Influence of the type of viscosity-modifying admixtures and metakaolin on the rheology of grouts

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Abstract. The Viscosity-modifying admixtures (VMAs) contribute to the control of the rheology of grouts and are used to enhance plastic viscosity, cohesion, stability, and resistance to bleeding of cement-based systems. This paper reports the results of an investigation on the effect of type of VMAs, namely two types of diutan gums and a welan gum and metakaolin (MTK), plus a superplasticiser, on the rheology behaviour of cement grouts. All mixes were made with polycarboxylic superplasticiser at 0.6% and 0.9%. The dosages of VMAs were 0.05%, and 0.10%, with a fixed water-to-binder ratio of 0.40. The investigated fresh properties of the grouts included the mini-slump flow, plate cohesion, and rheology parameters: namely yield value and plastic viscosity. The rheological parameters were obtained using a vane viscometer. Control grouts (with and without superplasticiser and VMA) were also tested and compared to mixes containing VMAs. The results indicated that the incorporation of MTK reduced the fluidity and increased the plate cohesion and yield stress, and plastic viscosity due to the higher surface area of MTK. The diutan gum grouts improved the grout fresh properties and rheology compared to the welan gum grouts.

1 Introduction

Grouts are widely used in injection grouting of cracks in massive structures since their physical and mechanical properties can be easily controlled. Viscosity-modifying admixtures (VMAs) are commonly used in conjunction with superplasticiser (SP) where highly flowable, yet stable and homogeneous, cement-based grouts are needed for applications, such as injection grouting, post-tensioning grouting and anchorage sealing, etc. [1, 2]. Grouts containing VMA are also used for filling ducts, where it is important to ensure high resistance to sedimentation and bleeding, hence ensuring corrosion protection of stressed tendons.

Moreover, VMAs are widely used in concrete applications, such as self-compacting concrete, underwater concrete, and shotcrete [1-7]. VMAs are highly effective in controlling bleeding as the long-chain molecules of VMA adhere to the periphery of water molecules, thus it adsorb and fix part of mix water which increase the yield value and plastic viscosity of the cement-based grouts. Several researchers have related the improvement in rheological properties and the performance of cement-based grout to the addition of VMA and SP [1-7]. Most VMA solutions are shear thinning which means that an increased shear rate causes a progressive decrease in plastic viscosity [6, 7].

VMAs can adsorb on particles, thus causing a bridging-flocculation effect. Some VMAs such as diutan gum and welan gum contain anionic groups in their backbone, which propagate electrostatic adsorption on aluminate and ferrous phases in the cement's pore solution. Such adsorption is assumed to be avoided largely by using adsorptive superplasticizers, however, particularly over the course of time interactions between superplasticizers and VMAs can occur, which affect the rheology and the setting of cementitious systems. [8, 9].

This investigation aimed to characterise the flowability and the cohesiveness measured by mini-slump, Lombardi plate cohesion and the rheological parameters of diutan gums and welan gum and to evaluate the influence of the dosages of VMAs and SP on the fresh properties and the rheological parameters of grouts made with a water-to-binder ratio (W/B) of 0.40. The effect of the replacement of cement by 7% metakaolin (by mass) is also investigated with the variation of the dosages of VMAs and SPs. A similar OPC control grout and another one made with MTK and without VMA and SP were investigated in order to compare the rheological parameters to VMA-grouts.

2 Experimental program, materials and test methods

2.1 Experimental programme

In this investigation, fifteen grouts were made with W/B of 0.40 (Table 1). Fresh properties of cement-based grouts made with 7% of metakaolin, incorporating three types of VMAs welan gum (WG), and two diutan gums (DGs), namely DG-1 and DG-2, were investigated. Two dosages of the VMAs were used (0.05% and 0.10% by the mass of mixing water) along with two dosages of SP (0.6% and 0.9% by the mass of cement, Table 1). Additionally, two systems: one without any SP and VMA and another with MTK were tested. The following properties of the grouts were examined: the mini-slump flow, Lombardi plate cohesion, and rheological properties (yield value and plastic viscosity).

2.2 Materials used

Portland cement CEM I in accordance with BS EN 197-1: 2000 was used in all mixes. The chemical and physical characteristics of the cement and metakaolin (MTK) are given in Table 2. A polycarboxylate based superplasticiser (SP) with solid content of 42% and specific gravity of 1.08 was used. The water content in the mixes was adjusted to take into account the water contained in the SP. Two types of DGs: DG-1 and DG-2 and one WG were employed as VMAs (their quantities are expressed per mass of the mixing water).

Both welan and diutan gums are high molecular weight, long chain microbial polysaccharides. Welan gum has monosaccharide side-chain (L-rhamnose, partially replaced by L-mannose), while diutan gum incorporates disaccharide L-rhamnose side-chain. In both cases, the side-chain is linked to one of the two glucose units [10 -12]. The molecular length of diutan gum is up to three times longer than that of the welan gum. The molecular weights of diutan and welan gum are about 2.88 to 5.18 million Daltons and 0.66 to 0.97 million Daltons, respectively [12]. Diutan and welan gums are compatible with cement hydration products. According to the supplier of the VMAs, the viscosity obtained with tap water of DG-2 was higher (3000-6000 mPa•s) than those of DG-1 and WG (>2800 mPa•s and 1000-2000 mPa•s, respectively). This indicates that DG-2 has higher polymerisation degree (longer chains) than the two other VMAs [12].

Table 1. Mix composition of the grouts.

Description	OPC	MTK (%)	$SP^{\#}$ (%)	VMA* (%)
Ref1-No VMA/SP/MTK	100	0	0.0	0.00
Ref2-No VMA/SP-7%MTK	93	7	0.0	0.00
MTK-6% SP	93	7	0.60	0.00
DG-1 =0.05% DG-1 =0.10%	93	7	0.6 & 0.9	0.05 0.10
DG-1 =0.05% DG-1 =0.10%	93	7	0.6 & 0.9	0.05 0.10
WG =0.05% WG =0.10%	93	7	0.6 & 0.9	0.05 0.10

- by weight of cement, * - by weight of water

Table 2. Chemical and physical properties of cement and metakaolin.

	Cement	MTK
SiO_2	20.8	51.7
Al_2O_3	5.0	43.2
Fe_2O_3	3.2	0.4
MgO	2.6	--
CaO	63.7	--
Na_2O eq	0.39	--
SO_3	2.83	--
LOI	0.65	0.16
Specific gravity	3.08	2.2
% passing 45 µm sieve	85	--
Mean particle size [µm]	22	1.4
Specific surface area [m^2/kg]	360	13200

2.3 Mixing and testing procedures

The grouts were prepared in a 5 litres planar-action high-shear mixer, in 2 litres batches. Tap water (16 ± 0.5 °C) and SP were added together to the mixer and mixed one minute at a low speed (140 rpm). Next, premixed solid components, such as cement, MTK and VMA, were introduced within 2 min, at the end of which the mixer was stopped and any possible lumps of solids formed were crushed (1 min). Then, the grout was mixed again for 2 min at a higher speed (285 rpm) and for 1 min at the low speed (140 rpm). The temperature of the grouts after mixing was 20 ± 1 °C.

For all tests, the timing is given from zero time – that is, the time when the cement particles come into contact with the mixing water. The mini-slump flow test was started at 6 min (immediately after the end of mixing). The transparent cone-shaped mould described elsewhere [13] was placed in the centre of a smooth Plexiglas plate. After filling with grout, the cone was gently lifted (approximately 30 s after finishing of placing of the grout). When the flow stopped, the spread of the grout was measured with a ruler in two perpendicular directions.

The cohesion of the grout was determined at 8 ± 1 min with a Lombardi plate cohesion meter [14]. A thin galvanized steel plate (100×100×1 mm) was immersed in the grout and hung on a stand placed on an electronic balance. The mass of the grouts that remains on the plate were recorded when the dripping of the grout had stopped. This test was followed by the fresh density measurement of the grout with a mud balancer, as specified in Reference [15]. Knowing the fresh density of the grout, it is possible to calculate the mean thickness on the grout of the plate.

The rheological measurement was carried out with a computer-controlled vane viscometer (Haake VT550). At 13 ± 1 min, approximately 800 ml of the sample was introduced into a plastic container where the vane was plunged. After 30 seconds rest, the test was started, and the same testing parameters as above (velocities and their durations) were followed. The shear rate steps used in this investigation are presented in Fig. 1. For each step, when the equilibrium was reached, the strain rate was increased from an initial value of 0.188 s^{-1} to a top value of 41.6 s^{-1} (ascending curve), and afterward, it is decreased to ending the descending curve.

The two rheological parameters, yield stress (τ_0) and plastic viscosity (μ_p), were obtained with Herschel-Bulkley model by fitting the shear stress-shear rate data. This model is given by equation (1):

$$\tau = \tau_0 + k\gamma^n \qquad (1)$$

where τ_0 is the yield stress, k is the consistency, and n is the characteristics of the mix's shear thinning behaviour. n < 1 indicates shear thinning, and n > 1 shear thickening.

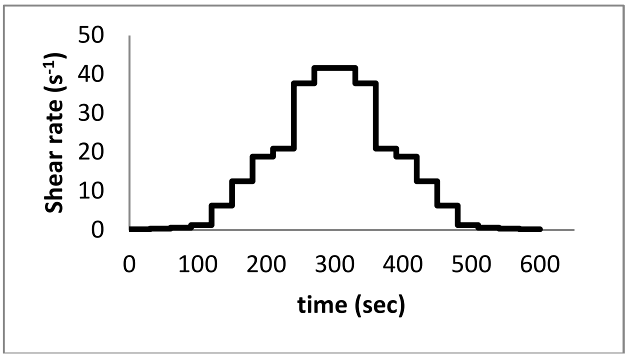


Fig. 1. Shear rate steps applied to paste using step-by-step procedure.

3 Results and discussion

3.1. Effect of dosages of VMAs, SP, and MTK on mini-slump

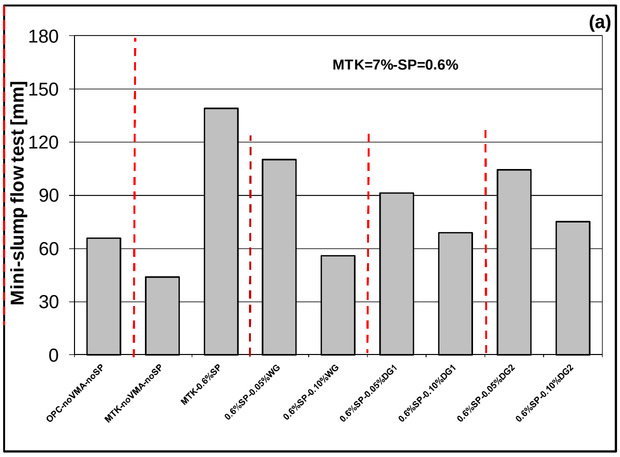
Results of the mini-slump flow are shown in Figure 2. The reference mix Ref1 (No SP/VMA/MTK) had a low spread, whereas the incorporation of the 0.6% (Fig. 2(a) or 0.9% (Fig. 2(b) of SP dramatically increased the spread. The increase of dosage of SP is shown to exhibit the greatest effect on the mini-slump. This is attributed to steric and a better electrostatic repulsions among cement particles that adsorb SP which leads a better deflocculation of the particles in the paste.

The replacement of cement by 7% MTK led to a significant reduction of fluidity from 66 mm (Ref1) to 44 mm due to the high surface area of MTK. It can be noted that the large surface area of MTK is likely to reduce the amount of SP per unit surface area so that Van der Waals based particle-particle attractions may eventually become increasingly important.

The addition of any VMA decreased the spread. An increase of VMA (0.05% and 0.10%) at a fixed SP dosage caused a gradual reduction of the spread for both systems of MTK grouts (SP=0.6% and 0.9%, Fig. 2). VMAs appear to have adsorbed and fixed part of free water, so this water is no longer available for lubrication of particles.

The trends obtained for both diutan gums (DG-1 and DG-2) in similar fashion. Even low dosage of DG-1 and DG-2 (0.05%) in grouts containing 7% MTK and 0.6% SP significantly decreased the spread flow (93 mm and 105 mm, respectively), compared to the systems without VMA (139 mm). It was not so significant in the case of WG (126 mm).

In comparison with the DGs, consecutive dosages of the WG resulted in a sharper decrease in the mini-slump flow for any given dosage of SP. Therefore, the rheological behaviour of the systems incorporating DGs were easier to control than those with WG. Worth mentioning, no significant difference was observed between the two DGs.



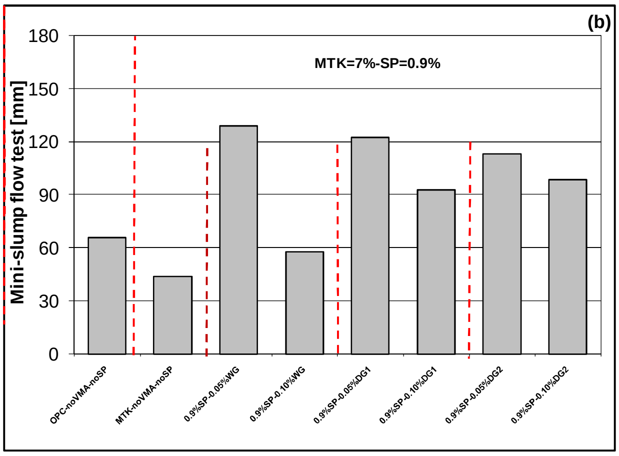


Fig. 2. Variation of mini-slump with type of VMAs, SP and MTK.

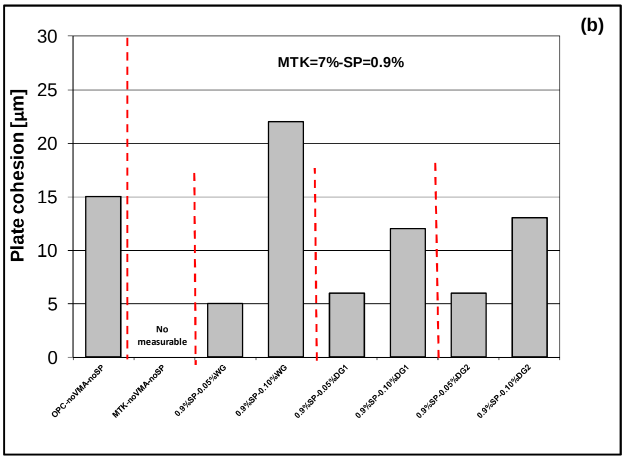


Fig. 3. Variation of plate cohesion vs. VMAs, SP, and MTK

3.2 Effect of dosages of VMAs, SP, and MTK on plate cohesion

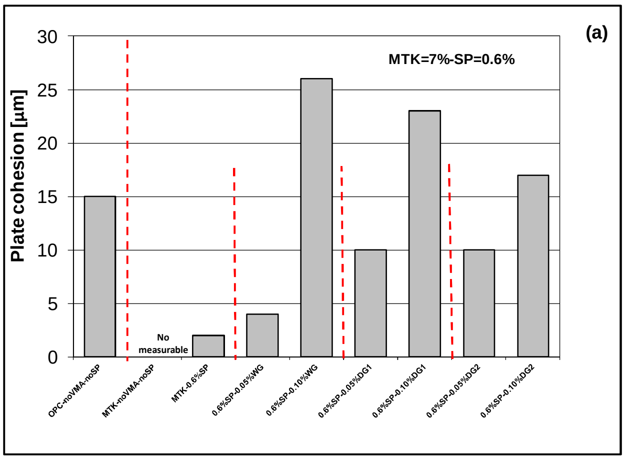
As expected, the addition of any VMAs affects significantly the cohesion plate values. An increase of VMA (0.05% and 0.10%) caused a gradual increase in the thickness of plate cohesion (Fig. 3). The increase in cohesion was very sharp for grouts containing the welan gum. This can be attributed to the entanglement and intertwining of adjacent polymer chains. For any given dosage of SP and VMA, it can be noted that DG2 exhibited lower values of plate cohesion compared to grouts with DG1.

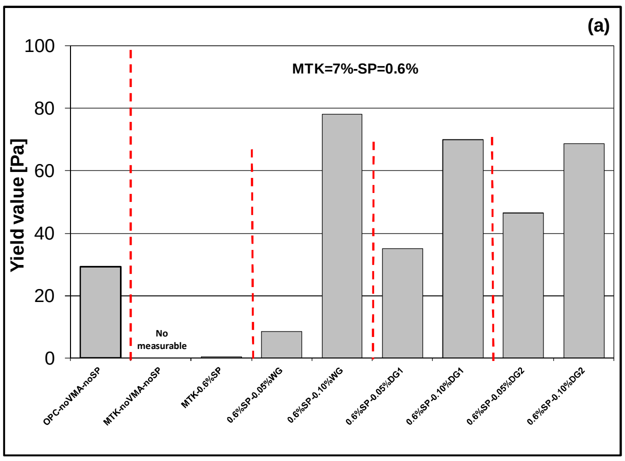
Conversely, for any given VMAs, an increase in SP from 0.6% to 0.9% (Fig. 3(a) vs. Fig. 3(b)) led to a reduction in cohesion plate values. The addition of MTK is shown to increase the cohesion plate value. This can be attributed to high surface area of MTK which resulted in an increase of cohesion.

The effects of SP and VMAs confirm other findings on the effect of these chemical admixtures on cement grouts containing fly ash and limestone powder [6, 15].

3.3 Effect of dosages of VMAs, SP, and MTK on yield value

Figs. 4 (a) and (b) present the yield stress results of grouts made with OPC, and 7% MTK and two dosages of VMAs at 0.05% and 0.10% for dosages of SP of 0.6% (a) and 0.9% ((b), respectively. The Ref1 mix (No-VMA/SP) had a value of yield stress of 29.3 Pa. In none superplasticised mix, the addition of 7% MTK increased dramatically the yield value so the mix was very cohesive and it was impossible to measure the yield stress with the viscometer. This was due to the high surface area of MTK. Similar findings for MTK were also observed in previous work [16] using metakaolin blended cements. The incorporation of MTK resulted in increased yield stress in the case of MTK, whereas yield stress values decreased with the addition of SP. The addition of 0.6% SP decreased significantly the yield value due to the dispersion effect of SP on cement particles. Addition of SP produces a thicker adsorbed polymer layer and consequently weaker van der Waals attractions between the particles, therefore lower energy is needed to disperse the particles and secure lower yield stress [17].





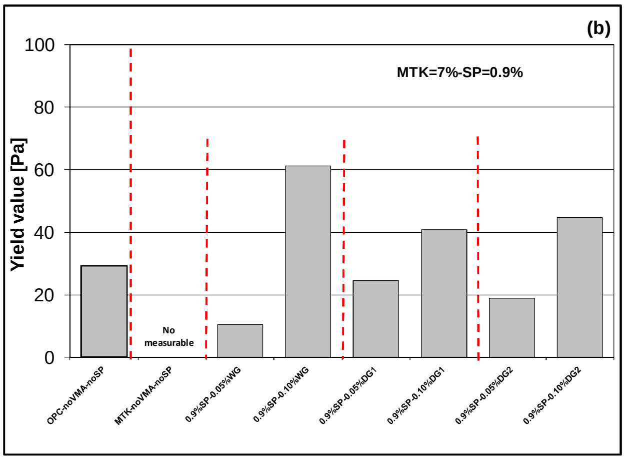


Fig. 4. Variation of yield value vs. VMAs, SP, and MTK.

In general, for any given dosage of diutan gums or welan gum, the increase in the dosage of SP resulted in a reduction of yield stress. For any given dosage of SP, the introduction of VMAs (DG1, DG2 or welan gum) resulted in significant increase in yield stress results. For example, for grout containing 0.6% of SP, the increase in concentration WG from 0.05% to 0.10% resulted in an increase in yield stress from 8.5 Pa to 78.2 Pa (9 times increase). In the case of DG1 and DG2, the increase in yield stress compared to the reference mix were approximately twice and half, respectively.
At low shear rate, where mini-slump flow and yield value are believed to characterise cement-based system rheology [15 18], the polymer chains entangle and intertwine, thus increasing the apparent viscosity of the grout [7].
The comparison between the results of yield stress of diutan gums and welan gum indicates in general that for similar dosage of VMA the grouts containing diutan gums led to greater values of yield stress than those of welan gum particularly for a low dosage (VMA=0.05%). It can be attributed to the diutan's molecular weight [12] and water retention. Furthermore, the carboxylic group attached to the backbone can be assumed to bridge particles and to competitively adsorb or complex with SP, thus reducing their dispersing effect. The increase of molecular weight led to improvement of water retention [19]. Thus, to achieve a similar viscosity, diutan gum required lower dosage than welan gum.

3.4 Effect of dosages of VMAs, SP, and MTK on plastic viscosity

Figure 5 describes the effect of MTK, VMAs and SP dosages and type of the corresponding VMAs on the plastic viscosity of grouts. The VMAs dosage had the greatest influence on plastic viscosities. The dosage of SP and MTK replacement level also influenced the plastic viscosity values.
An increase in VMAs dosage led to an increase in the plastic viscosity values for all of the grouts considered in this study. Adding 0.05% of WG, DG1, and DG2 to the mix made with 0.6% SP resulted in an increase in plastic viscosity of 380%, 815%, and 735%, respectively.
An increase in SP dosage induced a decrease in plastic viscosity values for any given dosage of VMAs. At 0.05% of VMAs, it appears that the plastic viscosity reduced significantly when the dosage of SP increased from 0.6% to 0.9% particularly for both diutan gums (DG1 and DG2).
It can also be observed that the addition of MTK resulted in a substantial increase in plastic viscosity due to the high surface area of MTK. Adding 7% MTK to the control mix without any SP and VMA led to very stiff mix and it was impossible to measure the plastic viscosity with vane viscometer.

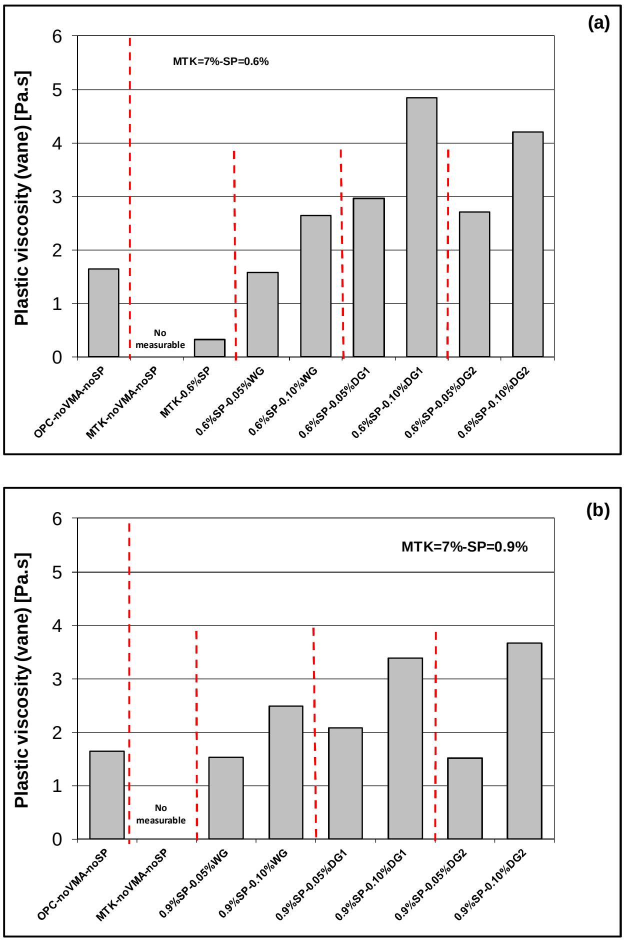


Fig. 5. Variation of plastic viscosity vs. VMAs, SP, and MTK.

In general, the plastic viscosities of diutan gums indicate that for similar dosage of VMA, the grouts containing diutan gums had greater values of the plastic viscosities compared to those of welan gum. It can be attributed to the diutan's molecular weight and polymeric architecture [12] and water retention ability [18].

4 Conclusions

Based on the results presented in this paper, the following conclusions have been drawn:
The addition of all three VMAs caused an increase in the yield values and a reduction in the corresponding fluidity compared to the reference mix.

Both plastic viscosity and cohesion plate values increased with the addition of all three VMAs.
The increase of SP led to an improvement of fluidity and a reduction of the plate cohesion, yield stress, and plastic viscosity values. This has attributed to better steric and electrostatic repulsions among the cement particles that react with SP which leads a better deflocculation of the particles in the paste.
The addition of MTK resulted in a reduction of fluidity and an increase in plate cohesion, yield stress, and plastic viscosity due to the high surface area.
DGs were better in controlling grouts fluidity and flowability. No significant difference was observed between DG-1 and DG-2.

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