Working mechanism of viscosity-modifying admixtures

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20.1 Introduction

Viscosity-modifying admixtures (VMAs) are essential to control the stability and cohesion of concrete with very specific rheological requirements, such as self-compacting concrete, underwater concrete, or shotcrete. In self-compacting concrete, high amounts of fine powder materials such as fly ash, silica fume, or limestone have been normally used to prevent segregation and bleeding. However, these fine powders are not always locally available and/or might have a variable composition. For this reason, the use of VMAs has progressively increased in recent years to provide more robust mix designs. In addition, some VMAs, such as cellulose and guar gum derivatives, have water retention properties and they are mainly used in rendering mortars. They reduce the adsorption of water into a porous substrate, increasing cement hydration and mechanical strength of the mortar.

As explained in Chapter 9 (Gelardi et al., 2016), there is a high variability of VMAs. Inorganic VMAs such as colloidal silica are frequently used; however, in this chapter, we mainly focus on polymeric VMAs because they allow a greater deal of structural variations. Polymeric VMAs enhance the stability of the mix by increasing one or several rheological parameters at the same time, such as plastic viscosity, yield stress, shear thinning behavior, and thixotropy. Their mode of action depends on their physico-chemical properties, dosage, and the presence of other admixtures in the mix.

A comprehensive review of the effects of VMAs on the rheological properties of cementitious systems has recently been given elsewhere (Khayat and Mikanovic, 2012). Here, we will focus mainly on the working mechanism of these admixtures, their compatibility when they are used in the presence of superplasticizers, and their effect on the hydration of cement.

20.2 Performance of VMAs

20.2.1 Mechanisms of action of VMAs

VMAs increase the stability of cementitious systems due to a combination of different physico-chemical phenomena that depend on the nature of the VMA and its concentration (Khayat and Mikanovic, 2012). Polymeric VMAs are highly hydrophilic and have high capacity to bind water molecules, increasing their effective volume in

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solution. This leads to an increase of the dynamic viscosity of the interstitial solution and to an increase of the macroscopic viscosity of the cement suspension (Brumaud, 2011; Brumaud et al., 2013).

In addition, depending on the nature and concentration of the polymer, the following mechanisms can occur (see Figure 20.1):

- *Bridging flocculation* involves the adsorption of a chain of a high-molecular-weight polymer onto two or more cement particles, physically holding them together (Fellows and Doherty, 2005). This mechanism involves an increase of the yield stress of cement suspensions.
- *Polymer–polymer association.* Associative polymers contain segments distributed along the chain that have a tendency to interact with each other. As a consequence, intramolecular and intermolecular associations between the polymer chains can develop, producing a three-dimensional network and an increase of the viscosity of the interstitial solution (Chassenieux et al., 2011).
- *Entanglement.* At high concentrations, the chains of VMA polymers can entangle and increase the apparent viscosity of the interstitial solution and cement suspension (Khayat and Mikanovic, 2012).
- *Depletion flocculation* occurs because nonadsorbed polymers are depleted from a "volume exclusion shell" around larger particles. The difference of polymer concentration in bulk solution with respect to the depleted zone leads to an increase of the osmotic pressure in the system, which causes its flocculation. This mechanism does not modify plastic viscosity of suspensions, but it leads to an increase of the yield stress (Palacios et al., 2012).

20.2.2 Impact of VMAs on the rheology of cementitious systems

A common feature of all polymeric VMAs is that they increase the apparent viscosity of the aqueous solution, being higher the increase with the dosage of polymer.

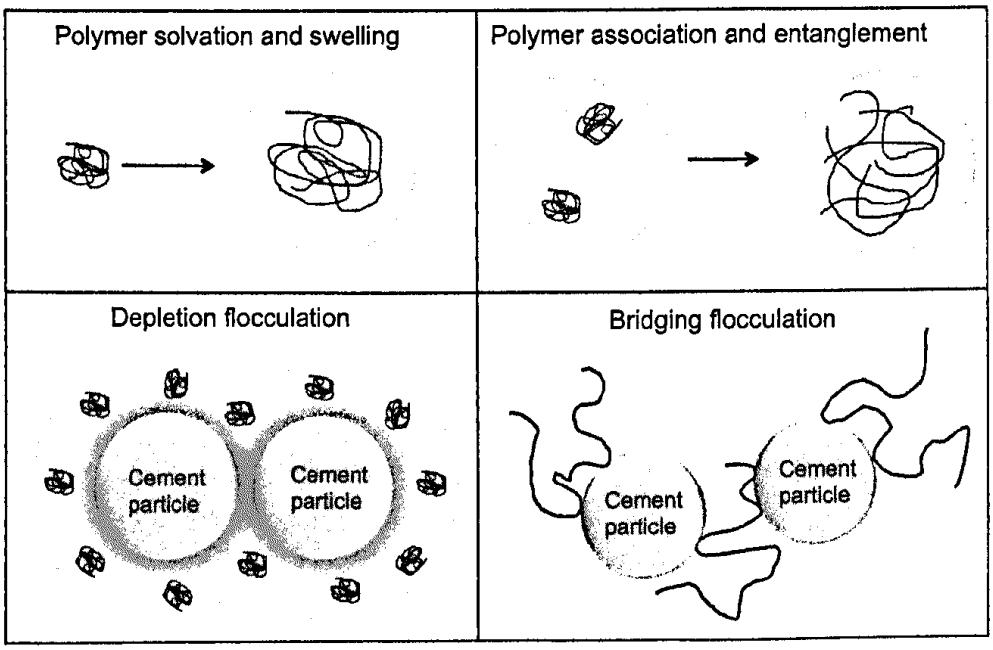

Figure 20.1 Sketch of the different mechanisms of action of polymeric VMAs.

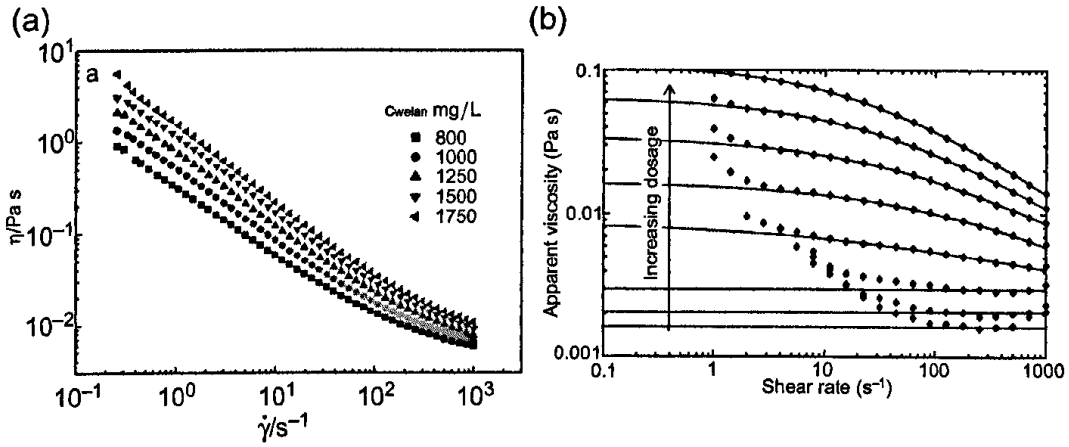

Figure 20.2 Examples of shear thinning behavior induced by (a) welan gum on aqueous solutions and (b) hydroxypropylguar on mortar pore solution.
Reproduced from Xu et al. (2013) and Poinot et al. (2013), respectively, with permission.

As shown in Figure 20.2, aqueous systems (as cement pore solutions) containing VMAs have a shear-thinning behavior where apparent viscosity decreases with shear rate. At low shear rates, disruption of polymer entanglements is balanced by the formation of new interactions and no effect on the viscosity is observed. At higher shear rates, the disentanglement of polymers predominates and chains align in the direction of the flow, consequently decreasing the apparent viscosity with the shear rate. This shear thinning behavior is observed not only in aqueous solutions but also in cementitious systems containing VMAs. This is highly desirable in concrete production, as VMAs increase the stability of the concrete once it is placed and enhance fluidity during mixing and pumping operations.

There are very few studies on the rheology of cementitious systems containing VMAs as the only admixture, and most of them deal with water retention agents. Brumaud (2011) showed that cellulose derivatives increase the viscosity of cement pastes.

Regarding the impact of water retention agents on the yield stress, contradictory results have been found in the literature. Some authors confirm that cellulose derivative (CE) admixtures slightly decrease the yield stress (Patural et al., 2011; Hossain and Lachemi, 2006). Patural et al. (2012) explained this decrease in base of the steric hindrance induced by the CE adsorbed onto cement particles. On the contrary, Brumaud (2011) observed an increase of the yield stress of cement pastes due to bridging flocculation prompted by the adsorbed admixture (see Figure 20.3). The difference obtained in the literature might come from the different structure and molecular weight of the CE polymers used. For example, Brumaud used CE with higher molecular weight than Patural et al.

20.2.3 Performance of VMAs in the presence of superplasticizers

In applications such as self-compacting concrete, it is essential to accomplish opposing rheological requirements, in particular high fluidity during casting and high viscosity

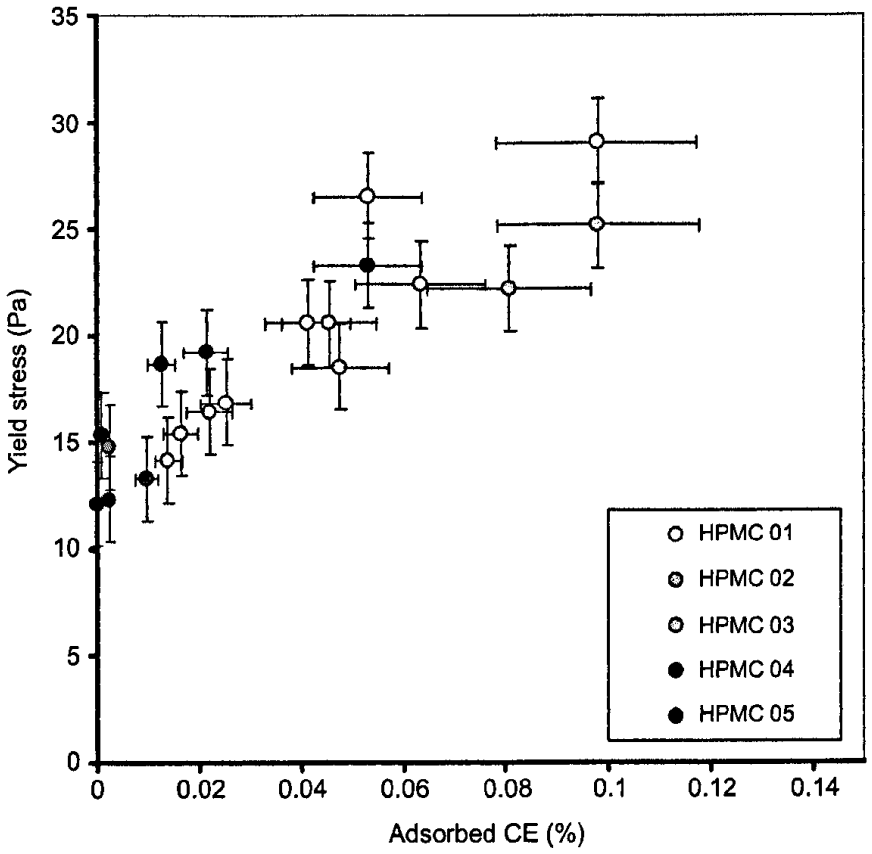

Figure 20.3 Yield stress of cement pastes with a w/c = 0.4 as a function of HPMC adsorption. Reproduced from Brumaud et al. (2014) with permission.

at rest to avoid segregation. For that reason, a combination of superplasticizers and VMAs is widely used. Chemistry and mechanism of action of both types of admixtures are different and problems of incompatibility might appear in practice. For example, adsorbing VMAs might compete with superplasticizers to absorb onto cement particles, reducing their dispersing properties.

20.2.3.1 Impact of VMAs on the rheological properties in the presence of superplasticizers

As observed in Figure 20.4, for a fixed dosage of superplasticizer, the addition of VMAs increases the plastic viscosity and/or yield stress. In practice, this increase of yield stress is normally corrected by the addition of extra water or more superplasticizer. In the cases illustrated in Figure 20.4(a), the CE shows a much more marked increase of plastic viscosity than yield stress. This observed effect might come from a specific combination of cellulose with a superplasticizer, but it is not necessarily a general behavior. In contrast, the other polymers show similar relative increases in both plastic viscosity and yield stress, as can be seen in Figure 20.4(b).

Welan gum and diutan gum are VMAs commonly used in combination with superplasticizers. Shear-thinning behavior is more pronounced in the presence of diutan

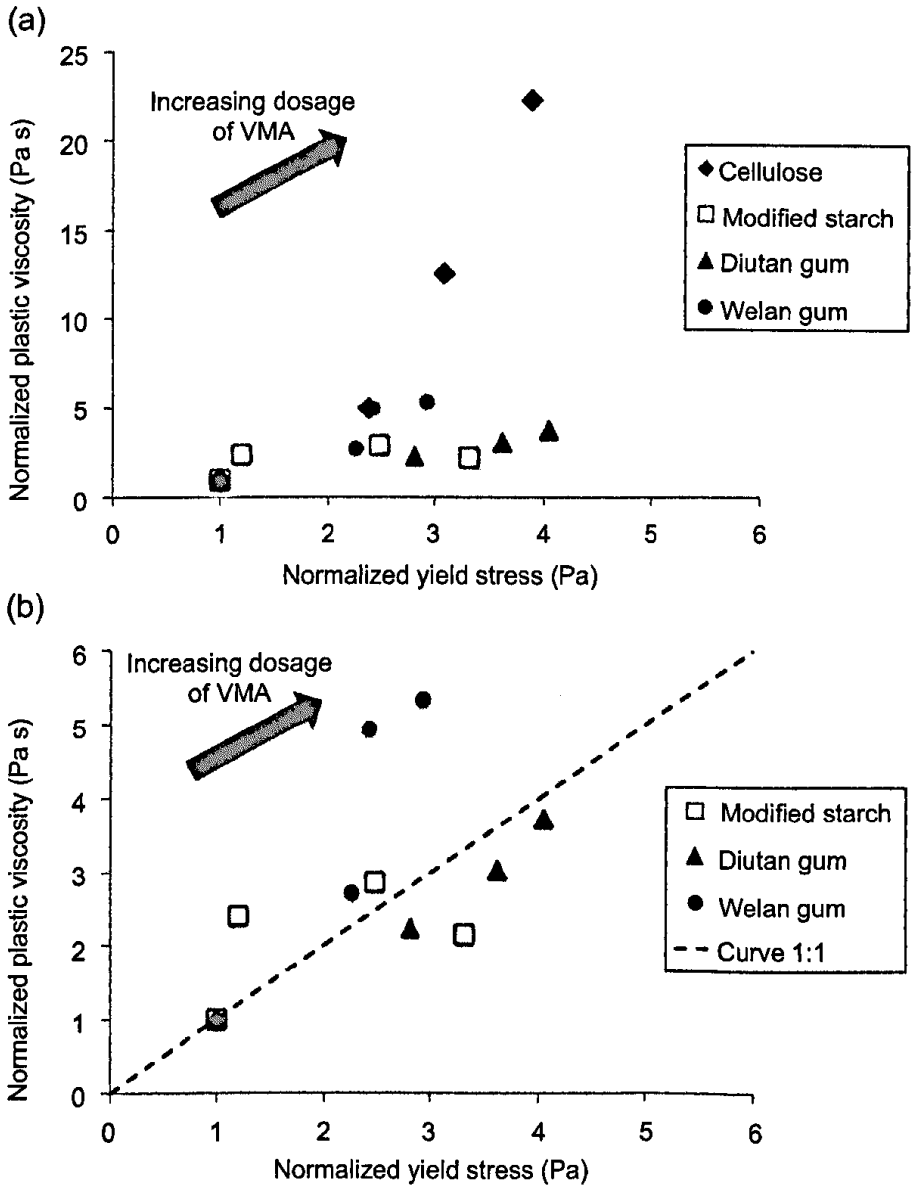

Figure 20.4 (a) Effect of type and concentration of VMAs on the rheological parameters of concrete-equivalent mortar of Self-compacting concrete (SCC) consistency. Dosage of superplasticizer was kept constant. (b) Image shown in detail.
Adapted from Khayat and Mikanovic (2012).

gum than welan gum because of its higher molecular weight (Sonebi, 2006). As shown in Figure 20.4(b), both gums and modified starch increase 2—5 times the plastic viscosity and yield stress of cement mortars with respect to those without VMA (Khayat and Mikanovic, 2012). This contrasts with the previously mentioned behavior of the cellulose derivative admixtures that mainly control the stability of the cementitious systems by significantly increasing the plastic viscosity. It should, however, be emphasized that these differences are illustrated on systems containing specific superplasticizers. Therefore, these observations should be taken as illustrations of possible

differences between combinations of a superplasticizer and a VMA rather than a general rule.

As explained before, polymeric VMAs physically adsorb large amounts of water by hydrogen bonds, increasing their effective volume and consequently the viscosity of the interstitial fluid of cementitious systems (Brumaud, 2011; Brumaud et al., 2013; Oosawa and Asakura, 1954). Apart from this specific effect on the continuous phase, the increase of yield stress observed in presence of welan gum and diutan gum could be explained by a combination of two mechanisms. On one hand, both gums have an anionic character and can also adsorb onto cement particles (see Figure 20.5 or Plank et al., 2010). For basic information on factors governing polymer adsorption as well as more specifically the role of molecular structure of PCEs on their adsorption, readers are referred to Chapter 10 (Marchon et al., 2013, 2016).

In the presence of a PCE superplasticizer, a competition between welan gum and superplasticizer to adsorb onto cement particles may occur as both polymers have a similar affinity for cement surface in the range of dosage of polymers normally used in concrete (see Figure 20.5). In this situation, yield stress would increase because of bridging flocculation. However, if not all the welan gum polymer is adsorbed, this polymer still remains in solution and could contribute to the increase of the yield stress by the depletion flocculation mechanism explained at the beginning of this chapter. However, first-order calculations of the depletion flocculation force do not seem large enough to explain the magnitude of yield stress change. More careful calculations would be needed. Furthermore, the competitity adsorption between PCE superplasticizer and a cellulose-based VMA has been probed by Bessaies-Bey et al. (2015) by using a combination of two techniques, total organic carbon (TOC) analyzer and dynamic light scattering (DLS).

In the case of modified starch VMAs, several studies have concluded that they significantly increase the yield stress. Again, this increase could be explained by a combination of both bridging and depletion flocculation. However, the effect of modified starch on the plastic viscosity is not clear. While Palacios et al. (2012) concluded that this VMA does not increase significantly the plastic viscosity of cement pastes, Figure 20.4(b) shows that starch-modified VMAs triple this rheological parameter.

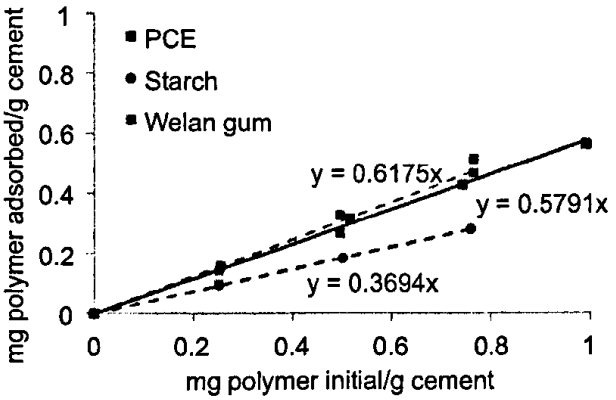

Figure 20.5 Adsorption of PCE superplasticizer and starch-modified and welan gum VMAs in the range of concentrations normally used in concrete.
Reproduced from the American Concrete Institute (Palacios et al., 2012) with permission.

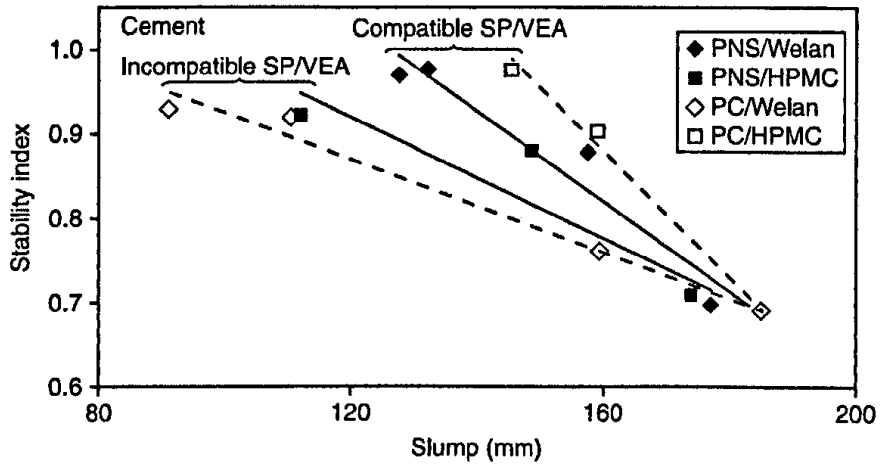

Figure 20.6 Stability of cement pastes as a function of spread flow (w/c = 0.65 and constant dosage of superplasticizer).
Reproduced from Khayat and Mikanovic (2012) with permission.

20.2.3.2 Compatibility of polymeric VMAs with superplasticizers

Kawai and Okada (1989) confirmed that cellulose-derivative VMAs are compatible with melamine-based and PCE superplasticizers. On the contrary, Figure 20.6 suggests certain incompatibilities of these VMAs with naphtalene-based superplasticizers (PNS) as the addition of cellulose derivatives decreases the slump flow (increases the yield stress) without much improvement in the stability of the mix (Khayat and Mikanovic, 2012). For the same reason, Figure 20.6 also reveals that PCEs and welan gum are incompatible while welan gum seems to be compatible with naphtalene- and melamine-based superplasticizers (Khayat and Mikanovic, 2012).

20.3 Working mechanisms of water retention agents

In building materials, cellulose ether (CE) and hydroxypropylguar (HPG)-derived polymers are normally used to improve the ability of a render or plaster to retain its constitutive water. In particular, they reduce the water loss due to capillary absorption into the porous substrate, onto which an overlay material is applied. This makes it possible for cement to hydrate and for adhesive and mechanical properties to develop (Brumaud et al., 2013; Marliere et al., 2012).

The working mechanism of both types of polymers has been proven to be similar. Firstly, CE and HPG admixtures increase the viscosity of cement pore solution. Brumaud et al. (2013) measured the influence of different CEs on the viscosity of distilled water and synthetic cement pore solutions. They confirmed that hydroxyethoxy methoxy cellulose (HEMC) and hydroxypropoxy methoxy cellulose (HPMC) increase the viscosity of these solutions; this increase depends on the molar mass, nature of the ether(s), and its dosage. However, as shown in Figure 20.7, at dosages lower than 1%, the viscosity increase does not depend on the molecular parameters, such as degree of substitution (DS) or mass substitution (MS). Only at very high

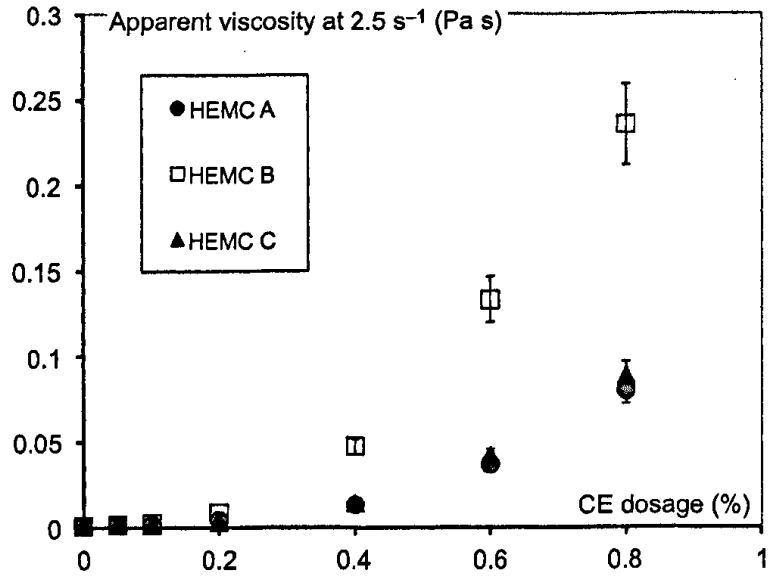

Figure 20.7 Apparent viscosity at 2.5 s^{-1} for various dosages of hydroxyethoxy methoxy cellulose (HEMC) in distilled water. HEMC B has a molar mass that is 2.5 times higher than the molar mass of HEMCs A and C. HEMCs A and C have an equivalent mass substitution (MS) and a different degree of substitution (DS) whereas HEMCs A and B have a different MS and similar DS.
Reproduced from Brumaud et al. (2013) with permission.

CE dosages (higher than 1%) is there a slight dependency on these molecular parameters and viscosity of the aqueous solution.

Water retention of cementitious systems increases with the molecular weight and dosage of CE admixtures. Several studies (Brumaud et al., 2013; Bülichen et al., 2012) have confirmed that the mechanism controlling the water retention of CE polymers depends on the concentration used. Below a critical concentration corresponding to the overlap of the polymer coils, water retention of mortars is dictated by the increase of the viscosity of the interstitial solution, no matter the polymer structural parameters (Brumaud et al., 2013). Most of the studies conclude that the increase of the viscosity induced by CE admixtures may reduce the mobility of the interstitial solution and increase water retention.

In contrast, Patural et al. (2012) showed by nuclear magnetic resonance dispersion measurements that the surface diffusion coefficient of water is not modified by the presence of CE, despite the high increase of the solution viscosity induced by these polymers. However, CEs transiently increase the fraction of mobile water molecules present at the solid hydrate surfaces.

At dosages above the critical concentration, the associative nature of the CE molecules mainly governs their water retention ability. There are two reasons for this. The first is that CEs form aggregates in solution, increasing the viscosity of the interstitial fluid. The second is that these polymer aggregates are a few micrometers in size (see Figure 20.8), so that they may jam and/or plug the porosity of the fresh paste or mortar (Sonebi, 2006; Patural et al., 2011; Brumaud et al., 2013). In addition, Jenni et al. (2003, 2006) found that methyl hydroxyethyl cellulose (MHEC) is transported through

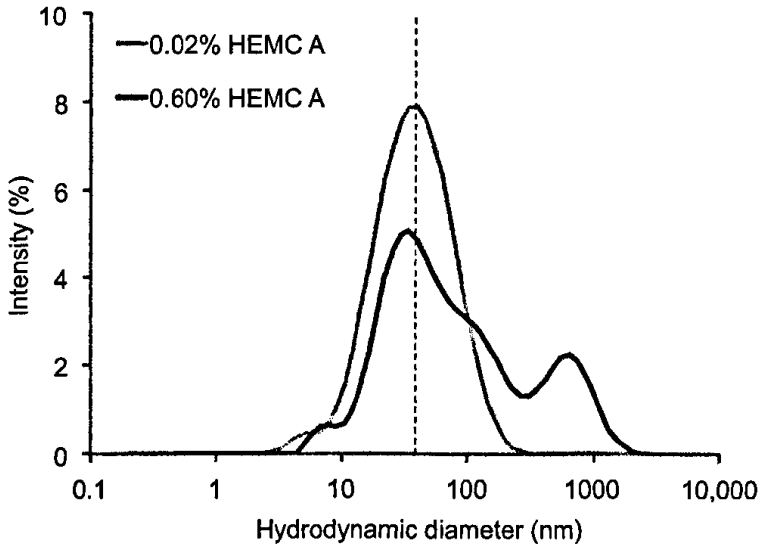

Figure 20.8 Hydrodynamic diameter of HEMC in aqueous solution below and above the overlapping concentration.
Reproduced from Brumaud et al. (2013) with permission.

the capillary pores of mortars and accumulated at the interface between the layer in contact with the substrate and the substrate surface, reducing the porosity.

Similar results as those presented above for CE have been obtained by Poinot et al. (2014) for HPG. They confirmed that water retention of cement mortars depends on HPG concentration. They also found that at concentrations higher than the overlapping concentration, a high increase of the water retention is induced due to the formation of polymer aggregates. However, at dosages below the critical concentration, almost no effect of HPG on water retention is observed. This last result contrasts with the case of CE polymers (see Figure 20.9) (Poinot et al., 2014). The reasons for this are not clear but may be to be found in the lower intrinsic viscosity of the selected polymers.

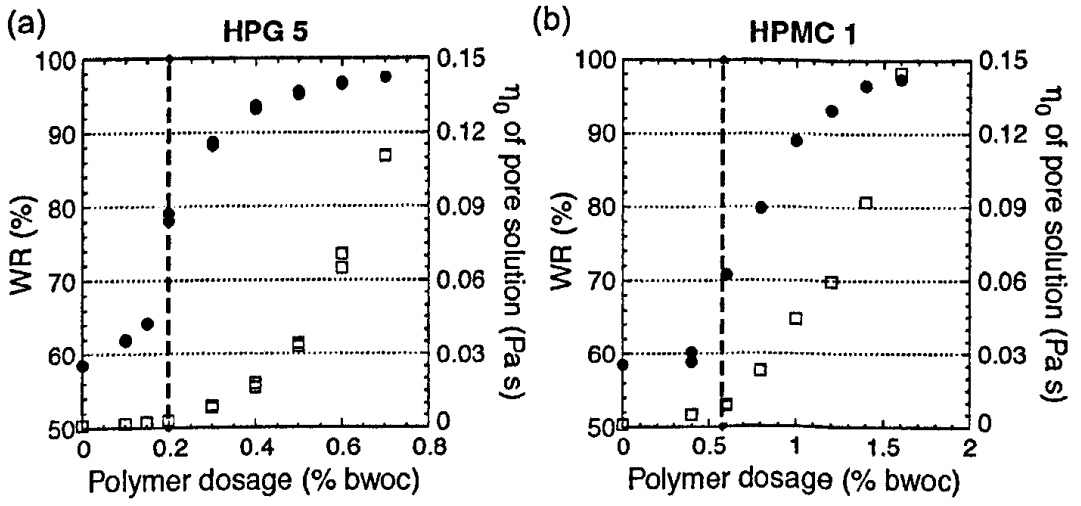

Figure 20.9 Effect of polymer agglomerates formation on water retention for (a) hydroxypropylguar (HPG) and (b) hydroxypropoxy methoxy cellulose (HPMC).
Reproduced from Poinot et al. (2014) with permission.

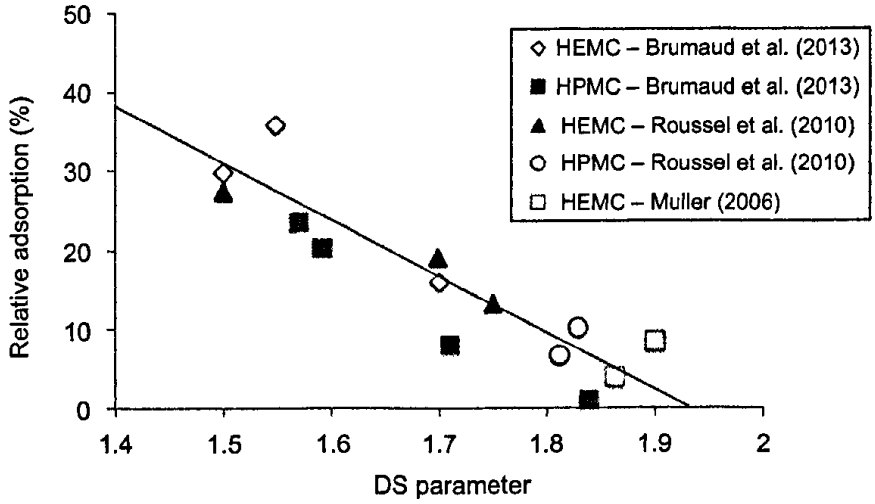

Figure 20.10 Relative adsorption of CE as a function of DS for a CE dosage of 0.2% (Roussel et al., 2010; Muller, 2006; Brumaud et al. (2013)).
Reproduced from Brumaud et al. (2013) with permission.

In cement pastes containing CE polymers, Brumaud (2011) determined that the viscosity of the interstitial solution was lower than expected from the dosage used. This difference was explained by a partial adsorption of these polymers onto the surface of cement particles, causing a decrease of polymer concentration in the pore solution and therefore also of the viscosity. Other authors have also confirmed that CE polymers can adsorb on cement particles (Bülichen et al., 2012; Khayat and Mikanovic, 2012; Brumaud et al., 2013) and that the extent of this depends on DS, as shown in Figure 20.10.

However, because CEs are nonionic polymers, the origin of this adsorption is unclear. According to Bülichen et al. (2012), the adsorbed polymer may not correspond to the cellulose derivative but to byproducts present in commercial MHEC that are able to adsorb onto cement particles. In any case, authors agree that the water retention properties of CE are not related to CE adsorption onto cement particles.

At this point, it is worth mentioning that adsorption measurements of CEs are not easy to perform by the depletion method without introducing artifacts, specifically at dosages above the critical concentration where CE aggregates could be trapped within the porosity of the cement pastes (Brumaud et al., 2013; Bülichen et al., 2012).

20.4 Influence of polymeric VMAs on hydration of cement

Most of the studies on the impact of VMAs on cement hydration have been done using cellulose derivatives or hydroxypropylguar retention agents. They were done by conductivity measurements on highly diluted systems and isotherm calorimetry using lower water–cement (w/c) ratios. In this section, we propose only a brief review of some findings of the literature concerning these specific cases. More detailed information on cement hydration mechanisms and how chemical admixtures can affect them can be found in Chapters 8 and 12, respectively (Marchon and Flatt, 2016a,b).

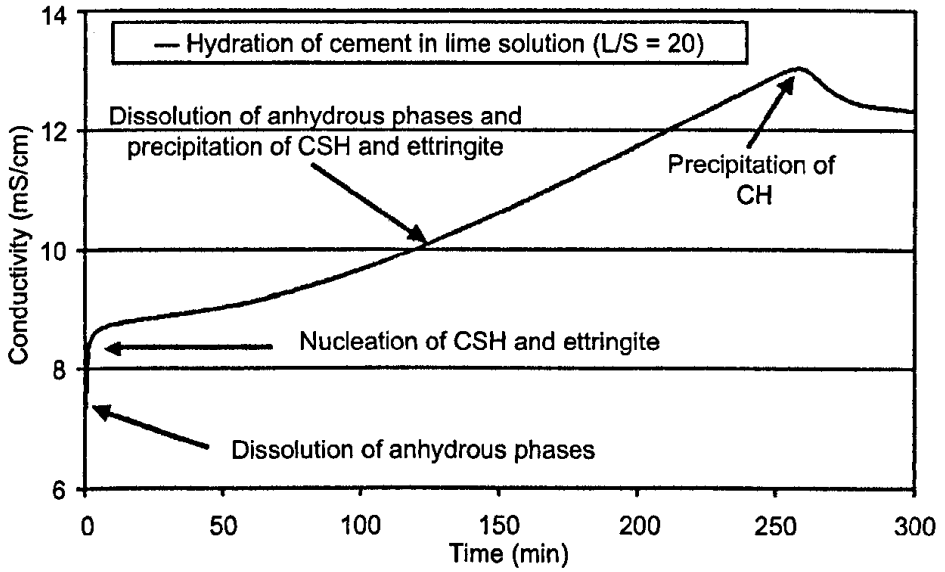

Figure 20.11 Example of a conductivity curve of cement hydration (liquid–solid ratio = 20). Reproduced from Pourchez et al. (2006) with permission.

Figure 20.11 shows the typical conductivity curve of cement reaction where the initial precipitation of portlandite involves a drop of the electrical conductivity (Comparet, 2004; Pourchez et al., 2010). In the presence of CE and HPG, a delay in the time of portlandite precipitation is observed, indicating a delay of C_3S hydration that is higher with the dosage of polymer (see Figure 20.12) (Pourchez et al., 2010).

Pourchez et al. (2010) analyzed the concentration of silicate and calcium as dissolution of C_3S progressed in highly diluted systems. They found that CE polymers had almost no influence on the dissolution of pure C_3S. These authors measured the concentration of calcium and silicates over time and calculated the amount of initial C–S–H nuclei based on the decrease of silicate concentration during the hydration of C_3S where the calcium concentration is constant. This was calculated according to Eqn (20.1) based on the works of Garrault and Nonat (2001) and Pourchez (2006):

$$\text{C–S–H initial nuclei} = \frac{\Delta\left[H_2SiO_4^{2-}\right]}{\frac{1}{3}\left(\frac{C}{S}\right) - 1} \tag{20.1}$$

where C/S is the calcium-to-silicon ratio of the C–S–H.

As shown in Figure 20.13, the amount of initial C–S–H nuclei decreases in the presence of CE polymers.

Additionally, Figure 20.12(a) shows that CEs have very limited impact on the rate of C–S–H growth, as the slopes in the stage of hydration are relatively similar to the reference. On the contrary, HPGs (see Figure 20.12) decrease the slope of the curve, indicating that they mainly slow down the growth of hydrate phases rather than their nucleation (Poinot et al., 2013). For both polymers, these authors have proposed that the adsorption onto C–S–H and portlandite is the main reason for the induced delay. They also indicated that the increase of the viscosity of the aqueous media, and possible decrease of water migration, does not play any role on the slowing down of the hydration induced by CEs and HPGs.

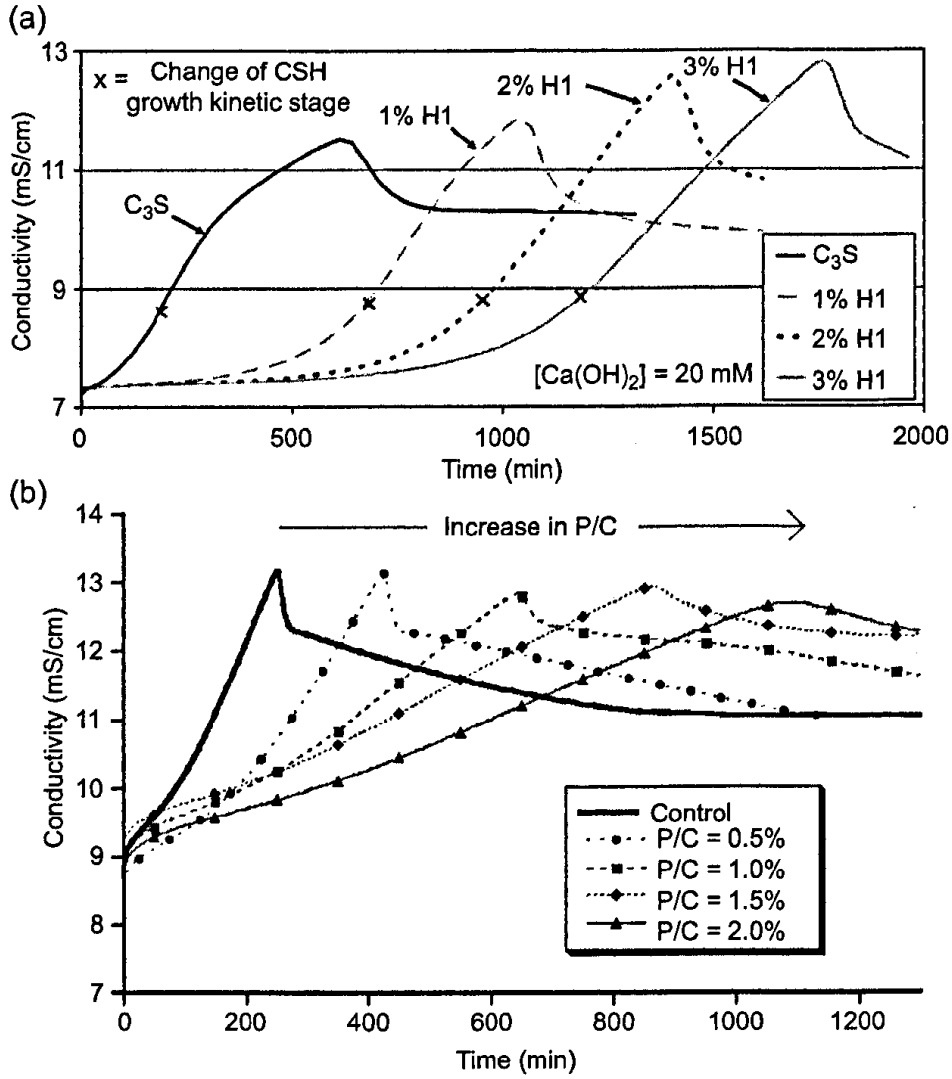

Figure 20.12 Conductometric curves of C_3S hydration in the presence of (a) cellulose derivatives and (b) hydroxypropylguars.
Reproduced from Pourchez et al. (2010) and Poinot et al. (2013), respectively, with permission.

The effect of other VMAs on the hydration of cement still remains unclear. Leemann and Winnefeld (2007) showed that in mixes containing both PCE-based superplasticizer and VMAs, the presence of polymeric VMAs does not significantly modify cement hydration (see Figure 20.14). On the contrary, Khayat and Yahia (1997) observed a clear delay of the setting time of cement grouts containing a naphtalene-based superplasticizer and a welan gum VMA.

Finally, we can note that the addition of inorganic VMAs, such as microsilica or nanosilica slurries, accelerates cement hydration as they introduce additional nucleation and/or growth surfaces that can consume ions released by the dissolving anhydrous phases (Leemann and Winnefeld, 2007). From this point of view, when retardation is an issue, such compounds may be valid alternatives, provided they are effective enough in modifying the other more essential properties.

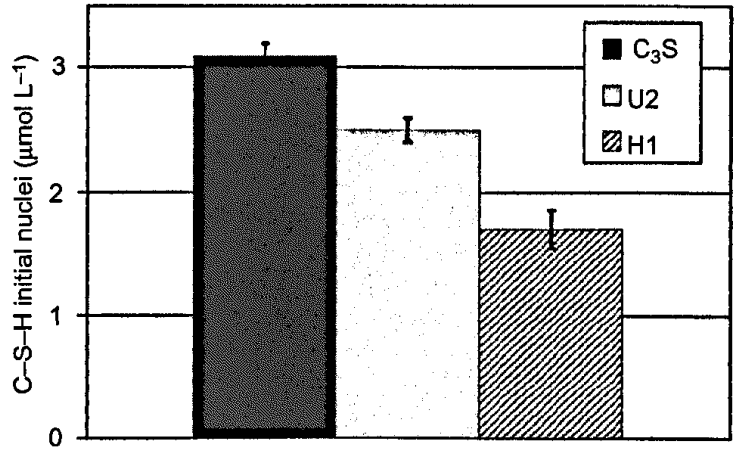

Figure 20.13 The impact of CE on the amount of initial nuclei of C–S–H after 30 min of C_3S hydration (liquid/solid = 100, polymer/solid = 2%, $Ca(OH)_2$ = 20 mM).
Reproduced from Pourchez et al. (2010) with permission.

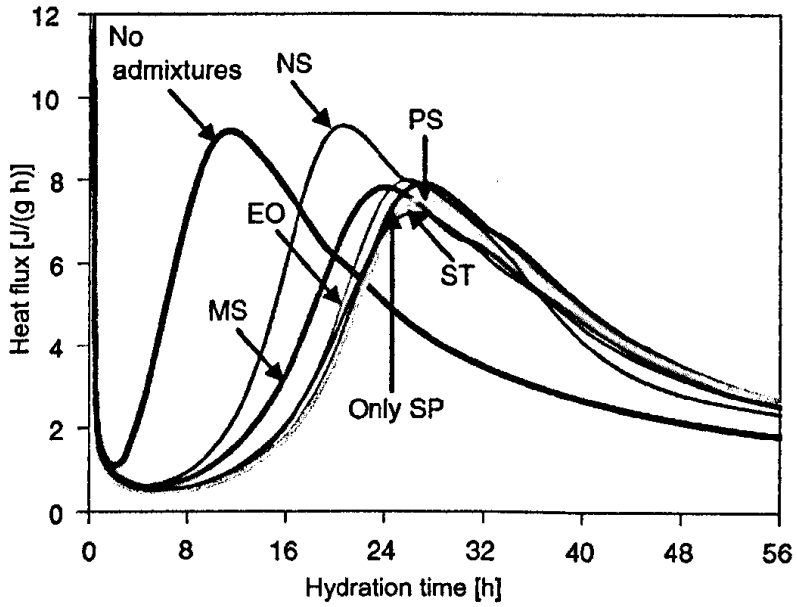

Figure 20.14 Isothermal heat flow curve of cement pastes with w/c = 0.4% and 1% of superplasticizer (SP) and different VMAs (ST, starch derivative; PS, natural polysaccharide; MS, microsilica; NS, nanosilica; EO, ethylene oxide derivative).
Reproduced from Leemann and Winnefeld (2007) with permission.

20.5 Use of VMAs in SCC formulation

In recent years, SCC application has progressively increased. Table 20.1 shows the concrete mix design of three SCCs containing different types of VMAs used in Canada. The three concretes had a compressive strength of 35 MPa at 28 days (Table 20.2).

SSC1 was used in the Fermont in Quebec Province to build a special tank. The high density of steel reinforcement (see Figure 20.15) required the use of an SCC. This SCC

Table 20.1 Composition of SCC

Nomenclature	Sand (kg)	Aggregates (kg)	Water (L)	Cement (kg)	Fly ash (kg)	Water/binder	Superplasticizer (L)	VMA (L)	Water reducer (L)	Retarder (L)
SCC1	794	885 (5–14 mm)	168	378[a]	42	0.40	5.0[c]	1.0[e]	0.80	–
SCC2	762	793 (2.5–10 mm)	179	460[b]	–	0.40	4.0[d]	3.0[f]	–	–
SCC3	810	889 (2.5–10 mm)	153	400[a]	–	0.40	3.5[d]	1.0[e]	0.75	1.0

[a]Cement containing 7–7.5% of silica fume.
[b]Ternary cement containing 20% of fly ash and 5% of silica fume.
[c]PNS.
[d]PCE.
[e]Biopolymer.
[f]Welan gum-based.

Table 20.2 Fresh and hardened properties of SCC

Nomenclature	Spread (mm)	Air content (%)	Compressive strength at 28 days (MPa)
SCC1	650 ± 50	6–8	35
SCC2	675 ± 50	6–8	35
SCC3	625 ± 50	6–8	35

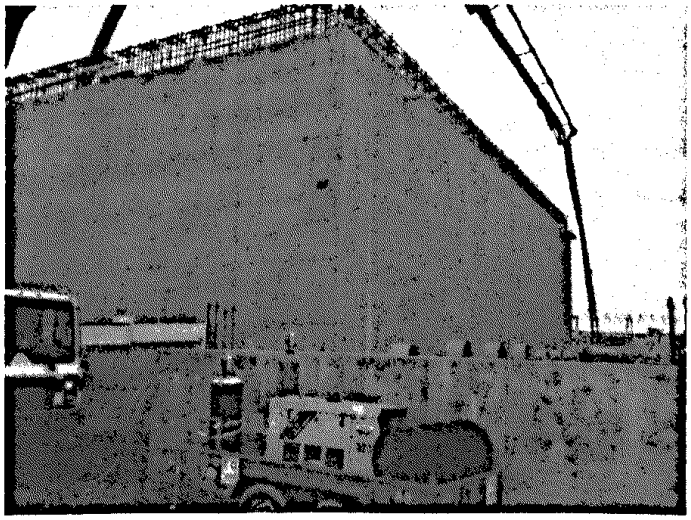

Figure 20.15 Construction of Fermont tank in Quebec using SSC1.

was prepared using a mix of several chemical admixtures, a PNS superplasticizer, a water-reducing admixture, and a biopolymer-based VMA.

SCC2 was used to build a retaining wall at Les Escoumins in Quebec Province (see Figure 20.16). In this case, the use of the SCC allows observation of the defects of the

Figure 20.16 Retaining wall at Les Escoumins in Quebec.

formwork. Highly fluid and stable SCC was obtained by using a PCE superplasticizer in combination with a welan gum-based VMA.

Finally, SCC3 was used in Parc Forillon in Quebec Province. Again, a mix of different chemical admixtures was required to obtain the suitable fresh properties of the concrete. Specifically, a PCE superplasticizer, a water reducer, a retarder, and a biopolymer based VMA were used.

20.6 Conclusions

Modern concrete, such as self-compacting concrete, underwater concrete, or shotcrete require very specific rheological properties. The addition of VMAs allows a reduction of the amount of fine powder materials in concrete at the same time that its stability, cohesion, and robustness are substantially increased. The understanding of the working mechanism of VMAs promotes the design of robust concrete mixes that can provide the best fresh and hardened state properties.

This chapter focuses on polymeric VMAs as they allow a higher variability of structural variations. The mechanism of action of these admixtures and their impact on the rheological properties depends on the nature of the VMA and the presence of other admixtures in the mix. In general, water retention admixtures delay cement hydration while the influence of other VMAs on cement hydration depends on its chemical composition.

In practice, problems of incompatibility between specific combinations of VMAs and superplasticizers must be avoided. These could lead to a quick loss of fluidity without much improvement in the stability of concrete. An understanding of the mechanism of action of the different types of polymers may decrease the risk of having such problems on site.

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