$ content

Table 2
Mix proportion of geopolymers (g).

Sample	% $Al(OH)_3$	Fly ash	$Al(OH)_3$	Na_2SiO_3	NaOH	NaOH concentration (M)
100FBC	0	40	–	40	20	10/12/15
2.5Al	2.5	39	1	40	20	15
5Al	5	38	2	40	20	15

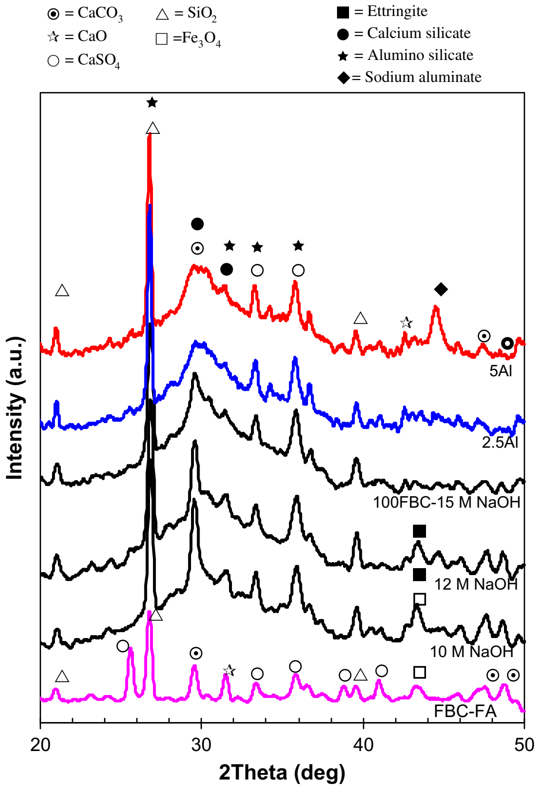

Fig. 1. XRD pattern of as-received FBC, FBC geopolymers and blend geopolymers prepared with 15 M NaOH.

of 5 wt.%, sodium-aluminate compound was detected in the composite with a prominent peak at 44.5° 2θ. With high alkaline concentration, this compound could subsequently convert to zeolite as an intermediate phase and could weaken the geopolymer.

3.2. Compressive strength of geopolymer mortars

The results of compressive strength of FBC fly ash geopolymer mortar are presented in Fig. 2. The 7-day strengths of FBC fly ash geopolymers were low at 7, 8 and 12 MPa for the mixes with 10, 12 and 15 M NaOH, respectively. This was due to the low reactive amorphous phase and high crystallinity of the as-received starting material. The compressive strength increased with the curing age owing to the high calcium content of FBC fly ash and the formation of calcium silicate hydrate (C–S–H) in the composite. In addition to alumino silicate compound, C–S–H was another significant factor enhancing the strength of FBC fly ash geopolymer. The leaching of minerals such as silicon and aluminum ions occurred when fly ash came into contact with NaOH and sodium silicate solutions [16] leading to the formation of calcium silicate and alumino-silicate gels. The calcium silicate hydrate (C–S–H) co-existed with the geopolymer products [18,19] and helped to develop the strength of geopolymer as a function of time. The increase in the NaOH concentration led to the higher strength gain since high NaOH concentration could better leach out the Si^{4+} and Al^{3+} ions resulting in the better formation of geopolymer gel [20]. The highest concentration of 15 M NaOH resulted with the geopolymer having a 90-day compressive strength of 26.0 MPa. In addition, the change in the NaOH concentration affected the SiO_2/Na_2O ratio. The increase in the NaOH concentration resulted in low SiO_2/Na_2O ratio and led to the formation of solid sodium silicate compound which was a weak compound and contributed to a relatively low strength matrix [14].

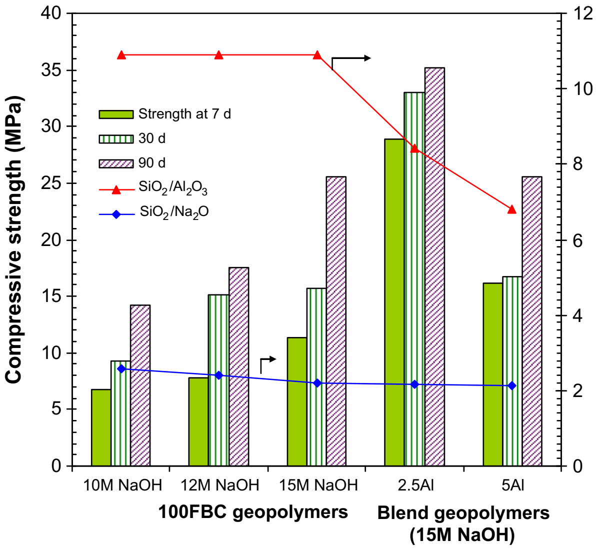

Fig. 2. Compressive strength of geopolymers.

Compressive strengths of $Al(OH)_3$-FBC blend geopolymer prepared with 15 M NaOH are also presented in Fig. 2. Addition of 2.5 wt.% of $Al(OH)_3$ enhanced the strength of the geopolymer owing to the increase in the alumina which led to the reduction of the SiO_2/Al_2O_3 mole ratio. The higher Si/Al ratio gave geopolymer with a relatively low strength [21]. For the incorporation of 2.5 wt.% of $Al(OH)_3$, the strength of geopolymer at 90 days was thus increased to 36 MPa. The aluminum ion from $Al(OH)_3$ reacted with silicon ion to form the additional alumino-silicate gel. However, the incorporation of the high amount $Al(OH)_3$ of 5 wt.% resulted in the reduction of the strength of the geopolymer and the strengths were similar to the geopolymer without $Al(OH)_3$. The excess aluminum ion reacted with NaOH solution and formed the sodium aluminate compound as detected in the XRD pattern and it seems that this lowered the geopolymer strength.

3.3. Microstructural study

The results of microstructure study of FBC fly ash and geopolymers are shown in Fig. 3. The composite consisted of the unreacted fly ash particles, geopolymer matrix and other compounds. The needle-like ettringite was found in FBC fly ash geopolymer prepared with 12 M NaOH and less (Fig. 3a) and was in accordance with the XRD result. Ettringite was observed in crack and void of the geopolymer matrix. It could be converted to calcium aluminate monosulfate in the presence of moisture and high content of

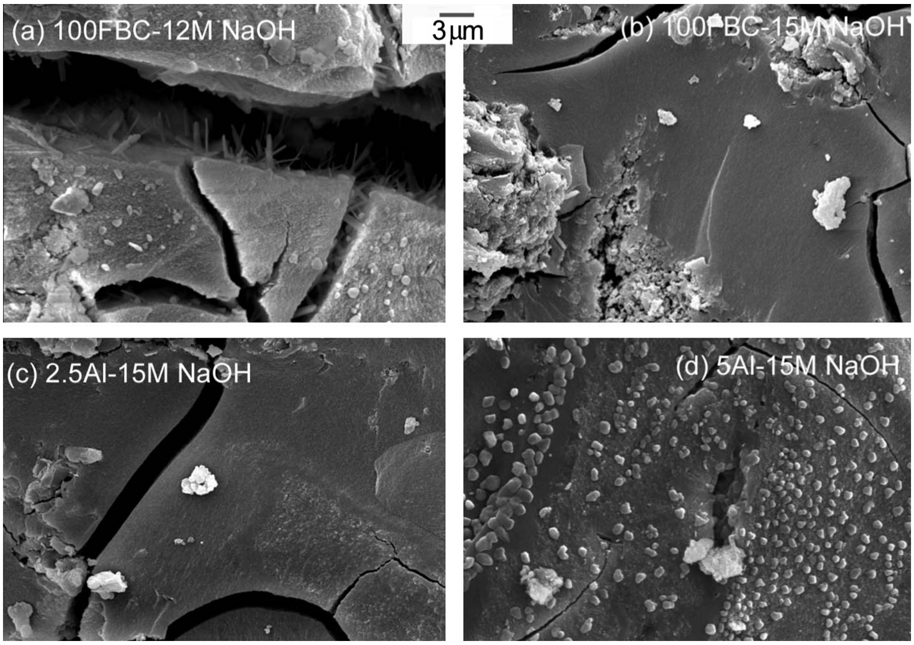

Fig. 3. SEM micrographs of geopolymer pastes at the age of 90 days.

calcium sulfate in the matrix. For the FBC fly ash geopolymer prepared with 15 M NaOH, no ettringite formation was observed (Fig. 3b). As mentioned, the high NaOH concentration helped the dissolution of calcium sulfate and formed calcium hydroxide. The pozzolanic reaction could subsequently carry out through the reaction between this calcium hydroxide and silica and alumina from the FBC fly ash particles resulting in more C–S–H in the matrix. With 2.5% $Al(OH)_3$, the prepared sample with 15 M NaOH also showed the dense and homogeneous matrix with no sign of ettringite formed in the cracks and voids (Fig. 3c). For the incorporation of 5 wt.% of $Al(OH)_3$ with 15 M NaOH, the matrix consisted of sodium silicate (Fig. 3d) and excess gibbsite ($Al(OH)_3$) with a small amount of cross linked geopolymer leading to a lower strength matrix [14]. Sodium aluminate zeolite could be found as indicated by the XRD peak at 44.5° 2θ.

3.4. Degree of reaction

Fig. 4 shows the degree of reaction of blend geopolymer pastes prepared with 15 M NaOH. The test was based on the dissolution of product, the remaining unreacted fly ash was determined. The FBC fly ash geopolymer has the degree of reaction of 21.9%. With $Al(OH)_3$ content of 2.5%, more products were formed in the composite leading to less unreacted material remaining in the sample. For the high dosage of 5% of $Al(OH)_3$, excess $Al(OH)_3$ was available and was difficult to be dissolved in chemical reagents. The degrees of reaction were 24.3% and 23.7% respectively for the samples with 2.5% and 5.0% $Al(OH)_3$. The high degree of reaction of the geopolymer with 2.5% $Al(OH)_3$ agreed with the results of strength in Fig. 4. The optimum $Al(OH)_3$ content was, therefore, 2.5% by weight of the powder and this mix gave a dense matrix with high degree of reaction and high strength.

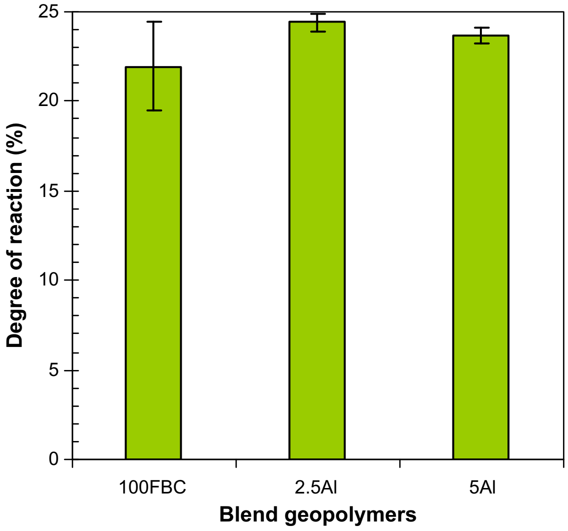

Fig. 4. Degree of reaction of geopolymer pastes at 90 days.

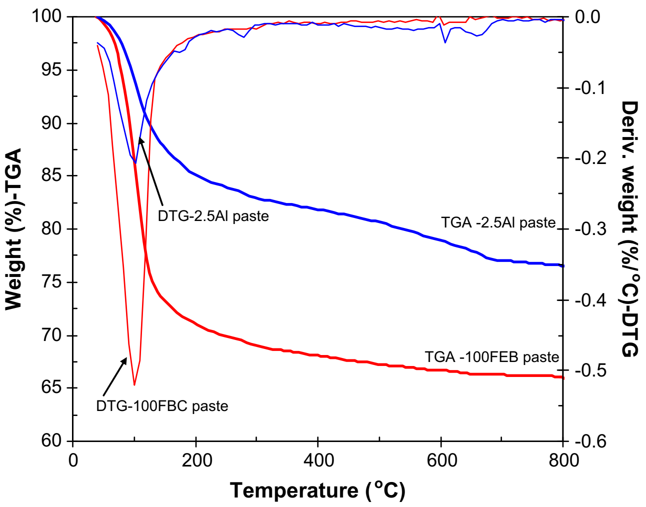

Fig. 5. TGA/DTG curves of geopolymer pastes at 90 days.

3.5. Thermal stability of geopolymers

Thermal stability of geopolymer pastes was measured by thermogravimetric analysis (TGA) and differential thermogravimetry (DTG), results are shown in Fig. 5. TGA/DTG monitored the weight change during heating of specimen. FBC geopolymer showed higher weight loss than the 2.5Al blend geopolymer. This was due to the reaction between free lime in FBC fly ash and $Al(OH)_3$ in base condition forming the more binding materials (i.e. aluminosilicate and calcium aluminate compounds) in matrix. Weight loss was found at 100 °C owing to the evaporation of water. Two peaks at 300 and 580 °C, respectively, presented the starting and finishing dehydroxylation of $Al(OH)_3$. Less decomposition of $Ca(OH)_2$ at 400 °C indicated that calcium compound reacted with aluminate ion and resulted in more complex compounds, i.e. calcium aluminate and alumino silicate compounds.

4. Conclusions

Based on the results of this study, the following conclusions could be drawn.

The concentration of NaOH affected the ettringite formation in FBC fly ash geopolymer. For NaOH concentration of 10 M and 12 M NaOH, the ettringite was detected in cracks and voids of the geopolymer matrix. With NaOH concentration of 15 M, the dissolution of calcium sulfate was facilitated resulting in the formation of calcium hydroxide. This resulted in the pozzolanic reaction and led to strength gain of the geopolymer. The incorporation of 2.5 wt.% of $Al(OH)_3$ in FBC fly ash geopolymer promoted the reaction and provided dense and homogeneous matrix with the formation of additional alumino-silicate compound. However, the high dosage of 5 wt.% of $Al(OH)_3$ resulted in excess $Al(OH)_3$ and formed sodium aluminate which weakened the geopolymer. FBC fly ash utilization in geopolymer offers a new effective method to recycle FBC fly ash and an alternative cementitious material for non-structural member which does not require high strength products such as pavement, block and wall panel.

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