Effect of NaOH activation on ettringite in concrete containing ground granulated blast furnace slag

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ABSTRACT

This paper reports the stability of ettringite in concrete containing ground granulated blast furnace slag (GGBFS). X-ray diffraction (XRD) was carried out to identify ettringite in GGBFS pastes mixed with de-ionized water, GGBFS pastes activated by NaOH solution, pastes of binary blends and activated binary blends containing GGBFS and Ordinary Portland Cement (OPC) at different proportions. Using the computer program Rietica, this paper further presents quantification of the relative crystalline proportion of ettringite formed in different pastes. XRD revealed that ettringite was formed in GGBFS pastes and binary blends pastes mixed with de-ionised water. However, it disappeared in all pastes activated by NaOH solution. The results further demonstrated that ettringite made up a significant proportion of the crystalline phases formed in pastes mixed with de-ionised water. This paper concludes that the high pH of the pore solution in activated GGBFS and binary blend pastes causes the ettringite to decompose.

Key Words: Alkalis; NaOH; Geopolymer; Activators; GGBFS

1. INTRODUCTION

Gypsum reacts with aluminates after mixing to form ettringite. This early ettringite forms homogeneously throughout the mix and thus its formation does not provide any significant adverse effects on concrete properties. However, delayed ettringite formation causes deterioration in concrete subjected to external or internal sulphate attack condition. When concrete suffers sulphate attack, freeze and thaw action or alkali silica reaction, ettringite may crystallise in microcracks and thus causes expansion and further cracking of the concrete (Baweja and Roper et al. 1997; Collepardi 2003). If concrete is cured at elevated temperature, ettringite decomposes (Lewis and Scrivener et al. 1995; Diamond 1996; Yang and Lawrence et al. 1999). Heat curing also results in holding the sulphate and alumina tightly in the calcium silicate hydrate gel and thus retards early ettringite formation(Brown and Bothe 1993). However, after several months or years when such concrete experiences the presence of water or sulphate, delayed ettringite starts to form heterogeneously which leads to the formation of non-uniform localised expansion in hardened concrete. Concrete

suffering delayed ettringite formation undergoes loss in mechanical properties and in extreme cases the concrete become crumbly and soft (Diamond 1996; Collepardi 2003).

Ground granulated blast furnace slag (GGBFS) has been extensively used as a cementitous material and it is also well known to possess sulphate resisting property (Higgins 2003; Song and Saraswathy 2006) . Many theories have been proposed regarding the reason why GGBFS concrete is effective in resisting sulphate attack (Ogawa and Hyodo et al. 2008; Rozière and Loukili et al. 2009). With the introduction of geopolymer concrete, several pozzolans, among which is GGBFS, have been proposed and researched as the base material forming activated binders. A very common alkali activator has been NaOH. The reported research into the effects of alkalis and in particular NaOH on Portland cement has shown that NaOH causes the disappearance of early formed ettringite in Portland cement concrete (Way and Shayan 1989). This disappearance is considered a deleterious occurrence as far as sulphate attack is concerned (Stark and Bollmann 1999). In such situations, delayed ettringite forms later and provides a destructive process to the concrete. To the knowledge of the authors, no research has been reported on the possible interaction between the NaOH if used to activate GGBFS in geopolymer concrete, and early formed ettringite. This paper explores this relationship and further postulates on the reason why GGBFS provides a sulphate resisting as well as chloride resisting concrete.

2. MATERIALS AND TESTING

2.1 Materials

This study used GGBFS and OPC as cementitious materials. The chemical analysis and specific gravity values of GGBFS and OPC are shown in Table 1.

Table 1. Chemical and Physical Properties of GGBFS and OPC

Chemical and physical properties	Cement (wt.%)	GGBFS (wt.%)
SiO_2	21.10	31.14
Al_2O_3	5.20	13.10
Fe_2O_3	4.30	0.66
CaO	64.20	38.94
MgO	1.20	11.6
Na_2O, K_2O	0.05, 0.47	0.24, 0.25
SO_3	2.60	3.46
Loss of Ignition	0.80	0.02
Specific Gravity	3.13	2.89

2.2 X-ray Diffraction (XRD)

XRD was carried out to:

1. Identify ettringite in GGBFS pastes. For this purpose, GGBFS was mixed with de-ionised water (DW) and this mixture is referred to here as DW_GGBFS. GGBFS was activated by 4M NaOH to observe whether ettringite is still present in the activated paste and this mixture is designated as 4M_GGBFS.
Identify ettringite in binary blends containing GGBFS and OPC at different proportions. To do this, mixes were prepared containing 25%, 50% and 70% GGBFS by mass of cementitious material which are designated here as GGBFS_25, GGBFS_50 and GGBFS_70 respectively. Furthermore, three other mixes with the same composition were activated by 4M NaOH and are referred to here as 4M_GGBFS_25, 4M_GGBFS_50 and 4M_GGBFS_70 respectively.
2. Quantify the relative proportions of ettringite formed in different pastes. For this purpose, a computer program Rietica (Hunter 1998) that is based on Rietveld method (Rietveld 1969) was used.

All the aforementioned pastes were cast in plastic vials with sealing caps using a liquid to binder ratio of 0.35. The samples were demoulded after 24 hours before placing in a controlled environment room at 50% relative humidity and 23°C.

All the samples for XRD analysis were crushed to powder at the required ages. Samples were analysed using two X-ray diffractometers both of which used Cu-Kα radiation with wavelength of 0.15418 nm. One was a SIEMENS D501 Bragg-Brentano diffractometer hosted at the Australian National University which ran at 40 kV and 40 mA, scan range 6-65° and 0.02° 2θ step size with a speed of 1°/min. Samples were loaded in side-packed sample holders. The other diffractometer was a SIEMENS X-ray diffractometer which operated at 40 kV and 25 mA, scan range 5-65° and 0.1° 2θ step size with a speed of 1°/min. This diffractometer is hosted at the School of Physical, Environmental and Mathematical Sciences at the University of New South Wales, Canberra.

3. RESULTS AND DISCUSSION

3.1 The Stability of Ettringite in GGBFS Pastes

The XRD patterns of DW_GGBFS at different ages are shown in Figure 1. Ettringite was observed even after 6 hours of mixing and it gradually appeared with time at 9°, 15.5° and 23° as expected and reported in the literature (Myneni and Traina et al. 1998). The broad peak at 29.5° indicated the formation of poorly crystalline calcium silicate hydrate. Furthermore, hydrotalcite was observed at 11.5°, 22.9°, 34.7° and 60.6° while aluminium rich gehlenite appeared at around 31°.

It can be seen that calcium hydroxide was formed at 7 and 14 days only. It gradually disappeared due to its consumption by pozzolanic reaction to produce extra calcium silicate hydrate gel (Sidney Mindess and J. Francis Young et al. 2003). Moreover, magnesium hydroxide (brucite) and magnesium oxide (periclase) were observed at 38° and 43° respectively at 7 and 14 days only and both of the solids disappeared after 28 days. This might be due to the formation of additional hydrotalcite as both of these hydration products form hydrotalcite in the presence of alumina (Wang and Morales et al. 1999; Ahari and Sharp et al. 2002).

Figure 2 displays the XRD patterns of 4M_GGBFS at different ages. Ettringite was observed after 6 hours of mixing; however, it completely disappeared after 1 day. This is expected in the presence of NaOH activator as it causes ettringite to decompose and thus ettringite releases sulphate to the pore solution (Berger 1974; Brown and Shi 1991/1992; Brown and Bothe 1993).

GGBFS is however, known to provide sulphate resisting property. Higgins and Crammond (Higgins and Crammond 2003) studied the sulphate resistance property of concrete containing 70% (by mass) GGBFS. Their results demonstrated that GGBFS concrete subjected to strong sulphate solution showed no evidence of sulphate attack even after six years. Whether this property would persist in cases where GGBFS had been activated using NaOH solutions may, in view of above discussion, be debatable.

It has also been reported that hydrotalcite is produced in significant amounts during hydration of GGBFS activated by NaOH (Kayali and Khan et al. 2012). Hydrotalcite is an anionic clay and its inter-layer anions can be replaced with a wide range of anions due to its distinct anion exchange property (H. Y. Zhu and J. Orthman et al. 2001). In a recent publication, Kayali and Khan have reported that hydrotalcite plays a dominant role in the remarkable chloride binding ability of GGBFS concrete (Kayali and Khan et al. 2012). Their finding provides strong indication that it is the hydrotalcite which is the main responsible agent that results in the resistance of GGBFS concrete to chlorides. The authors therefore, postulate that hydrotalcite formation may be the reason for the improved sulphate resisting property of GGBFS concrete at it is capable of adsorbing sulphate ions from surroundings by using its anion exchange property (Esumi and Yamamoto 1998). This reflects the proposition that the sulphate in the pore solution resulting from the decomposition of ettringite is likely to be locked in hydration products especially in hydrotalcite and this sulphate is therefore, no more available in the pore solution to cause delayed ettringite formation, even in a strong sulphate environment. Furthermore, at relatively high pH, calcium silicate hydrate contains high amounts of sulphate and at the same time performs as a sink in which aluminates are accommodated (Brown and Bothe 1993; Taylor and Famy et al. 2001)
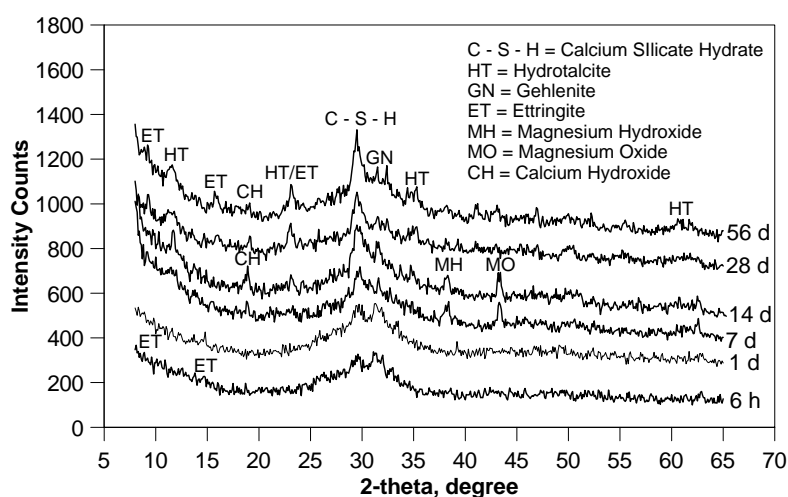

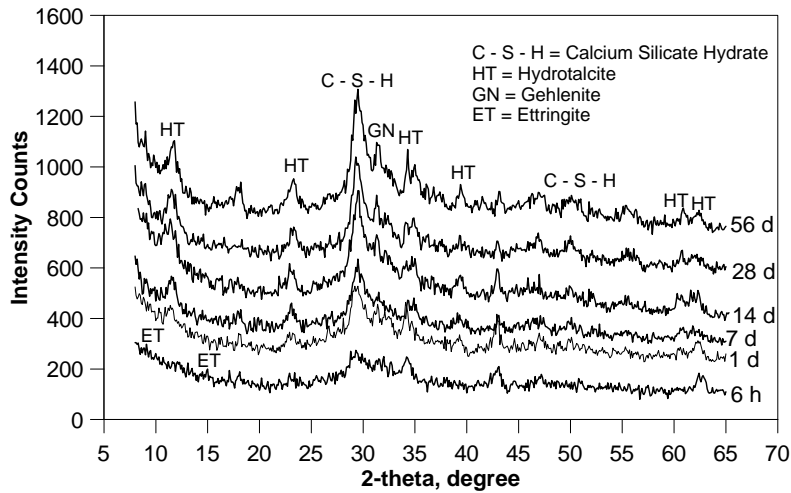Figure 1. XRD patterns of DW_GGBFS pastes

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Figure 2. XRD patterns of 4M_GGBFS

Moreover, similar to their occurrence in DW_GGBFS; hydrotalcite, calcium silicate hydrate and gehlenite were also observed here as shown in Figure 2. However, the intensity peaks for each of these three aforementioned hydration products in 4M_GGBFS were higher than those in DW_GGBFS. This is due to the fact that the addition of NaOH into the mix increases the pH of the pore solution which inhibits the formation of thin film around GGBFS particles and thus promotes the hydration reactions (Escalante-Garcı´a and Fuentes et al. 2003; Sidney Mindess and J. Francis Young et al. 2003).

3.2 The Stability of Ettringite in Binary Blend Pastes

Figures 3(a), 3(b) and 3(c) represent the XRD patterns of GGBFS_25, GGBFS_50 and GGBFS_70 respectively at different ages. Ettringite was detected at 9°, 15.5^{o} and 23° in all of the three Figures similar to its formation in plain GGBFS pastes. The formation of hydrotalcite was recorded at 11.5^{o} and 22.9^{o} at 56 days only for GGBFS_25 while it appeared at 11.5^{o} and 22.9^{o} from 14 days onwards for both GGBFS_50 and GGBFS_70.

Furthermore, calcium hydroxide was observed at 18.5^{o}, 34°, 48°, 51° and 63°. It is interesting to note that the intensity peaks of calcium hydroxide gradually decrease with the incremental increase of GGBFS in the binary blends. This is attributed to the consumption of calcium hydroxide by pozzolanic reaction. In addition, an increase in GGBFS proportion in the binary blend results in loss of OPC content which is largely contributing to form calcium hydroxide. Moreover, calcium silicate was observed at 30° and 33° and the peak at 29.5^{o} indicated the formation of calcium silicate hydrate as expected.
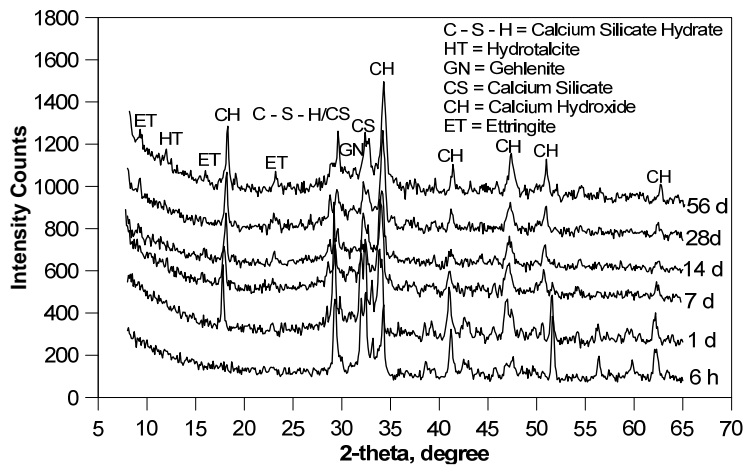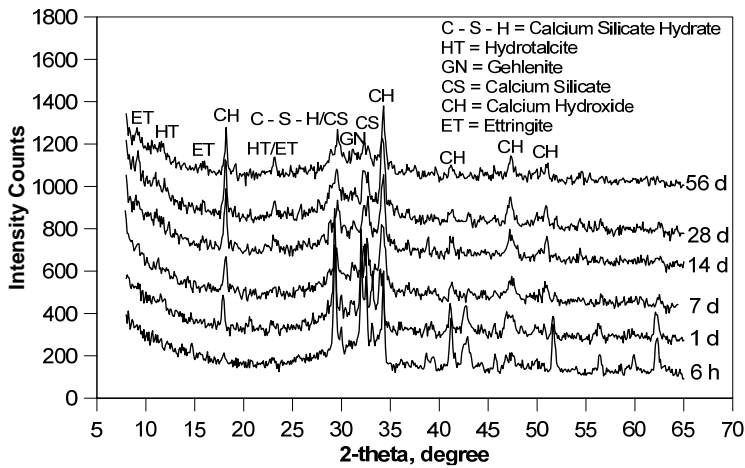
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Figure 3 (a). XRD patterns of GGBFS_25 pastes

Figure 3 (b). XRD patterns of GGBFS_50 pastes

Figures 4(a), 4(b) and 4(c) illustrate the XRD patterns of 4M_GGBFS_25, 4M_GGBFS_50 and 4M_GGBFS_70 respectively at different ages. The figure reveals that ettringite was present after 6 hours of mixing and it completely disappeared after 1 day similar to its occurrence in activated GGBFS pastes as shown in Figure 2.

Furthermore, similar to their occurrence in the binary blends, hydrotalcite, calcium hydroxide, calcium silicates, calcium silicate hydrate and gehlenite were observed. However, the intensity peaks of all of the aforementioned minerals in the activated binary blends were higher than those formed in binary blends mixed with de-ionised water. This is due to the accelerated hydration reactions caused by adding NaOH.
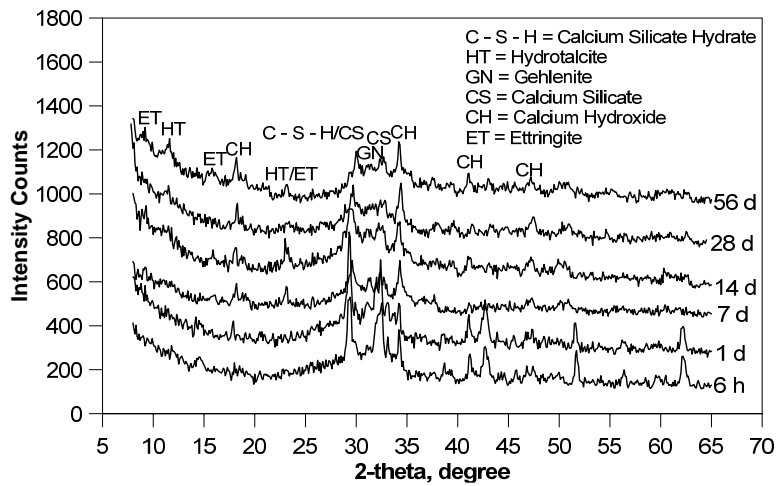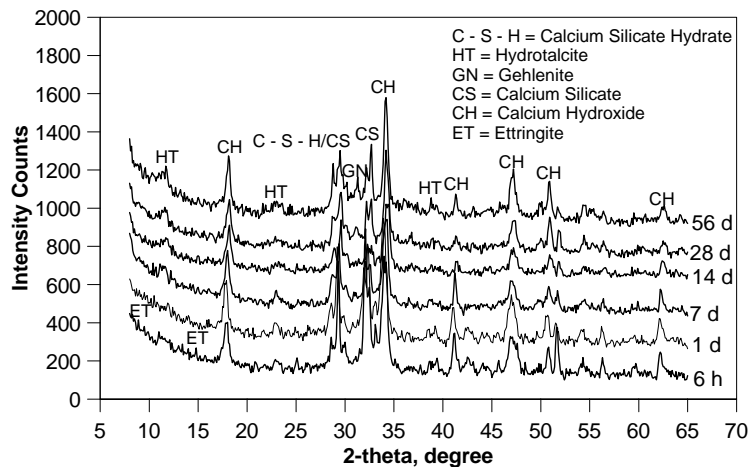
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Figure 3 (c). XRD patterns of GGBFS_70 pastes

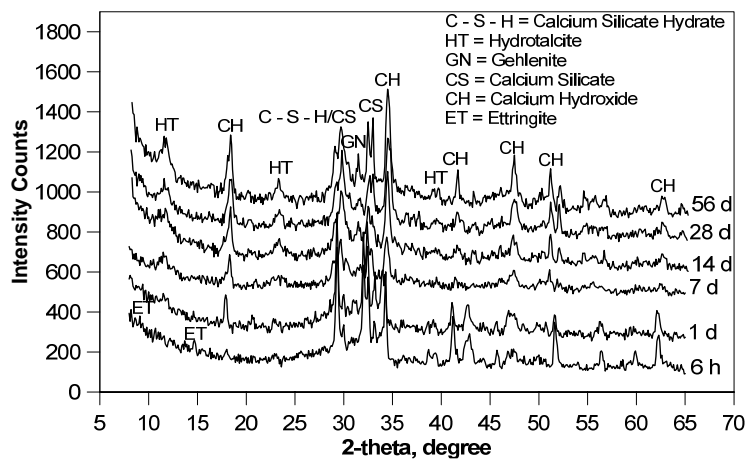Figure 4 (a). XRD patterns of 4M_GGBFS_25 pastes

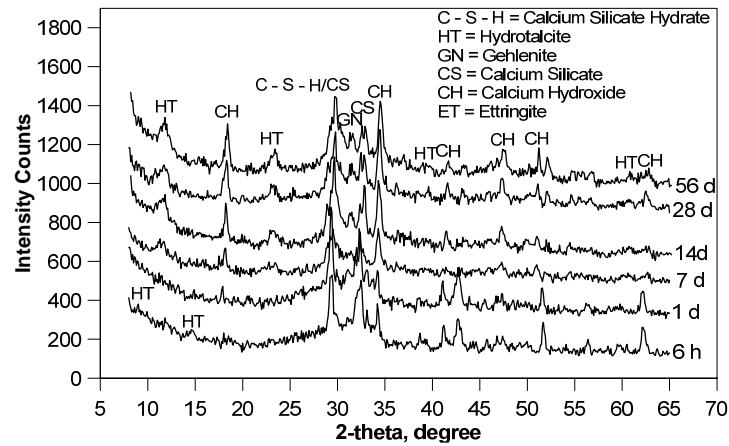Figure 4 (b). XRD patterns of 4M_GGBFS_50 pastes

Figure 4 (c). XRD patterns of 4M_GGBFS_70 pastes

3.3 Quantification of Ettringite

The relative crystalline proportions of ettringite in different pastes at 56 days are shown in Figure 5. The Figure reveals that ettringite comprises about one-third of the crystalline phases in DW_GGBFS.

Furthermore, all the three binary blends contain significant amounts of ettringite. However, ettringite disappeared in all pastes activated by NaOH. This reflects the high efficiency of NaOH solution to decompose ettringite.
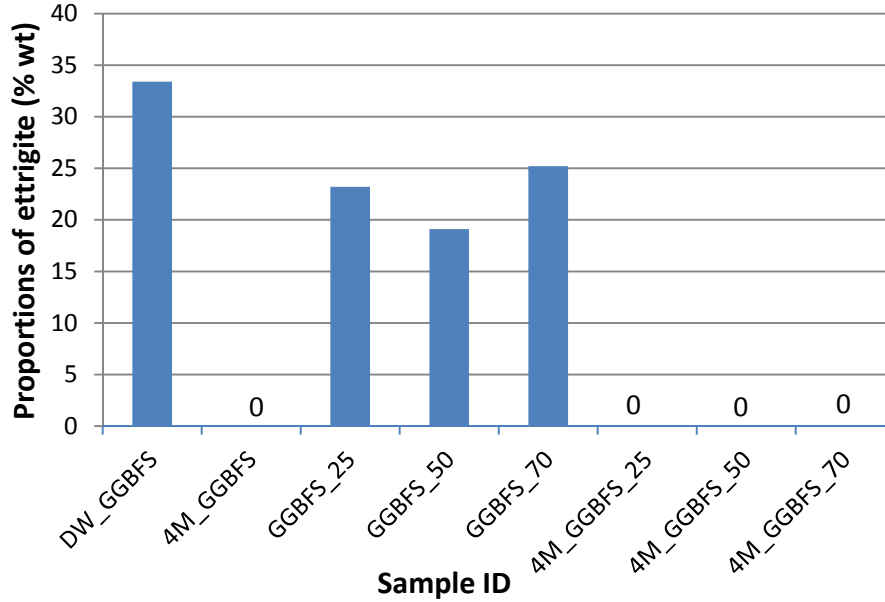

Figure 5. The relative crystalline proportions of ettringite at different pastes at 56 days

4. CONCLUSIONS

1. XRD analysis reveals that ettringite is formed in GGBFS pastes and binary blends pastes. However, it completely disappears when the pastes are activated by NaOH. The NaOH activator causes ettringite to decompose into the pore solution.

2. Quantification of the crystalline phases demonstrates that ettringite is formed in significant amounts in both GGBFS pastes and binary blends pastes. However, the high pH of the pore fluid in activated pastes causes ettringite to decompose into the pore solution.

3. The improved sulphate resisting property of GGBFS concrete may be attributed to the adsorption of sulphate from the pore solution by hydrotalcite due to its anion exchange property. Although this proposition appears to explain the observed sulphate resistance quite reasonably, the possibility of delayed ettringite formation in activated GGBFS concretes remains to be further investigated. The authors postulate that due to hydrotalcite formation in GGBFS, the sulphate ions are likely to remain adsorbed, and hence immobilised within the hydrotalcite layers. Further research into this postulation is highly recommended.

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