Effect of Curing Conditions on Strength Development of Geopolymer Mortar Using Fly Ash and Ground Granulated Blast Furnace Slag

Yosaku Ikeo*

Summary

Geopolymers have attracted attention as one of the innovative materials, because geopolymers are low CO_2 emissions compared with conventional cement. This paper describes the results of an experimental work conducted to investigate the effect of curing conditions on strength of geopolymer mortar using fly ash and ground-granulated blast furnace slag. Compressive strength development was found to be greatly influenced by the curing conditions. Drying ambient conditions significantly reduced the strength potential of geopolymer mortar. Furthermore, the curing conditions and microstructures and compressive strength of geopolymers were related to each other. These results demonstrate that temperature of curing and moisture curing duration are very important to increase strength of geopolymers.

Keywords: geopolymer, fly ash, ground granulated blast furnace slag, curing, compressive strength, microstructure

1. Introduction

The production of Ordinary Portland cement (OPC) not only consumes significant amount of natural resources and energy but also emits substantial quantity of CO_2. To reduce the use of OPC, the use of supplementary materials to partially replace OPC and alternative cementing materials should be developed. In recent years, the construction industry has taken interest in geopolymers as an alternative to OPC. Geopolymers are inorganic polymeric, ceramic-like materials formed through the reaction between aluminum silicate powder and alkaline silicate solution. Byproducts such as fly ash and ground-granulated blast furnace slag (GGBFS) are used as aluminum silicate powder. Consequently, geopolymers have gained considerable interest as a material that can aid in the suppression of CO_2 emissions and effective utilization of byproducts.

The reaction mechanism of geopolymers is generally considered to be a structural polycondensation, as shown in Figure 1. It is believed that the aluminum (Al) and silicon (Si) contained in aluminum silicate powder such as fly ash are dissolved and ionized in the alkaline silicate solution. This metal ion (M^{m+}) further reacts with the solution components to polymerize [1]. Thus this reaction varies substantially in its reaction with cement. Accordingly, much of the relationship between materials, strength, and durability is still unclear. There are relevant studies, which include studies on the effects of aluminum silicate powder and alkaline silicate solution types on compressive strength [2, 3], set retarders [4], and acid resistance [5]. Studies have reported increased strength in geopolymers containing a large volume of fly ash when cured under high temperatures [6]. Contrarily, few studies show the effects of drying and humidity during the curing process on compressive strength.

Thus, this study focuses on the compressive strength of geopolymers cured under different environments, including a dry environment. The compressive strength of geopolymer mortars prepared with fly ash and GGBFS was evaluated. In addition, the relationship between strength and microstructure was investigated.

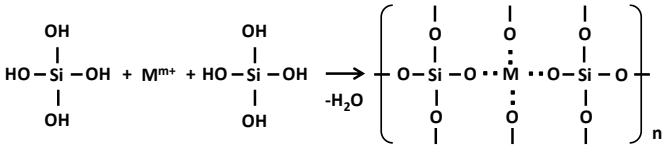


Fig.1 Reaction mechanism of geopolymers

＊1 Chief Researcher, Research & Development Institute

2. Experimental Method

2.1 Preparation of materials and mortar

Table 1 shows the main physical properties of the materials used in the experiment. Fly ash (FA) and ground-granulated blast furnace slag (GGBFS) were used as powder. JIS standard sand (S) was used as fine aggregate. Sodium silicate solution (WG) and 10 mol/l sodium hydroxide solution (NH) were used as an alkaline solution.

Table 2 shows the mix proportions of geopolymer mortars. The ratio of fly ash to GGBFS was two types. FA50 and FA75 are mixtures with 50% and 75% fly ash content in the powder respectively. The alkaline solution (AS) consisted of sodium silicate solution (WG), 10 mol/l sodium hydroxide solution (NH), and tap water (W). The solution/powder ratio (AS/P), which is the mass ratio of the alkaline solution (AS) and the powder (P), was set to 0.6. The amount of fine aggregate to paste was adjusted to a volume ratio of 60%.

Table 1 Physical properties of materials

Type	Material used	Main physical propeties
Powder (P)	Fly ash (FA)	Density: 2.28g/cm^3 Blaine fineness: 3670cm^2/g
	Ground-granulated blast furnace slag (GGBFS)	Density: 2.91g/cm^3 Blaine fineness: 4320cm^2/g
Sand (S)	Standard sand (S)	Oven-dry density: 2.64g/cm^3
Alkaline solution (AS)	Sodium silicate solution (WG)	Density: 1.50g/cm^3
	10mol/l sodium hydroxide solution (NH)	Density: 1.33g/cm^3
	Tap water (W)	-

Table 2 Mix proportions of geopolymer mortars

Mixes	AS/P	kg/m^3					
		FA	GGBFS	S	WG	NH	W
FA50	0.60	378	378	990	355	23	76
FA75	0.60	551	184	990	262	132	46

2.2 Mixing and curing method of mortar

The materials were placed in a mortar mixer and mixed for 3 min. The cylindrical test specimens (ϕ50 × 100 mm) were then prepared for the compressive strength test.

Table 3 presents the curing conditions. Specimens were cured under sealed at 20 ℃ for 3 days, and then under the five conditions: sealed curing (S) at 20 ℃, underwater curing (W) at 20 ℃, steam curing (ST) at 65 ℃, air curing (A) at 20 ℃ and 60% relative humidity (R.H.), and dry curing (D) at 65 ℃. Steam curing condition was warming rate of 15 ℃/h, maximum temperature of 65 ℃, maintained curing period of 12 h, and cooling rate of 15 ℃/h. After steam curing, the specimens were stored in a 20 ℃ and 60% R.H. environment until it reached the age to undergo the compressive strength test. An oven was used to perform dry curing at 65 ℃.

Table3 Curing conditions

Code	Pre-curing	Curing conditions
S	Sealed curing at 20℃ for 3days	Sealed curing at 20℃
W		Underwater curing at 20℃
ST		Steam curing for 12 hours at 65℃ → Air curing at 20℃ and 60% R.H.
A		Air curing at 20℃ and 60% R.H.
D		Dry curing at 65℃

2.3 Test items

(1) Flow test

The mortar flow was measured immediately after mixing the mortar in accordance with JIS R 5201: Physical testing methods for cement (global).

(2) Compressive strength test

Performed in accordance with JIS A 1108: Method of test for compressive strength of concrete. The testing material age was set to 3 days, 1 week, 4 weeks, 13 weeks, and 26 weeks for sealed curing; and 1 week, 4 weeks, 13 weeks, and 26 weeks for other curing methods.

(3) Analysis of pore size distribution

After the compressive strength test, the mortar was crushed to 2.5–5.0 mm. The reaction was stopped by soaking them in acetone, and D-drying was performed. The pore size distribution was then analyzed by mercury porosimetry. The target material age for testing was set to 3 days, 1 week and 4 weeks for sealed curing; and set to 4 weeks for other curing methods.

(4) X-ray diffraction measurement

After the compressive strength test, the mortar was crushed to 2.5–5.0 mm, and the reaction was stopped by soaking them in acetone. Subsequently, the mortar was further crushed and X-ray diffraction was measured. The target material age for testing was set to 4 weeks.

3. Experimental Results and Discussion

3.1 Mortar flow

Figure 2 shows the mortar flow. The FA75 mortar flow was larger than that of FA50. Prior studies [3), 6)] reported that mortar flow increased with higher ratios of fly ash and in solutions using sodium hydroxide. In this study, similar trends were seen for FA75, which has a high ratio of fly ash and high ratio of sodium hydroxide in the alkaline solution.

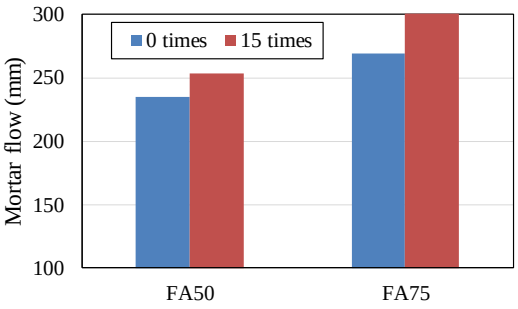
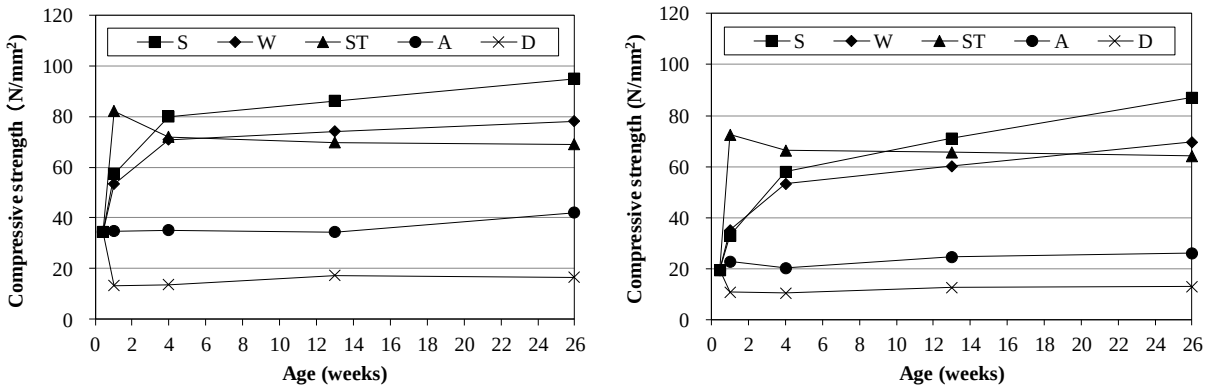


Fig.2 Mortar flow

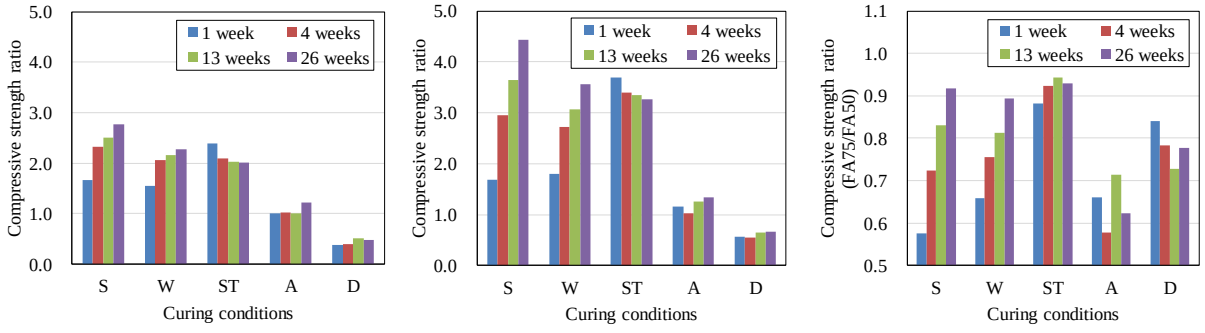
3.2 Compressive strength

Figure 3 shows compressive strength. The specimens were switched to curing under 5 differing conditions at an age of 3 days and cured in each curing method. In FA50, the strength after the initial three days of sealed curing was approximately 35 N/mm^2. Thereafter, the strength tended to increase with age for sealed (S) and underwater curing (W). With steam curing (ST), the strength exceeded 80 N/mm^2 post-curing after 1 week but decreased slightly after 4 weeks. When cured in air (A) at 20 °C and 60% R.H., there was almost no increase in strength. When dried (D) at 65 °C, the strength decreased at an age of 1 week and



(a) FA50 (b) FA75

Fig.3 Effect of curing time on compressive strength



(a) FA50 (b) FA75 (c) FA75/FA50

Fig.4 Compressive strength ratio

stayed at the same level thereafter. In FA75, the strength after the initial three days of sealed curing was approximately 20 N/mm^2, lower than that in FA50. Subsequent changes in strength by the curing method showed similar trends as FA50. However, a difference was seen at 4 weeks where sealed curing produced the highest strength in FA50 and steam curing produced higher strength in FA75. This was likely caused by the high ratio of fly ash in FA75, causing slower development of compressive strength at room temperature. Sealed curing produced the highest strength at 26 weeks in both FA50 and FA75, followed by underwater curing and steam curing. Underwater curing produced lower strength than sealed curing. This was probably due to some reaction components eluted into the curing water during this period. In addition, FA50 had higher strength than FA75 under all curing conditions. Studies have shown that higher GGBFS ratios produce higher strength [3]. Thus the differences in the ratio of fly ash to GGBFS contributed to the stronger compressive strength of FA50. Sealed curing and underwater curing (methods that retain moisture) caused the strength to significantly increase with age across both mixtures, while air curing at 20 ℃ and 60% R.H. or dry curing at 65 ℃ (methods that do not retain moisture) did not produce increased strength, but rather, caused it to decrease in some cases. The decreased strength in steam cured mortar after 4 weeks was affected by post-cure storage in a dry environment at 20 ℃ and 60% R.H.

Figures 4 (a) and (b) show the compressive strength ratio at each age when the strength at Day 3 is assumed to be 1. Figure 4 (c) shows the compressive strength ratio of FA75 to FA50. As described previously, Figures 4 (a) and (b) indicate that, in sealed curing (S) and underwater curing (W), the compressive strength increased with age in both FA50 and FA75, whereas, in steam curing (ST), the compressive strength decreased slightly with age after week 1. In air curing (A), there was an insignificant increase in strength after 3 days, and in dry curing (D), there was a slight change after an initial decline in strength at week 1. In addition, for sealed curing (S) and underwater curing (W), the compressive strength ratio was larger in FA75 than FA50 at each age, indicating large increases in strength for FA75 after 3 days of age. The compressive strength ratio increased with age for sealed curing (S) and underwater curing (W) in Figure 4 (c), and there was a sharper rise in the compressive strength over time for FA75 than FA50. The composition of the alkaline solution differed between FA50 and FA75. Since the level of sodium hydroxide was higher in the FA75 solution, the alkaline solution caused greater elution of reactive components in the powder, such as CaO and Al_2O_3. Therefore, the recombination of eluted components probably resulted in an increased long-term strength, despite the large proportion of fly ash, which has low reactivity.

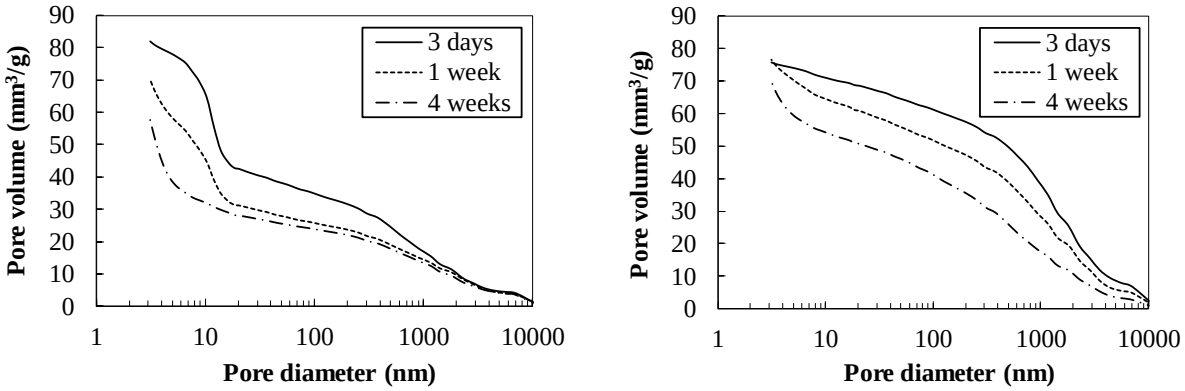
3.3 Pore size distribution

Figure 5 shows the relationship between curing time (for sealed curing) and pore size distribution. The difference in mixture ratio produced differences in pore size distribution. FA75 tended to have more pores of large size than FA50 at all ages. Conversely, pore size distribution changed with age regardless of the mixture type, indicating a decreasing trend in total pore volume, especially the larger size. This trend is similar to hardened cement [7], indicating that sealed curing increases the compressive strength of geopolymers as the microstructure densifies with age.

Figure 6 displays the relationship between curing condition and pore size distribution. In all cases, the total pore volume, particularly those with larger diameters, was largest when dried (D) at 65 ℃. Air curing (A) at 20 ℃ and 60% R.H. produced the second-largest volume of large pores. Sealed curing (S), underwater curing (W), and steam curing (ST) had fewer large pores compared to dry curing (D) at 65 ℃ and air curing (A) at 20 ℃ and 60% R.H., indicating a tendency for these curing methods to produce a denser structure. Studies show that the pore size distribution becomes coarse in hardened cement when dried at high temperatures [8], thus the properties of geopolymers are similar. When the pore size distribution in Figure 5 after three days of sealed curing and Figure 6 after four weeks of curing under various conditions is compared, large pores and overall pore volume decreased after 4 weeks of sealed curing, underwater curing, and steam curing. In contrast, large pores increased after dry curing at 65 ℃, and the total pore volume increased in FA75. This is considered to be a reason for the decrease in compressive strength after dry curing at 65 ℃.

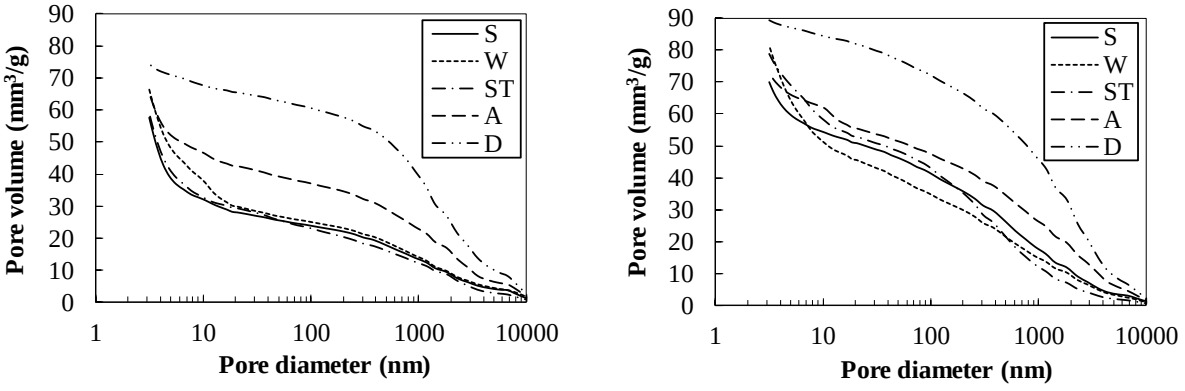
A coarsening of pore size distribution and lower compressive strength were observed when dried at 20 ℃ and 60% R.H. or 65 ℃. Thus, the relationship between pore volume and strength was examined. The pore size distribution in sealed curing shown in Figure 5 indicates decreasing pore volumes with age due to the densification of microstructure. As the pore size distribution varied considerably between FA50 and FA75, there may also be a difference in the pore size range that impacts compressive strength. Figure 7 shows the decrease in pore volume between 3 days to 4 weeks of sealed curing, categorized into five pore diameter ranges. The decrease in pore volume caused the strength to increase, however, this tendency varied between FA50 and

FA75. In FA50, the pore volume tended to decrease with a wider pore size range, with the largest decrease observed at a pore size of 10–10000 nm. Contrarily, in FA75, the decrease in pore volume was largest at a pore size of 500–10000 nm, revealing a tendency for wider ranges to ease the decline in pore volume. This suggests that pores of 10–10000 nm in FA50 and 500–10000 nm in FA75 substantially contribute to compressive strength. Therefore, the pore volume in the range of 10-10000 nm for FA50 and 500-10000 nm for FA75 was calculated from the pore size distribution in Fig. 6 with observed differences by curing condition. Figure 8 shows the relationship between pore volume and compressive strength after four weeks of curing under each condition. In both FA50 and FA75, compressive strength tends to decrease with increased pore volume. This suggests that the formulation changes the impact of pore diameter range on compressive strength and that the pore size distribution is strongly related to the compressive strength.



(a) FA50 (b) FA75

Fig.5 Relationship between curing time and pore size distribution (Sealed curing at 20℃)



(a) FA50 (b) FA75

Fig.6 Relationship between curing condition and pore size distribution (Age:4weeks)

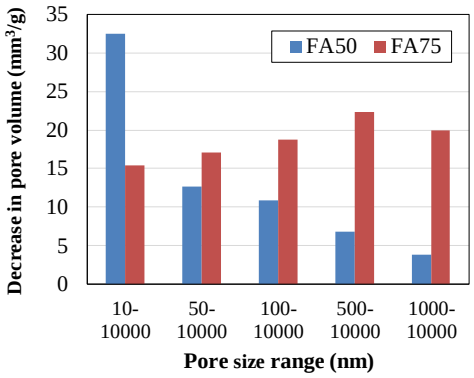


Fig.7 Relationship between pore size range and change of pore volume (Sealed curing at 20℃)

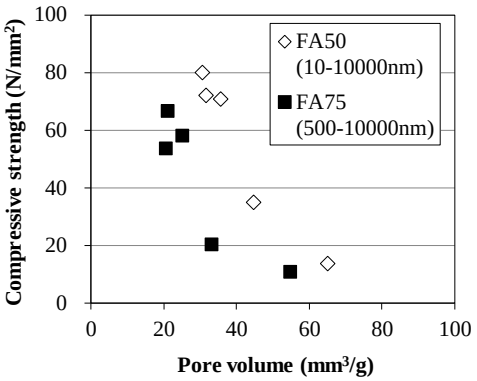
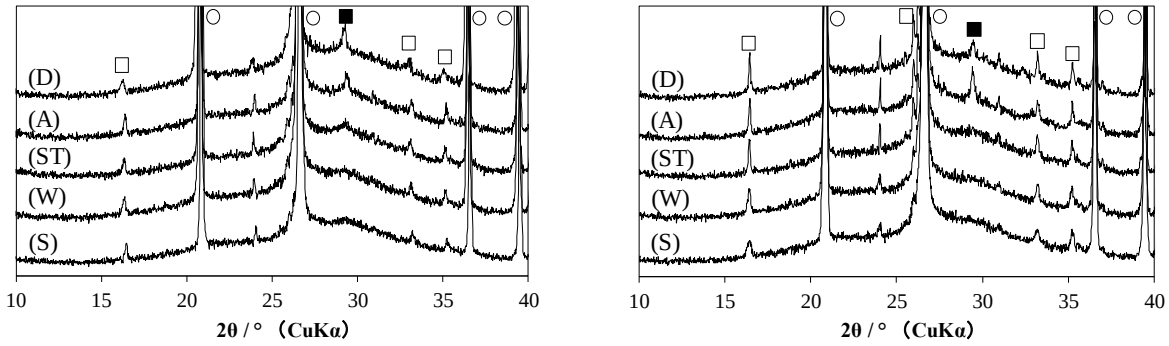


Fig.8 Relationship between pore volume and compressive strength

3.4 X-ray diffraction

Figure 9 shows the measurements of X-ray diffraction. Quartz, mullite, and calcite were recognized as crystalline substances. Quartz is derived from the fly ash and standard sand that were used as raw materials, whereas mullite is a mineral derived from fly ash. The halo around 20° to 30° was derived from amorphous minerals contained in the fly ash and GGBFS. In this experiment, no significant differences were observed due to the different formulations, and no distinct crystalline reaction products other than calcite were identified. Calcite was found in all mixtures during air curing (A) and dry curing (D). Calcite was not observed when cured in the absence of air, such as in sealed curing (S) and underwater curing (W). This indicated that the formation of calcite occurred through the carbonation of calcium-based reaction products during the curing period. Consequently, the reaction products of the geopolymers in this experiment are considered either amorphous or substances with low crystallinity.



(a) FA50 (b) FA75

○ : quartz, □ : mullite, ■ : calcite

Fig.9 X-ray diffraction patterns of mortar

4. Conclusion

In this study, the effect of curing conditions (including the drying environment) on compressive strength of geopolymers was examined. The compressive strength of geopolymer mortar prepared with fly ash and GGBFS and the relationship between strength and microstructure were investigated. Based on the experimental results, the following major conclusions can be drawn.

1) The strength of the geopolymer mortar varied considerably based on curing conditions. The mortar strength increased with age after sealed and underwater curing. Although mortar strength significantly increased immediately after steam curing, the strength could no longer increase with age.
2) The mortar strength did not increase with age after air curing at 20 ℃ and 60% R.H., and the strength decreased after dry curing at 65 ℃. This shows that drying during the curing process has a significant impact on and causes a decline in the development of the compressive strength.
3) There is a close relationship between curing conditions and the pore size distribution of the geopolymers, suggesting the impact of pore size distribution on compressive strength.
4) Most of the crystalline materials in the geopolymer mortar were minerals derived from raw materials. The only crystalline material derived from the reaction product was calcite, thought to be formed through carbonation. Therefore, the reaction products of the geopolymers used in this experiment are amorphous or substances with low crystallinity.

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