

Rapid fabrication of highly dense geopolymers using a warm press method and their ability to absorb neutron irradiation

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Abstract

A highly dense pure phase geopolymer was fabricated in only a few hours using a warm press technique. The resultant geopolymer had a high compressive strength of 149 MPa after pressing at 200 MPa and 130°C for 1 h. The heat and pressure applied during the processing accelerated the geopolymerization and solidification of the starting materials, which consisted of fly ash, a sodium hydroxide solution, and water glass. This highly dense geopolymer had an excellent ability to absorb neutron irradiation, compared to geopolymers fabricated by a conventional curing process.

1. Introduction

Large quantities of fly ash are discharged worldwide from coal-fired power plants every year[1]. A portion of this fly ash is used in cements and asphalts as a filler

material, but additional opportunities for reuse and new applications of fly ash should be developed in order to further reduce waste. Generally, fly ash is primarily composed of an amorphous aluminosilicate, quartz, and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). In addition, fly ash can contain small amounts of iron oxide, calcium oxide, magnesium oxide, sodium oxide, and potassium oxide. Recently, geopolymer materials have been investigated as an attractive method of fly ash reuse[2-8]. These geopolymers have good mechanical properties and excellent chemical stability[2]. However, acceptable mechanical properties only emerged after curing for 3 days to one week between room temperature and 50°C . In contrast, increasing the curing temperature to approximately 100°C decreased the hardening period of the geopolymers to less than one day. However, the mechanical strength drastically decreased due to the formation of many cracks within the hardened body. Therefore, in order to fabricate geopolymers without cracks in several hours, the authors considered a warm press method, in which the starting materials are pressed at high pressure while being heated to between 100 and 150°C . Using this method, highly dense geopolymer bodies without cracks can be obtained.

To date, acceleration of geopolymerization by the warm press technique has been studied as a lay-up technique for composites consisting of geopolymer and alumina fibers[9]. However, highly condensed single-phase geopolymers have not been fabricated using the warm pressing technique. In the present study, the effects of the heating temperature and pressing time on the density and compressive strength of the resultant geopolymers were investigated. In order to clarify the densification mechanism, X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared (FT-IR) spectroscopy, magic-angle-spinning nuclear magnetic resonance (MAS-NMR), and pore size distribution measurements were performed on the geopolymers.

Geopolymers may be useful as encapsulation materials for nuclear waste due to their high chemical corrosion resistance, resistance to high temperatures, water content that is comparable to that of zeolites[10,11]. Therefore, their ability to absorb neutron irradiation was evaluated and compared to that of conventionally cured geopolymers and cements.

2. Experimental procedure

Coal fly ash (JIS Type II) discharged from a Japanese power plant was used as a starting material. The chemical composition of the fly ash used is shown in Table 1. A slurry was formed by well mixing 100 g of the fly ash, 28 g of 10 mol/L sodium hydroxide solution, and 50 g of water glass, and this slurry was heated to 130°C for 2 h to form a dry starting material. The starting material was ground to a particle size finer than 500 μm , passed through a sieve, and then placed in a stainless steel mold. The steel mold was inserted into a warm press, and pressed at 200 MPa while being heated to between 75 and 140°C for various lengths of time to form a cylindrical sample, 15 mm in diameter and 30 mm in height. As a reference, a conventional geopolymer sample was also fabricated by curing at 50°C and 80% relative humidity for 3 days using the same starting slurry and a mold. The compressive strengths of the samples were measured using a universal testing machine (5582, Instron). The crosshead speed was 1 mm/min. The crystal phases in the samples were analyzed by XRD (XD-D1). In order to confirm the formation of a geopolymer, KBr pellets containing the sample were examined using FT-IR spectroscopy (Spectrum 100). In addition, the hardened samples and the original fly ash were investigated using solid-state ^{27}Al and ^{29}Si MAS-NMR spectroscopy (Unity Inova 400 Plus) at 104.2 and 79.6 MHz, respectively. The chemical shifts were

calibrated with respect to the zero reference of $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ for ^{27}Al and tetramethylsilane for ^{29}Si . The pore volume and pore size distribution in the samples were evaluated using N_2 sorption isotherm analysis (Autosorb-1). In particular, the porosities of the bulk samples were characterized using the Barrett-Joyner-Halenda (BJH) method[12]. The water content per unit volume of each sample was calculated from the weight loss after heating at 500°C and the apparent density of the samples.

To examine neutron transmission, geopolymer samples 45 mm in diameter and 10 mm thick were prepared by the warm press method. Gold filaments were attached to both sides of each sample. After neutron irradiation from one side of the geopolymer sample for 15 min, the radiant intensity of the gamma beam from the gold filaments was evaluated. Finally, the neutron transmission ratio was calculated from the difference between the radiant intensities of the gamma beams from the gold filaments at the top and bottom. The neutron irradiation intensity was $1.9 \times 10^4 \text{ n/cm}^2/\text{s}/\mu\text{A}$.

3. Results and discussion

3.1 Compressive strength

Figure 1 shows the compressive strength of geopolymer samples heated to various temperatures for 30 min under a uniaxial pressure of 200 MPa. Below 130°C , the compressive strength of the samples increased with increasing heating temperature, reaching a maximum value of 133 MPa at 130°C . However, increasing the heating temperature to 140°C decreased the compressive strength of the samples. **Figure 2** shows the compressive strength and bulk density of geopolymer samples pressed for different lengths of time at 130°C and 200 MPa. Increasing the pressing time increased the compressive strength of the geopolymer samples. The maximum compressive

strength was 149 MPa at 60 minutes. Furthermore, the bulk density of the geopolymer samples increased with increasing pressing time. In other words, sample densification progressed slowly with pressing time at 130°C and 200 MPa. According to the true sample density determined using a pycnometer, the relative density ($\frac{\text{apparent density}}{\text{true density}}$) of the geopolymer sample pressed for 60 min was 71%, which was relatively large compared to the value of approximately 50% for the conventionally cured sample. Hence, the increase in compressive strength with increasing pressing time was thought to be caused by an increase in the density of the geopolymer samples.

3.2 Effect of warm press on the local structure of the geopolymer

XRD analysis of the conventionally cured geopolymer sample and samples before and after warm pressing was performed. In all samples, XRD identified the crystal phases of quartz and mullite which were contained in the original fly ash. Therefore, warm pressing did not alter the crystal phases present in the geopolymer samples. FT-IR analysis of the conventionally cured geopolymer sample and samples before and after warm pressing was employed. A typical adsorption band around 990 cm^{-1} , which was assigned to the asymmetric stretch vibration of T-O (T: Si, Al), was observed for all samples. Thus, warm pressing did not alter the T-O (T: Si, Al) network structure. **Figure 3** shows (a) ^{27}Al and (b) ^{29}Si MAS-NMR spectra of samples before and after warm pressing. For reference, the spectra of fly ash are also displayed in the figure. In the ^{27}Al MAS-NMR spectra, a resonance peak associated with Al(VI) at 0-20 ppm was present in all processed samples. A peak due to Al(IV: AlO_4) at 50-70 ppm was also detected in the processed samples. It has been reported that upon geopolymerization of fly ash, a transformation from Al(VI) to Al(IV) occurs[14]. That is, the coordination number of Al changes to four, which is the same as that of Si(IV), due to the formation of an Al-O

network in the silica network chain. In contrast, in the ^{29}Si MAS NMR spectra of samples before and after warm pressing, the resonance peak around -90 ppm, which corresponds to Q^4_3 , did not change. However, in the conventionally cured sample, a ^{29}Si resonance peak, which seems to correspond to Q^4_2 , was detected around -97 ppm. This suggests that the Si coordination changed due to the heat treatment at 130°C , whether or not the sample was pressed at 200 MPa. Thus, warm pressing did not influence the local structure in the geopolymer samples.

3.3 Change in microstructure

Figure 4 shows the pore distribution of the conventionally cured geopolymer and the warm-pressed geopolymer formed at 130°C under 200 MPa in 60 min. Clearly, the warm-pressed geopolymer lost its 6 to 50 μm pores. This disappearance of pores was in accordance with the change to a dense micromorphology in the geopolymer after warm pressing. Thus, warm pressing did not influence the local structure and crystal phases of geopolymer samples; it only influenced their density.

3.4 Densification mechanism during warm pressing

During warm pressing, the weight of the sample decreased as a result of water evaporation. Therefore, the authors propose the following mechanism for the densification of the geopolymer during warm pressing. **Figure 5** shows a schematic of the bonding mechanism of geopolymer particles during warm pressing. It is likely that each geopolymer particle has some hydroxyl ions (OH^-) because the starting material still contains some water after being heated at 130°C for 2 h. Particles containing OH^- can bond to each other by a dehydration reaction, releasing water to form a larger particle. In three dimensions, this reaction forms a larger geopolymer grain. After warm pressing, a dense geopolymer with a high compressive strength is obtained. **Figure 6**

shows the compressive strength of geopolymer samples fabricated by warm pressing for various lengths of time, and that of a conventionally cured sample. When the geopolymer was fabricated by warm pressing, the porosity decreased to 30%, and the compressive strength exceeded 100 MPa. When the porosity was 29% (relative density 71%) after pressing at 130°C and 200 MPa for 60 min, the maximum value of the compressive strength of the geopolymer was 149 MPa. Moreover, Kearsley and Wainwright found that a multiplicative model of the relationship between compressive strength and porosity, as defined by Balshin, was in accordance with observations of the compressive strength and porosity of foam concrete [15]. Therefore, in this study, the relationship between the compressive strength (σ_c) and porosity (P) of the geopolymers was evaluated using the Balshin equation, as follows:

$$\sigma_c = \sigma_0(1-P)^n \quad (1)$$

where σ_0 is the intrinsic strength, or compressive strength at zero porosity (P=0), and n is a power coefficient. In Fig. 6, a Balshin curve is shown. According to the calculated curve, σ_0 was estimated to be 1560 MPa and n was determined to be 8.0. Here, the correlation coefficient R was 0.90, which indicates that there is a relatively quantitative relationship between the compressive strength and porosity of geopolymer samples prepared by warm pressing and conventional curing. In previous papers, σ_0 of OPC (Ordinary Portland Cement) mortar with and without mineral additives was estimated to range from 83.5 to 490.7[16]. Thus, the intrinsic compressive strength of the geopolymers is clearly higher than that of OPC materials.

3.5 Neutron absorption

Geopolymers are candidate encapsulation and immobilization materials for containing nuclear waste or radioactive elements, because geopolymers have a high

thermal resistance and a high chemical corrosion resistance[2,10,11]. Furthermore, geopolymers contain hydroxyl ions (OH^-), particularly protons (H^+) which can trap neutrons, potentially resulting in a high neutron absorption capability. OPC is a candidate encapsulation material for nuclear waste, because a calcium silicate hydrate (CSH)-hardened body contains many water molecules, and hence many protons.

Therefore, in this study, neutron absorption in a conventional OPC mortar sample and in dense geopolymer samples fabricated by warm pressing and by conventional curing was evaluated. **Figure 7** shows the neutron absorption ratio versus unit thickness and the water content per unit volume of the OPC and geopolymer samples. For reference, the results for a concrete sample produced 30 years ago were included in the figure. A material can be considered better if its absorption ratio is higher, because neutron transmission can be suppressed. Fresh cement had the highest absorption ratio, because many water molecules were contained within the hardened body. In contrast, as shown in the reference result, the neutron absorption ratio for aged concrete was the lowest. Generally, a dehydration reaction continues over time in cement and concrete materials, so the aged concrete contained very little water, as shown in Fig. 7.

Furthermore, the geopolymer samples fabricated by conventional curing had a lower neutron absorption ratio because geopolymerization is a dehydration reaction[2], so these samples contained less water than the fresh cement mortar, as shown in Fig. 7.

However, the highly dense geopolymer samples fabricated by warm pressing had a neutron absorption ratio comparable to that of the cement mortar. Thus, densification of the geopolymer increased its neutron absorption capability. In addition, the water contents of a 2-year-old cement and 2-year-old geopolymer fabricated by warm pressing were investigated and estimated to be 0.219 and 0.245 g/cm^3 , respectively, on the basis

of weight loss upon heating at 500°C. While the water content of 2-year-old cement decreased compared to that of fresh cement, the water content of the 2-year-old warm-pressed geopolymer did not decrease relative to that of the fresh warm-pressed geopolymer (see Fig. 7). Furthermore, the molecular structure of the geopolymer is similar to that of a zeolite, although it is thought to be amorphous[2]. Therefore, water molecules can remain for a long time inside the geopolymer body. Thus, geopolymers are good candidate materials for the encapsulation and immobilization of nuclear wastes.

4. Summary

Warm pressing enabled the fabrication of dense geopolymers. Furthermore, geopolymers with a high mechanical strength could be fabricated in several hours. First, a mixture consisting of 100 g of fly ash, 28 g of 10 mol/L sodium hydroxide solution, and 50 g of sodium water glass was heated at 130°C for 2 h. Subsequently, the dried samples were ground to particle sizes finer than 500 µm and placed in a steel mold within a warm press machine. While the samples were pressed, the press was heated to 130°C for 0-60 min. The maximum strength and relative density of the resultant geopolymers were 149 MPa and 71%, respectively, after warm pressing for 60 min. Finally, the dense geopolymer had an excellent neutron absorption capability, comparable to that of a fresh OPC mortar sample.

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Figure and table captions

Figure 1 Compressive strength of geopolymer samples heated to different temperatures for 30 min at 200 MPa.

Figure 2 Compressive strength and bulk density of geopolymer samples pressed for different lengths of time at 130°C and 200 MPa.

Figure 3 ^{27}Al and ^{29}Si MAS NMR spectra for samples before and after warm pressing. A conventionally cured sample is included for reference.

Figure 4 Pore distribution in a conventionally cured geopolymer and a warm-pressed geopolymer formed at 130°C and 200 MPa for 60 min.

Figure 5 Illustration of the bonding mechanism for geopolymer particles during warm pressing.

Figure 6 Compressive strength of geopolymer samples fabricated by warm pressing for various lengths of time and by conventional curing.

Figure 7 Neutron absorption ratio versus unit thickness for OPC samples, both fresh and 30 years old, and that of geopolymer samples formed by warm pressing and conventional curing treatment. The water content per unit volume of each sample was also indicated.

Table 1 Chemical composition of as-received coal fly ash (mass%)

Figure 1

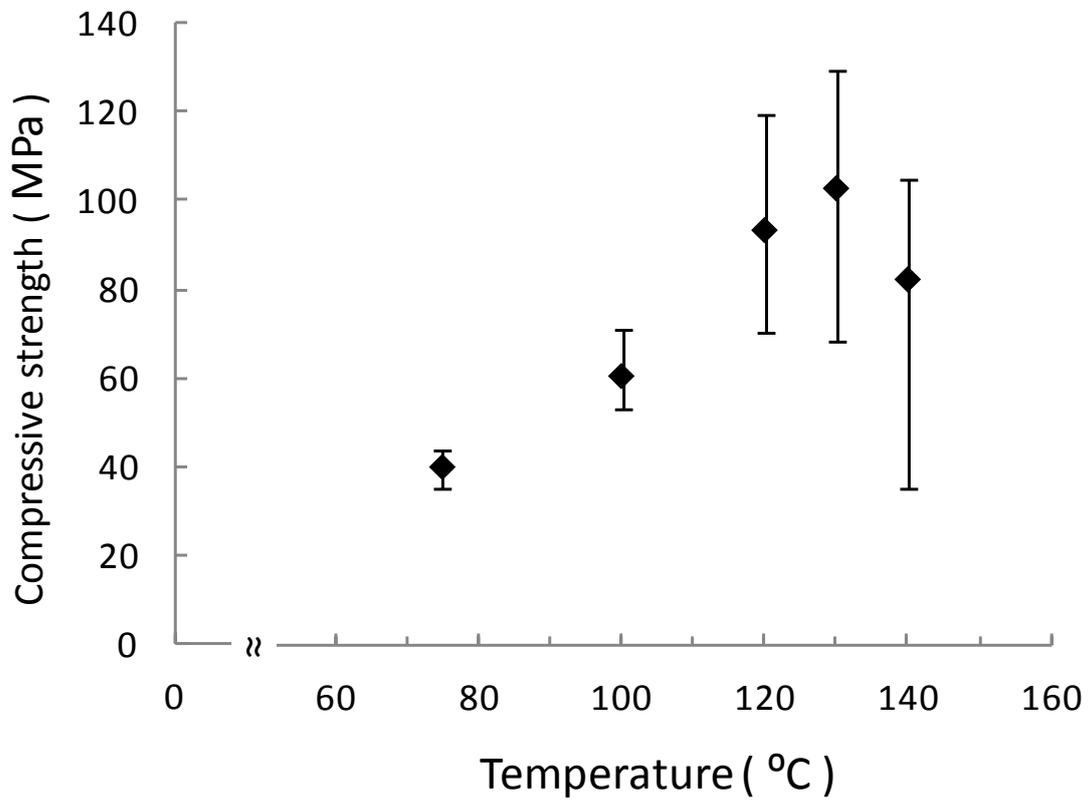


Figure 2

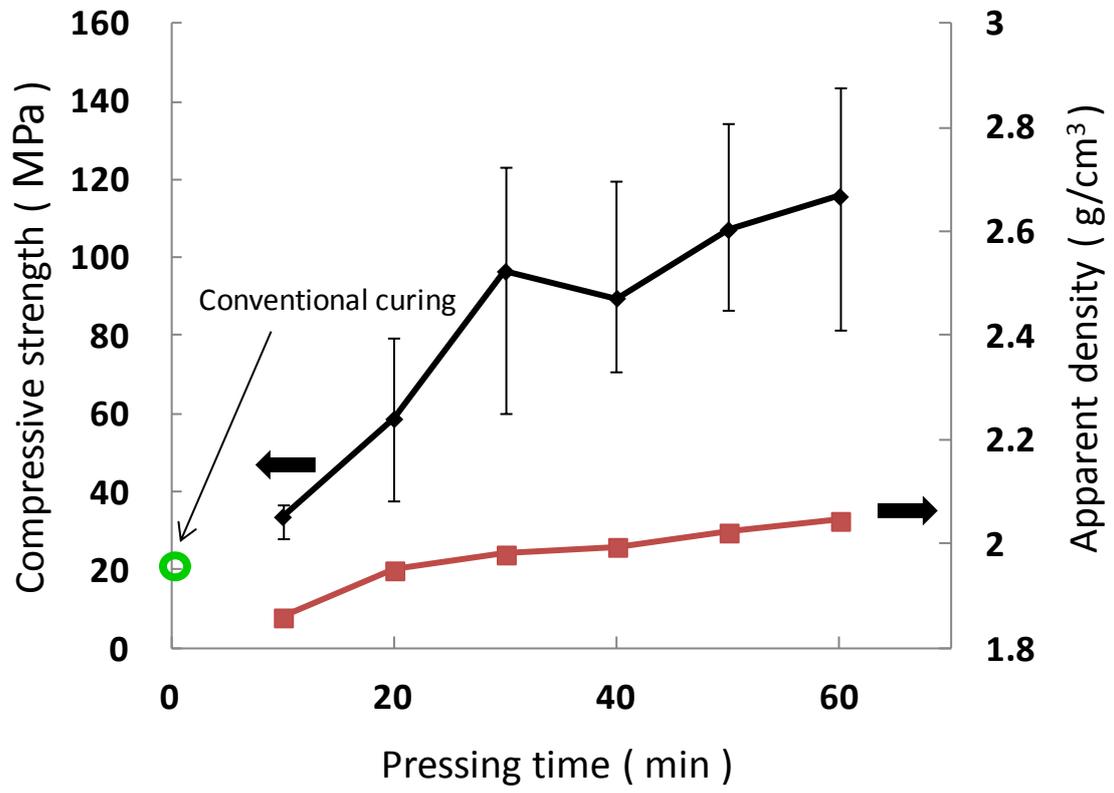


Figure 3

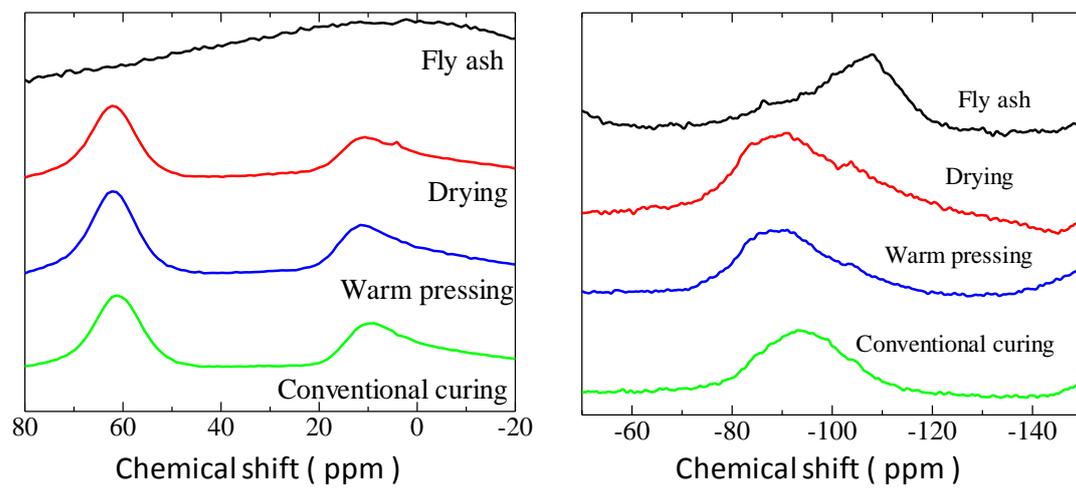


Figure 4

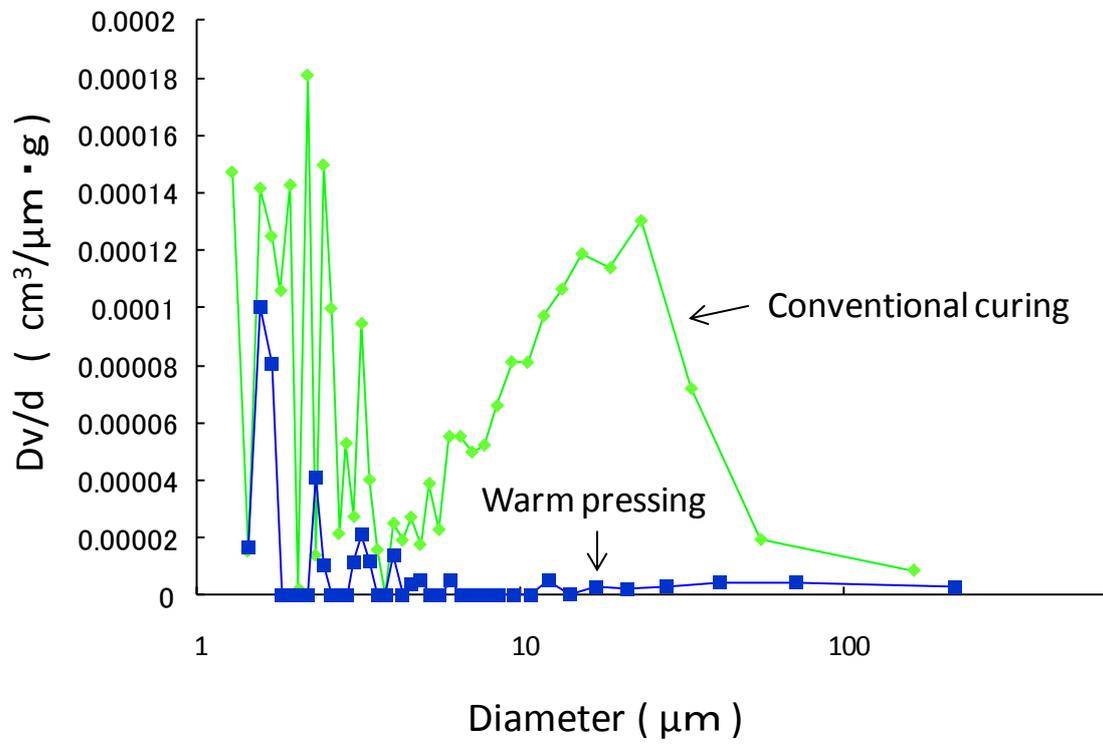


Figure 5

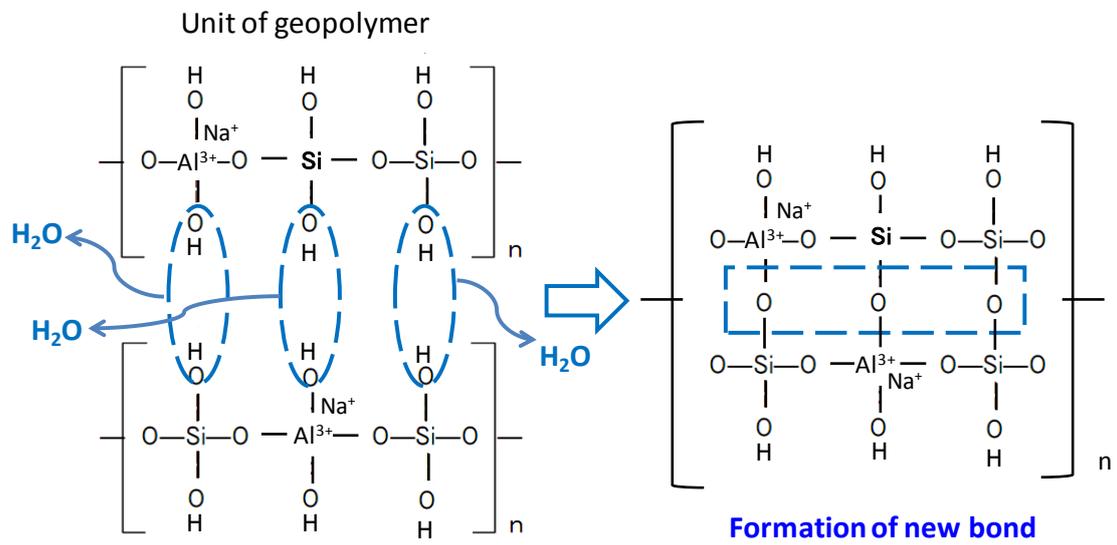


Figure 6

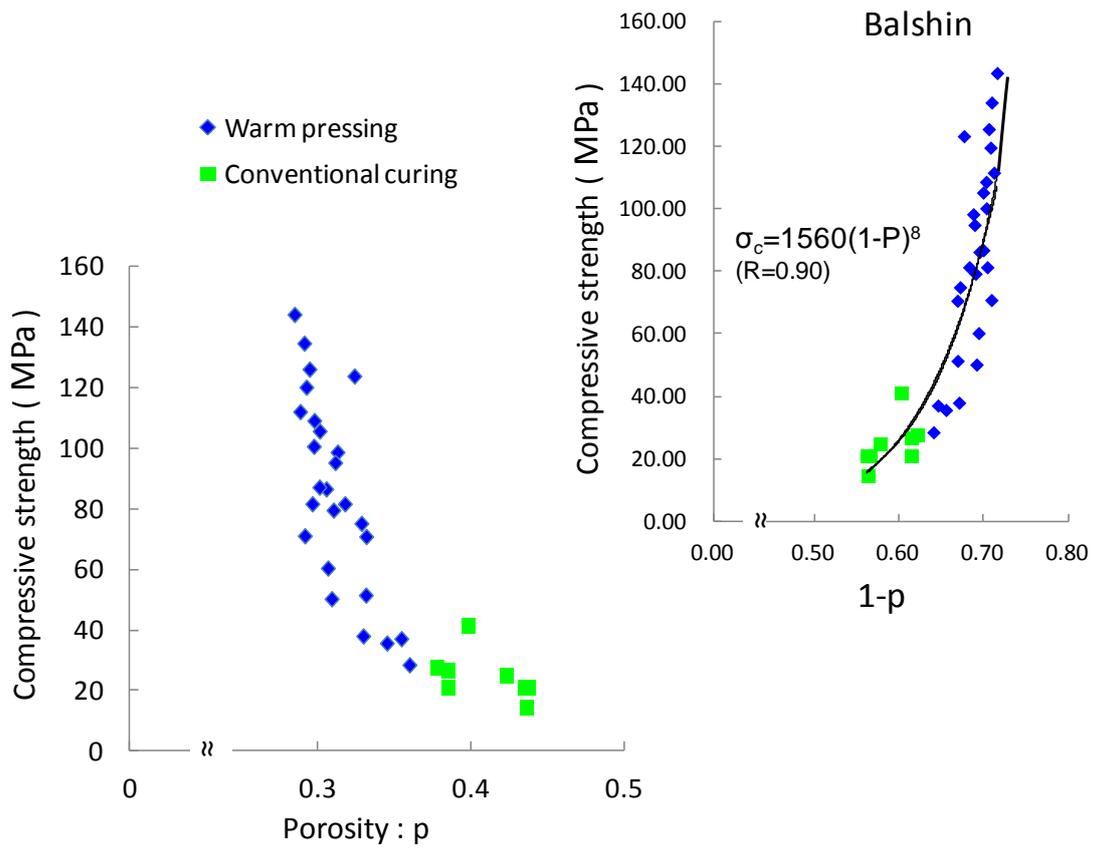


Figure 7

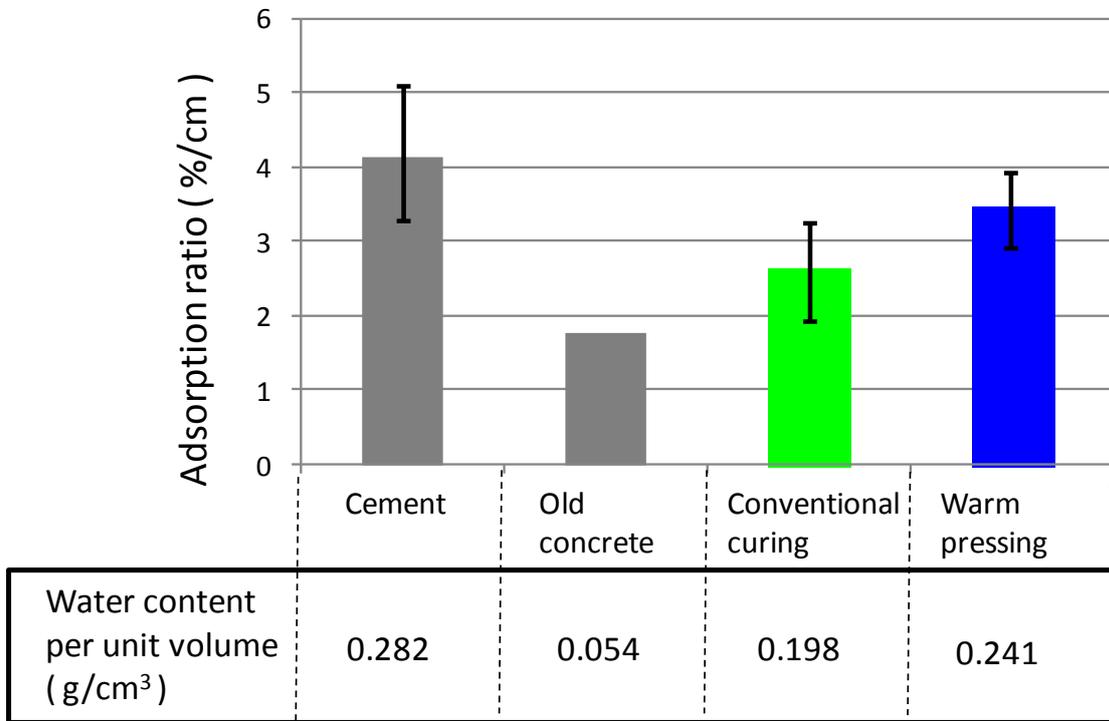


Table 1

Composition	Mass%
SiO ₂	56.2
Al ₂ O ₃	25.7
Fe ₂ O ₃	7.9
CaO	3.2
TiO ₂	2.9
P ₂ O ₅	2.2
K ₂ O	1.6
Total	99.7