Cement & Concrete Composites 23 (2001) 463–469

Cement & Concrete Composites

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Influence of key cement chemical parameters on the properties of metakaolin blended cements

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Abstract

The use of metakaolin (MK) as a mineral admixture for cement and concrete is a well-documented practice. The properties of cement pastes and mortars containing MK have been investigated as a function of key cement chemical parameters recognized as potential activators of the MK. Rheological behavior, initial setting time and compressive strength development have been compared by varying the total sulfate content, the nature of the added calcium sulfate and the free lime content (in the form of portlandite) in the cement. The results obtained indicate that it exists a compromise for the ratio performance/consistency in term of sulfate content and nature. Concurrently, a small addition of portlandite improves the consistency of the properties investigated. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Blended cement; Compressive strength; Metakaolin; Portlandite; Rheology; Setting time; Type of added sulfates; Total sulfate

1. Introduction

Metakaolin (MK) is a pozzolanic material that is essentially an anhydrous poorly crystallized aluminosilicate produced by calcining kaolin, a naturally occurring clay basically containing kaolinite ($Al_2Si_2O_5(OH)_4$) and, depending on the deposit, other minerals such as quartz, rutile etc. It is well recognized that blending such material with ordinary portland cement (OPC) leads to enhanced performance of mortars and concrete. Such benefits include higher level of long-term strength, lower permeability, reduced diffusion coefficients, increased sulfate resistance. Many of these features are linked to the refinement of the pore structure. Closely related to this, numerous references can be found in the literature [1–3]. The mineralogical properties of kaolin, the effects of calcination conditions, of the preparation and of the curing conditions on the mechanical strength of $MK/Ca(OH)_2$ pastes have been described previously [4–8]. Concurrently, the pozzolanic activation of MK as well as the properties of MK blended cements have also been extensively investigated elsewhere [9–13]. However, little information is available concerning the effects of variation (i.e., nature and/or content) of some key chemical parameters or substances contained in OPC, which are recognized as MK activators, and of their influence on properties. Therefore, in order to have insights on these aspects, the rheological behavior, initial setting time and compressive strength development of pastes and mortars made with MK blended cements have been compared by varying the total sulfate content, the nature of the added calcium sulfates and the free lime content of the cement. The results have been compared between them and, when appropriate, with those obtained on pastes and mortars prepared with neat OPC for reference. Please note that in this work, the effect of alkali sulfates in cement, recognized as MK activator has not been studied.

2. Materials and methods

2.1. Raw material selection for obtaining MK

A typical sample of a kaolin clay has been provided from a natural deposit and its composition has been determined by means of X-ray fluorescence and X-ray diffraction. Chemical composition in % by weight is as follows:

Mineralogical composition in % by weight is as follows: 65% kaolinite, 31% quartz, 2% muscovite-like micas and 2% rutile.

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SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	Na_2O	TiO_2	LOI	Total
59.4	25.5	1.4	0.2	0.2	0.1	1.9	11.7	99.8

2.2. Thermal treatment for obtaining MK

The following calcination procedure has been selected: samples of 400 g of kaolin clay were dried at 80°C, weighted in a platinum crucible and introduced in a laboratory furnace isothermally annealed at a temperature of 750°C (an optimal temperature for kaolin clay calcination recognized elsewhere [4–8]) for 120 min. At the end of this period, the calcined product was removed from the furnace and cooled down in a dessicator to ambient temperature. After this thermal treatment and prior to any blending, the samples were gently stirred to eliminate lumps. Full dehydroxylation of the kaolinite was ascertained by a differential thermal analysis of the sample.

2.3. Laboratory cement preparation

A sample from an industrial clinker has been provided for the study and its composition is shown in Table 1.

Starting from this clinker, two series of laboratory cements have been prepared.

Two OPC with and without the addition of 1% portlandite were prepared for reference purpose.

These references contain a total sulfate content of 3.5% and calcium sulfates added as a blend made of 50% gypsum – 50% hemihydrate. To obtain such cements, high purity (>95%) laboratory grade gypsum and hemihydrate obtained by dehydration of gypsum were suitably ground with clinker in a laboratory mill.

Since it was not possible to obtain another sample of industrial clinker with a higher level of free lime without altering other clinker parameters, an artificial addition of free lime was made in the form of portlandite: 1% (by weight of OPC) of high purity (>96%) laboratory grade portlandite was added after the grinding step by mixing with a sample of the ground material in a laboratory blender.

A series of 10 OPC were blended with 30% (by weight of blend) calcined clay. The blends were prepared by intergrinding.

The variables in the cements are the level of total sulfate content, the type of added sulfates and the level of portlandite. Three levels of total SO_3 content have been selected: 3%, 3.5% and 4% by weight of clinker, respectively. For each value of total SO_3, three types of added sulfate (100% gypsum or 100% hemihydrate or a blend of 50% gypsum – 50% hemihydrate) have been selected. Addition of 1% portlandite was also made after the grinding step.

Equal grinding mill speed has been applied regardless of the type of cement (30 rpm with a total of 2500 revolutions). Consequently, an average Blaine fineness of around 290 m^2/kg has been obtained for the neat Portland cements and around 580 m^2/kg for the corresponding blended cements having the same type of sulfates.

To avoid any influence of the grinding on the balance between gypsum and hemihydrate, the sulfates have been introduced in the mill after 1500 revolutions.

A summary of all the cement compositions is given in Table 2.

2.4. Rheological measurements

2.4.1. Background

The rheological behavior of cement paste is frequently described as a Bingham plastic behavior [14], for which the relationship between stress and rate of deformation can be expressed with two parameters, the yield stress (τy expressed in Pa or Nm^{-2}) and plastic viscosity (μ expressed in Pa s) as:

$$\tau = \tau y + \mu \times D, \tag{1}$$

where τ is the shear stress and D is the shear rate (in s^{-1}). τy is a measure of the force necessary to start a movement of the paste (i.e., the flow resistance) and μ is a measure of the resistance of the paste against an increase in the speed of movement (i.e., the viscosity).

The factor affecting the flow resistance is the extent to which particles are flocculated. Flocculation increases the yield stress considerably. The forces responsible for flocculation are often broken by shear. Usually, this breakdown is not complete and is often accompanied by

Table 1
Industrial clinker composition (% by weight) and subsequent Bogue calculation

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2	Mn_2O_3	P_2O_5
21.3	5.6	2.8	66.9	1.3	0.78	0.23	0.83	0.3	0.05	0.11
Free lime	Insol. res.	LOI	Total	K_2O soluble	Na_2O soluble	C_3S	C_2S	C_3A	C_4AF	
1.1	0.3	0.46	100	0.66	0.1	59.6	13.4	10.3	8.5	

Table 2
Summary of cements composition and their reference[a]

Type of cement	Total SO_3 (%)	Added sulfates type and balance	Addition portlandite (%)	Reference
OPC	3.5	50 G/50 HH		OPC
OPC	3.5	50 G/50 HH	1	OPC + p
B	3	50 G/50 HH		B3 G/H
B	3	50 G/50 HH	1	B3 G/H + p
B	3.5	100 G		B3.5 G
B	3.5	100 G	1	B3.5 G + p
B	3.5	50 G/50 HH		B3.5 G/H
B	3.5	50 G/50 HH	1	B3.5 G/ H + p
B	3.5	100 HH		B3.5 H
B	3.5	100 HH	1	B3.5 H + p
B	4	50 G/50 HH		B4 G/H
B	4	50 G/50 HH	1	B4 G/H + p

[a] Note for the abbreviations: B for blended, G for gypsum and H for hemihydrate and p for portlandite.

thixotropy. Thixotropy is a term used to describe the property exhibited by a system that is fluid under shear but develops a gel structure and becomes self-supporting when at rest [15]. Upon reagitation, the gel structure breaks and the paste is again fluid. Then, upon cessation of shear, the gel structure reappears with the self-supporting state. As a rule, thixotropic fluids behave as Bingham plastic fluids under shear and their behavior is defined by a yield stress and a plastic viscosity [16]. With thixotropic systems, the τy would be the shear stress necessary to initiate movement, i.e., measured at zero shear rate. For a nonthixotropic fluid, the yield value remains the same, whether the shear rate is increasing or decreasing. In the case of a thixotropic fluid, the yield stress is exhibited only upon withdrawal of shear. The process is frequently assumed to be reversible but it is seldom the case in cement fluids because there is a second source of time dependency – continuous chemical reactions which modify slurry properties with time in an irreversible manner. Nevertheless, the situation is somewhat simplified during the hydration induction period.

Since a cement paste incorporating finely divided particles, such as MK, may be prone to thixotropy [17], it has been decided to compare the evolution of the yield stress at almost zero shear rate in the different pastes.

2.4.2. Rheological measurement procedure

A shear vane rheometer has been used to characterize the yield stress. This method has been described elsewhere [18]. Here, a four-blade stainless steel vane has been used with the M150 torque-sensing head of a Haake Rotovisco RV 100 rheometer. Provided the vane is rotated at a sufficiently low speed, the sheared surface is cylindrical and the maximum torque can be used to calculate the yield stress. The advantage of this method is that the shear surface is within the material itself.

Yield stress values (τy) have been calculated from the maximum torque recorded τm occurring at a very low angular speed, using the following [17]:

$$\tau y = B \times \tau m \quad \text{with } B = 2/\pi \times D^3 \times (H/D + 1/3), \qquad (2)$$

where H is the height of the vane expressed in mm and D is the diameter of the vane expressed in mm.

Cement pastes with a W/C of 0.4 have been mixed with a laboratory paddle mixer at a constant speed of 180 rpm for a period of 5 min. Afterwards, the mixtures have been poured in a 10 mm diameter cup in which they have been allowed to stand for an overall period of time of 90 min in order to run the yield stress measurement. An angular speed of 0.5 rpm has been chosen for all the measurements.

Measurements have been performed at 5, 15, 30, 60 and 90 min. The vane was immersed in the cup containing the cement mixtures such that it was at least one blade height distant from both the cup bottom and the free surface of the cement paste. The time allowed for the recording of the maximum torque during a measurement was 15 s. Between each measurement, the paste was left in static conditions in the cup while the vane has been removed and cleaned.

On the basis of visual inspection of the pastes after mixing, an appropriate size of vane was selected to offer the best sensitivity. In case of fluid pastes (i.e., the plain OPC pastes), a vane of 75 mm height and 28.6 mm diameter was used. Since most of the pastes were somewhat stiff, a vane of 35.8 mm height and 22.3 mm diameter was used for the characterization of the yield stress of the MK mixtures.

2.5. Setting time measurement

Initial setting time has been measured on cement paste at a water to cement ratio of 0.4 using a Vicat needle apparatus. Such water to cement ratio has been selected to allow comparison with the rheological measurements.

2.6. Compressive strength

Compressive strength has been measured after 3 and 28 day curing periods on mortar prisms (series of 3) prepared as per the European standard EN 196-1. $40 \times 40 \times 160$ mm^3 prisms have been cast and demolded after 1 day and immediately immersed in a water bath at 20°C until the day of testing. For each set of prisms, the three results have been averaged.

3. Results and discussion

3.1. Rheological behavior

The rheological results obtained at 5 and 90 min are illustrated in Figs. 1–3. Fig. 1 shows the comparison of the yield stress between the two OPC (Fig. 1)(a) and the MK blended cements having the same sulfate content (Fig. 1)(b) at 5 and 90 min, respectively. Overall, the presence of MK increases significantly both the 5 and 90 min yield stress when compared to the neat reference cements. It confirms the well-known characteristics of the MK blended cements: their high water demand and subsequent thixotropic behavior, or their ability to build up a structure upon standing. In both the OPC (Fig. 1)(a) and the blended cement pastes (Fig. 1)(b), addition of portlandite provides a slight fluidification at 5 min. The effect of portlandite becomes more pronounced at 90 min in the blended cement pastes since less resistance to flow is observed.

The influence of sulfate type (with a total sulfate content of 3.5%) is illustrated in Fig. 2, rheological results obtained at 5 min indicate that the MK blended cement with 100% hemihydrate exhibits a much higher yield stress, likely related to a plaster set, than that observed in the two other systems for which the rheological behavior is similar. At 90 min, the situation is reversed with the 100% plaster system exhibiting a lower yield stress than the two other systems.

The addition of portlandite (Fig. 2) in the hemihydrate system leads to a stiffening effect while it leads to a slight fluidification in the two other systems at both 5 and 90 min.

The variation of the total sulfate content from 3% to 4%, as illustrated in Fig. 3, results in a slight increase of the 5 min yield stress while the addition of portlandite in such systems has little or no effect. Overall, the variation of total sulfate content does not much influence the consistency of the initial rheology.

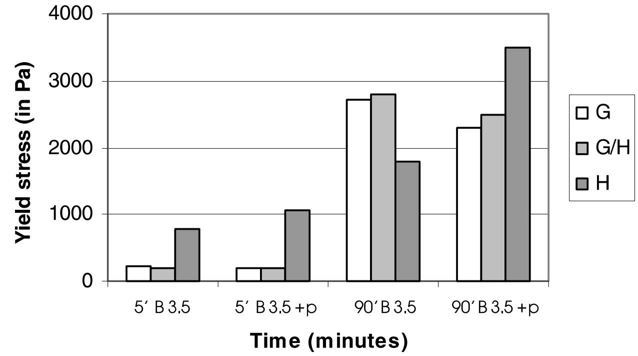

Fig. 2. Yield stress at 5 and 90 min in pastes containing blended cements with different type of sulfates (total sulfates content: 3.5%).

At a period of 90 min, the higher the total sulfate content, the lower the fluidity. The effect of portlandite is contrasted at 90 min (Fig. 3): the highest resistance to flow is observed with the lowest level of total sulfate and the lowest resistance to flow is observed with the highest level of total sulfate. However, the most interesting feature is that the portlandite addition seems to level off

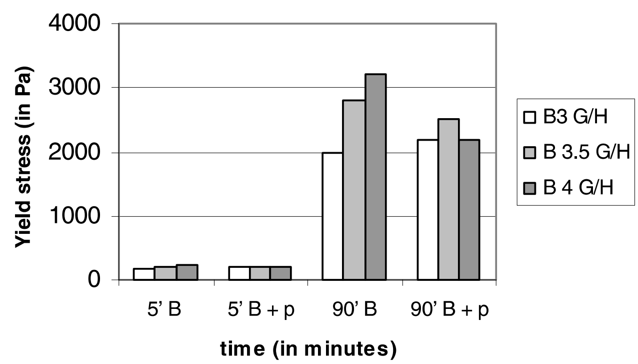

Fig. 3. Yield stress at 5 and 90 min in pastes containing blended cement with different total sulfates content (type of added sulfate: 50% G/50% SH).

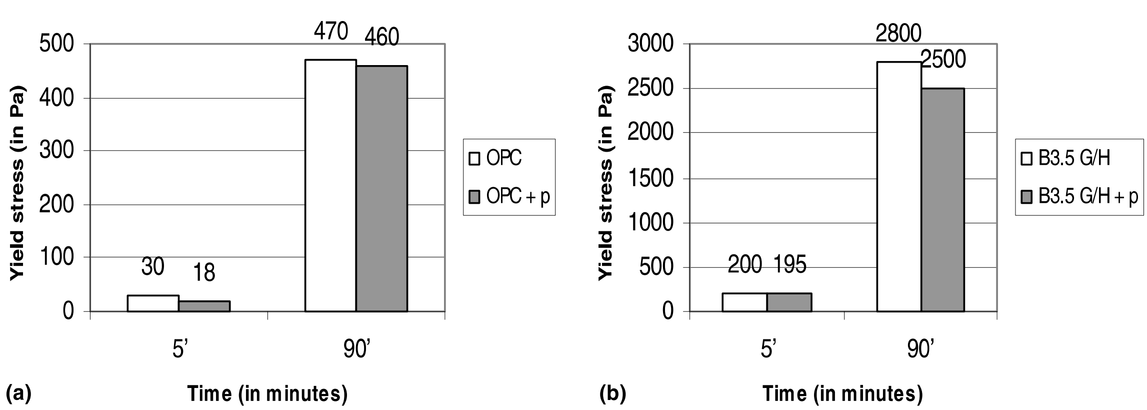

Fig. 1. Yield stress at 5 and 90 min in OPC pastes (a) and pastes containing blended cement with same type of sulfates (b).

the effect of the total sulfate variation and leads to a better consistency between systems.

3.2. The setting time

The setting time results are illustrated in Figs. 4 and 5(a) and (b).

Overall, the MK blended cements have a much shorter setting time compared to those obtained with the neat reference cements (Fig. 4). It is a confirmation of the well known accelerating effect of fine reactive MK on the hydration of the OPC. The marked stiffening rate observed during the rheological measurements may be partially linked to the faster hydration process.

Among the blended cements, setting time is somewhat similar regardless of the type of calcium sulfate or level of total sulfate (Fig. 5)(a) and (b). It appears that batch to batch variation due to sulfate does not have an effect on the setting time consistency. The addition of portlandite has a small accelerating effect in the OPC pastes (minus 16 min) as expected (Fig. 4). On the contrary, a small retarding effect (average of 7 min retardation) is observed in the MK blended cement pastes (see Figs. 4 and 5). The highest retarding effect (plus 20 min) is observed in the 100% gypsum system.

It is assumed that the setting time of each blended system corresponds closely to the time taken for the formation of a significant ettringite content [11]. With the addition of 1% portlandite, the formation rate of ettringite seems to be slightly hindered.

The rheological behavior, when portlandite is added, indicated a higher fluidity retention at 90 min and this feature may be partially explained by the retarding effect that delays the particle–particle bonds, hence the interactions.

3.3. Compressive strength

The compressive strength results are shown in Figs. 6 and 7(a) and (b), respectively. Please note that the accuracy is ±1.5 Mpa.

The compressive strength obtained with the OPC (see Fig. 6) is, as expected, higher than the one obtained with the corresponding blended cements having the same sulfates: plus 12 MPa at 3 days and plus 5 MPa at 28 days. Addition of the portlandite decreases the compressive strength of the OPC at 28 days (see Fig. 6). In

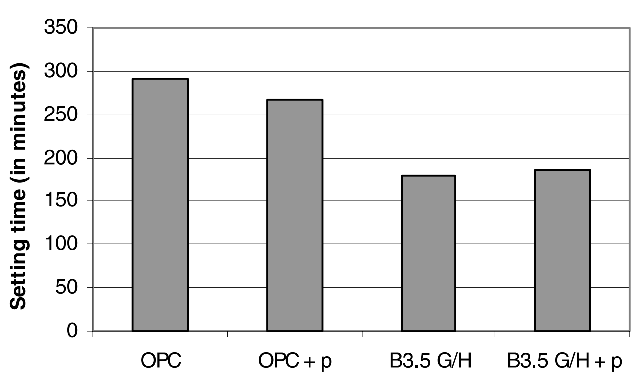

Fig. 4. Initial setting time comparison in OPC pastes and MK blended cements with same type of added sulfates and same total sulfates content.

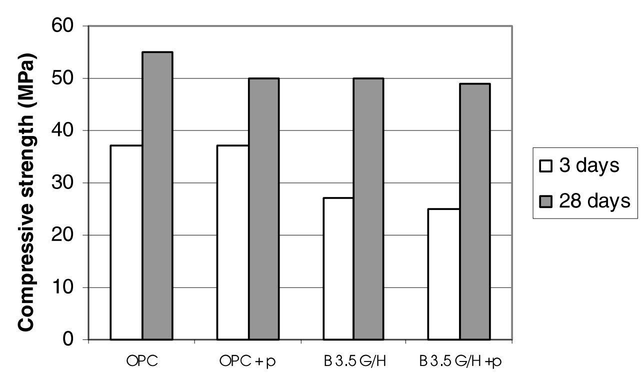

Fig. 6. Compressive strength comparison in OPC mortars and MK blended cements with same amount and type of added sulfates.

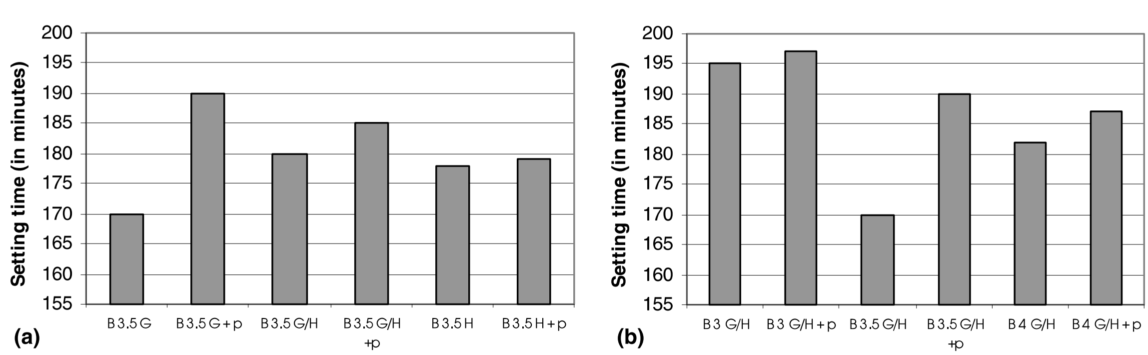

Fig. 5. Initial setting time comparison in pastes containing MK blended cements with different type of added sulfates (a) and different sulfates content (b).

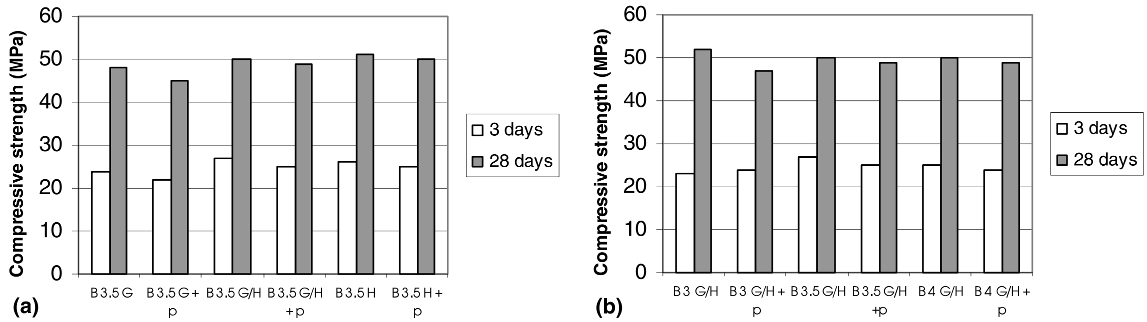

Fig. 7. Compressive strength comparison in mortars containing MK blended cements with different types of added sulfates (a) and different total sulfates content (b).

the MK blended cement mortars, the compressive strength is not significantly affected by the type of sulfate (see Fig. 7(a)). At 3 days, the 100% gypsum system exhibits slightly lower compressive strength when compared to the other systems.

Regarding the influence of the total sulfate level, little effect is observed (see Fig. 7(a)). However, the higher compressive strength at 3 days is obtained with 3.5% sulfate but with 3% sulfate at 28 days. Overall, it could be considered that the optimum for strength in terms of sulfate is obtained by selecting a total sulfate content of 3.5% along with a 50% gyspum/50% hemihydrate mix of added calcium sulfates. When portlandite is added, the highest compressive strength at 28 days is obtained with 3.5% total sulfate. It must be pointed out that the addition of portlandite decreases slightly the 28 day compressive strength, especially in the 100% gypsum system but the overall effect is less pronounced when compared to that observed with the reference OPC.

4. Conclusions

In this study, it has been observed that variations of key levers such as total sulfate content, nature of sulfates and addition of portlandite have a moderate effect on short term properties of the MK blended cements such as rheology, setting time and 28 days compressive strength. Rheology is the property most affected by those levers. Nevertheless, it appears that there is an optimum in terms of sulfate for the ratio performance/consistency that is, with this particular clinker, a total sulfate content of 3.5% along with the 50% gypsum – 50% hemihydrate mix of added calcium sulfates. Concurrently, the small effect of portlandite addition in such blended cements results in a slight decrease of the flow resistance, a small retardation effect and a slight lowering of compressive strength but overall it is accompanied with a better consistency of the properties when taking into account the sulfate variation. The effect of portlandite addition is minimized for a total sulfate content of 3.5% with a mix of 50% gypsum – 50% hemihydrate.

Acknowledgements

Permission for publication of this paper is gratefully acknowledged to Lafarge management.

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