INFLUENȚA TEMPERATURII ASUPRA REZISTENȚEI LA ATAC SULFATIC A BETONULUI CU FILER DE CALCAR
INFLUENCE OF TEMPERATURE ON THE RESISTANCE TO SULFATE ATTACK OF LIMESTONE FILLER CONCRETE

GUANGBIN QU[1*], AILIAN ZHANG[2]
[1]School of Architecture, Harbin Institute of Technology, Harbin 150001, China
[2]Department of Civil Engineering, Sichuan College of Architectural Technology, Deyang 618000, China

Cement mortar prisms were made with three different cementitious materials (with or without mineral admixture) plus 30% mass of limestone filler. After 28 days of curing in water at room temperature, these samples were submerged in 2% magnesium sulfate solution at different temperatures (5^{0}C, 20^{0}C and alternate temperature between 5^{0}C and 20^{0}C) for a year. The strength development was measured on these immersed prisms at intervals, and samples selected from the surface of prisms were examined by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR). The results show that the influence of temperature on the resistance to sulfate attack of mortar is related to the binder compositions. A higher temperature leads to a quicker strength loss of the mortar without mineral admixture. For blended cements, a higher temperature is favorable for the pozzolanic reaction of mineral admixture and the overall deterioration of mortar is reduced. After 1 year of exposure to magnesium sulfate solutions, the formation of thaumasite was checked in the OPC mortars at both 5^{0}C and 20^{0}C. It is concluded that the thaumasite formation is not limited to structures at low temperature (less than 15^{0}C).

Au fost realizate prisme de mortar cu trei diferite materiale liante pe bază de ciment (cu sau fără adaos mineral), plus 30% filler de calcar. După 28 de zile de păstrare în apă, la temperatura camerei, aceste probe au fost imersate în soluție de 2% sulfat de magneziu la temperaturi diferite (5^{0}C, 20^{0}C şi cicluri alternante între 5^{0}C şi 20^{0}C pe o durată de un an. Evoluția rezistențelor a fost măsurată la diferite termene. De asemenea, de la suprafața prismelor au fost prelevate probe care au fost examinate prin difracție de raze X (XRD) şi spectroscopie în infraroşu cu transformata Fourier (FTIR). Rezultatele arată că influența temperaturii asupra rezistenței mortarului la atacul sulfatic este în corelație cu compoziția liantului. Expunerea mortarului pe bază de ciment fără adaos la o temperatură mai mare duce la o pierdere de rezistență mai rapidă. Cimentul ca adaos are avantajul că o temperatură mai mare favorizează reacția puzzolanică, iar deteriorarea generală a mortarului este mai redusă. După 1 an de expunere la soluții sulfat de magneziu, formarea de thaumasit a fost verificată în mortare pe bază de ciment portland atât la 5^{0}C cât şi la 20^{0}C. S-a ajuns la concluzia că formarea thaumasitului nu se limitează la structuri de temperatură joasă (mai puțin de 15 ℃).

Keywords: *cement, mineral admixture, sulfate attack, temperature, thaumasite*

1. Introduction

In recent years, it has become a common practice to incorporate fine limestone powder as an additional constituent in the cement or concrete production. The European standard allows the use of the term "Portland-limestone cement" with incorporation of 5–35% limestone [1]. A high volume of limestone filler is also used frequently to increase the content of fine particles and optimize the particle packing in self-compacting concrete (SCC) mixes [2]. The use of limestone in cements or concretes seems to have many benefits, such as reducing water demand, improving strength development, and being economical [3-4]. However, it has been widely reported that another kind of sulfate attack, attributed to the formation of thaumasite ($CaSiO_3$•$CaCO_3$•$CaSO_4$•$15H_2O$), occurs in the cements and concretes containing limestone in recent years [5-7]. Though most researchers believe that thaumasite forms in cool conditions(lower than 15^{0}C) [8], there are some conflicting viewpoints on the effects of temperature on thaumasite formation and thaumasite induced attack in concretes containing limestone filler [9-10]. Therefore, more work is needed to verify the effects of temperature on sulfate attack of limestone filler cements and concretes.

2. Experimental

The cement used is ordinary Portland cement (OPC) with strength grade of 42.5, with a density of 3.1g/cm^3 and specific surface area of 350m^2/kg. The limestone was ground to a specific surface area of 400m^2/kg. Three mineral admixtures were used: fly ash (FA), with grade of Ⅱ according to Chinese Standard GB1596-2005; ground granulated blastfurnace slag (GGBS) with specific surface area of 400m^2/kg; silica fume (SF) with

* Autor corespondent/Corresponding author,
Tel.: +86-451-87070701, e –mail: gguangbin2011@163.com

Table 1

Mortar mixture proportions/*Compoziția mortarelor* (kg)

No.	OPC *Ciment porland*	SF *Silice ultrafină*	GGBS *Zgură granulată de furnal*	FA *Cenuşă zburătoare*	Water *Apă*	Sand *Nisip*	Limestone *Filer de calcar*
C0	1	0	0	0	0.6	2.2	0.3
C1	0.7	0.05	0.25	0	0.6	2.2	0.3
C2	0.6	0	0.25	0.15	0.6	2.2	0.3

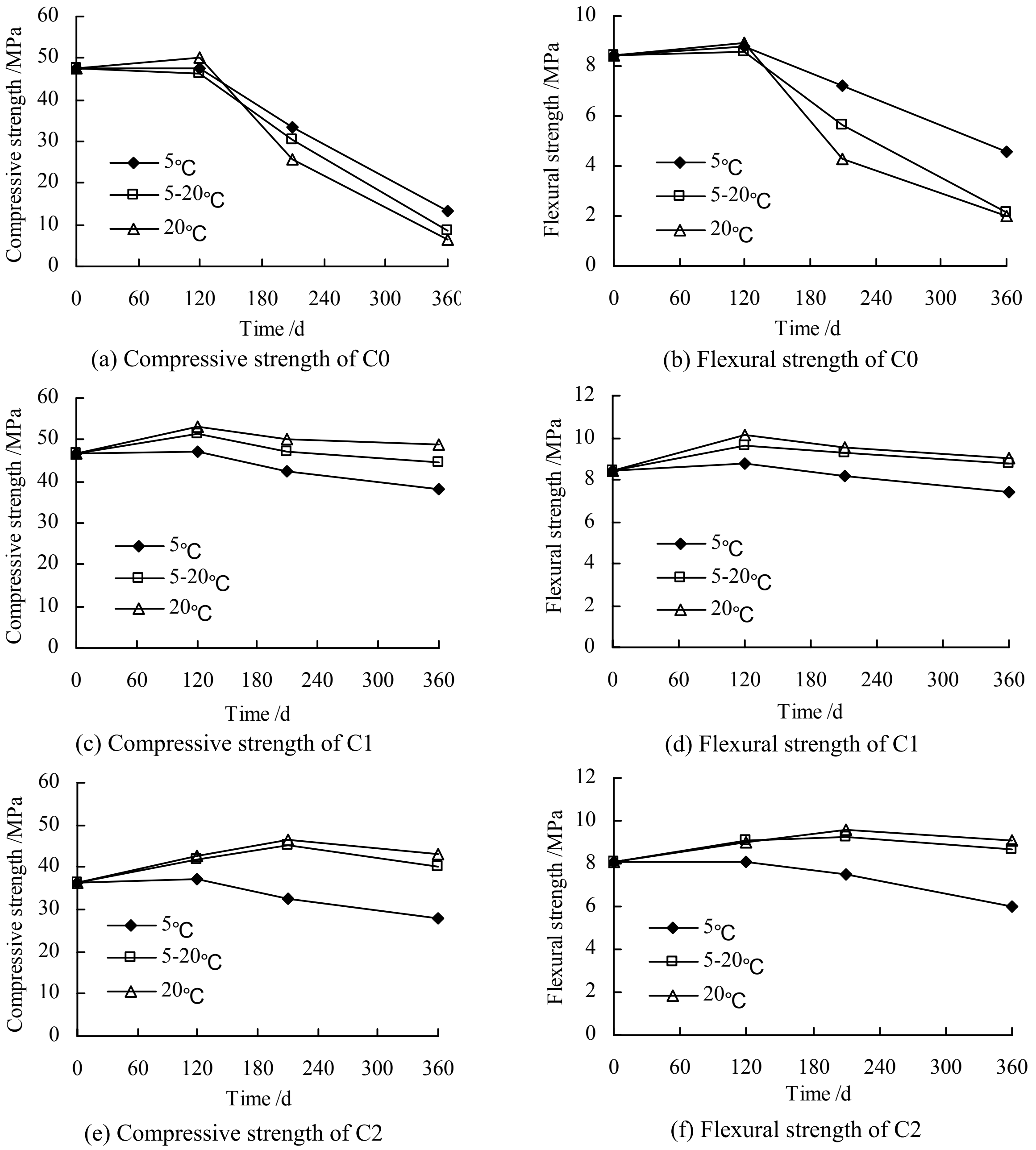

Fig. 1 - Strength development of the mortars with immersion times/*Evoluția rezistenței mecanice a mortarelor imersate în soluție 2% de sulfat de magneziu.*

specific surface area of 23000m^2/kg. A quartz sand was used with a fineness modulus of 2.6 and density of 2.65g/cm^3. Synthetic $MgSO_4$ was used to prepare the sulfate solutions.

Mortar prisms (40x40x160 mm) were cast according to the mixture proportions presented in Table 1. After 24 hours in a moist cabinet, they were removed from the mould and cured in water at room temperature (20±2^{0}C). After 28 days curing in water, the mortar specimens were stored into 2% $MgSO_4$ solutions with three different temperatures (with a fluctuation of ±1^{0}C): (1) 5^{0}C,

(2) 20^0C and (3) cycling temperatures of 5^0C and 20^0C (three days at each temperature). In each case, the sulfate solution was replaced every 2 months and the volume ratio of solution to mortar specimens was kept at about 2:1. The strength measurement of mortar specimen was performed at regular intervals up to 1 year. Samples were selected from the surface of prisms after strength testing at different immersion ages. X-ray diffraction (XRD) and Fourier transform infrared (FTIR) spectroscopy were used to analyze these samples and distinguish the degraded products of the limestone filler cement mortars after exposure to different sulfate environments.

The XRD analysis was conducted using an automated Japan D/MAX-□A X-ray diffractometer operating at 35 kV and 30 mA using CuKα radiation. Data was collected between 5° and 60° 2θ using a step-size of 0.02° and a count time of 0.6 s per step. Fourier transform infrared (FTIR) spectroscopy was carried out using a Nicolet 60 SXB FTIR Spectrophotometer. The wavenumber ranges from 400cm^{-1} to 4000 cm^{-1}.

3. Results and discussion

3.1. Strength development

Figure 1 presents the strength development of mortar specimens immersed in sulfate solution at different temperatures. No significant strength reduction occurred on the OPC mortar during the beginning 3 months at different temperatures, and even the flexural strength increased a little.

With the continued exposure to sulfate attack, the strength of OPC mortar began to decrease and the strength loss increased evidently with the increasing of immersion time. After 1 year of immersion, the OPC mortar showed 72.3%, 82.3% and 86.4% of compressive strength loss when exposed to sulfate solutions at 5^0C, cycling temperatures of 5^0C and 20^0C and 20^0C respectively. The flexural strength loss was 45.6%, 74.8% and 76.3% for the OPC mortar stored at 5^0C, 20^0C and cycling temperatures of 5^0C and 20^0C respectively. So the increasing temperature accelerates the deterioration and strength loss of OPC mortar under sulfate attack.

The two blended cement mortars showed some visible strength growth during the first several months of immersion in sulfate solutions, and the higher the solution temperature is, the more the strength growth is. Because fly ash has a slower reactivity and its pozzolanic reaction keeps up for a longer time than blastfurnace slag and silica fume, the immersed Mortar C2 had a more strength growth after the initial curing than Mortar C1, especially at the two higher temperature conditions. With the worsening of sulfate attack on mortar, the strength of the two blended cement mortars began to decrease during the later period of immersion. After one year immersion in sulfate solution at 5^0C , the compressive and flexural strength of Mortar C1 were decreased by 18% and 12.1% respectively. But for Mortar C1 being stored at 20^0C, the compressive and flexural strength were, however, increased by 4.8% and 7.9% respectively. A similar tendency was found on Mortar C2. Its compressive and flexural strength were reduced by 23% and 25.7% respectively after 1 year storage at 5^0C; but, were increased by 19% and 12.6% respectively after 1 year storage at 20^0C. It can be found that a high environment temperature improves the resistance to sulfate attack of the blended cement, and such influence is stronger when the used mineral has a slower potential reactivity. But in any case, the blended cement mortars showed a less strength loss than the OPC mortar, and it means that the addition of these mineral admixtures effectively improves the resistance of mortar to sulfate attack.

3.2. Mineralogy

The samples were selected from the surface of mortar prisms before immersion and after 1 year immersion into different sulfate solutions. Their XRD patterns are shown in Figure 2 (2 theta from 5 to 35 degree). In all samples, there are obvious peaks corresponding to quartz (SiO_2) from the sand and calcite ($CaCO_3$) from the limestone filler. Before immersion, some monocarboaluminate ($3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$) and a mass of portlandite ($Ca(OH)_2$) formed in the mortars as hydration products of cement and limestone filler, and their peaks are much stronger in the OPC mortar than in the blended cement mortar. After 1 year exposure to sulfate attack, only a small amount of portlandite can be found in the mortars at 5^0C, even no detectable trace of portlandite can be seen in the samples at 20^0C, and no monocarboaluminate existed in all the immersed mortars. At the same time, some sulfate-bearing substances including ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$), thaumasite ($CaSiO_3{\cdot}CaCO_3{\cdot}CaSO_4{\cdot}15H_2O$) and gypsum ($CaSO_4{\cdot}2H_2O$) formed instead. For Mortar C0, there is much more such sulfate-bearing substances, epecially gypsum and ettringite, which corresponds to a higher deterioration on the mechanical property, in the sample at 20^0C than that at 5^0C.

From the attack products formed in Mortar C1, no obvious difference can be found between the two immersed samples at different temperatures. Therefore it is expected that the consumption of portlandite is also attributed to, besides sulfate attack, the pozzolanic reaction of mineral admixtures in the blended mortar at 20^0C. On the other hand, a little brucite ($Mg(OH)_2$) was also detected from Motar C0 at 20^0C, and its formation accelerated the mortar damage. No trace of brucite was found in other samples because a limited magnesium attack occurred and

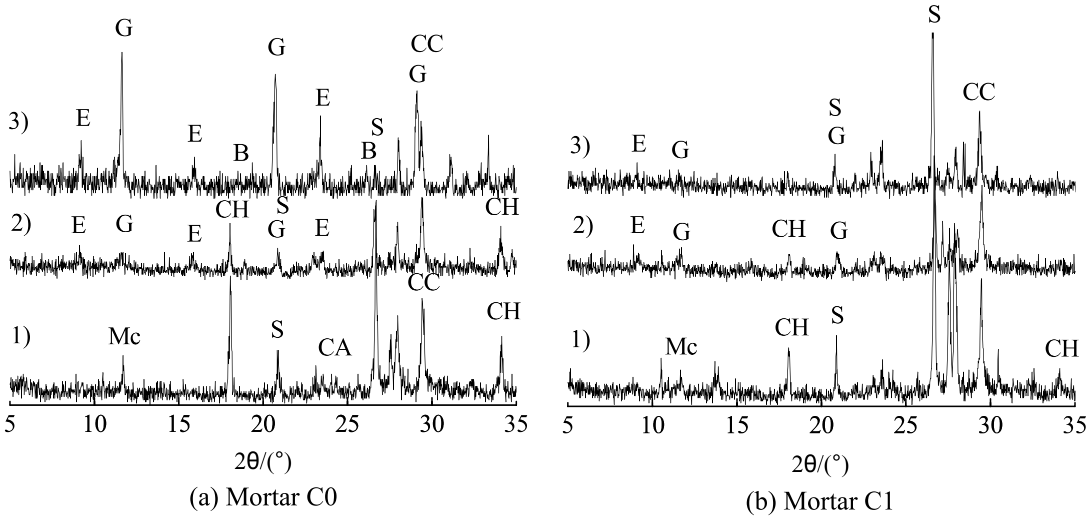

Fig. 2 - XRD patterns of the mortars before and after immersion in sulfate solutions with different temperatures. 1) before immersion; 2) at 5^{0}C for 1 year; 3) at 20^{0}C for 1 year. (E—ettringite and/or thaumasite; G—gypsum; CH—portlandite; Mc—monocarboaluminate; CC—calcite; S—quartz; B—Brucite) / *Difractogramele mortarelor înainte şi după imersia în soluție de sulfat de magneziu, la diferite temperature 1) înainte de imersie; 2) la 5^{0}C, timp de un an; 3) la 20^{0}C timp de un an.*

most of the formed brucite layers were peeled off from these samples.

Because it is not easy to distinguish between ettringite and thaumasite only by using XRD patterns [11], further investigation was made using FTIR spectroscopy as shown in Figure 3. According to the previously published document [12], the obvious peaks at 501 cm^{-1} and 669 cm^{-1}, which were detected in all the samples, are assigned to the presence of SiO_6 bonds. Octahedral Si is such an extremely rare co-ordination state for mineral silicates that the presence of these two peaks indicates the formation of thaumasite at three different temperatures. The strong peaks at around 1110 cm^{-1} associated with S-O show that a great deal of sulfate-bearing substances formed in all samples. The Mg-O peak [13] at around 470 cm^{-1} presents that the magnesium attack occurred and the transformation C-S-H into M-S-H happened in mortar C0 at all the three temperatures, and the higher temperatures seemed to enhance such attack on mortar. The C-O peaks at 875cm^{-1} and around 1400cm^{-1} are occurring in all the samples as expected, and they are attributable to the presence of carbonates (such as calcite and thaumasite).

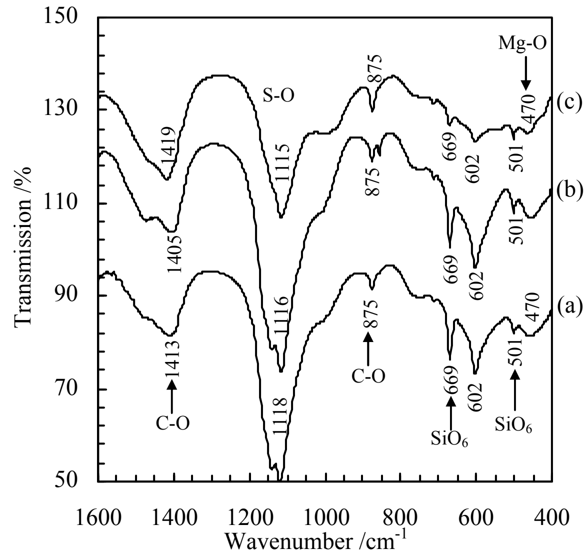

Fig. 3 - FTIR spectra of Mortar C0 after exposure to different sulfate solutions for 1 year. (a) at 5^{0}C; (b) at 20^{0}C; (c) at cycling temperature/*Spectrele FTIR ale mortarului C0 după expunerea timp de un an în soluție de sulfat: a) la 5^{0}C; b) la 20^{0}C, c) la temperaturi alternante.*

3.3. Discussion

From the visual observation and strength measurement reported in Section 3.1, it can be clearly found that the temperature has a different influence on the deterioration of OPC and blended cement mortar exposed to sulfate attack. In fact, there are two opposite chemical reactions happening in the mortar immersed in sulfate solution for a long time. On the one hand, the invasion of sulfate into mortar and its reaction with cement hydrates leads to the deterioration of mortar; on the other hand, the continuing hydration of cementitious material improves the property of mortar. For the OPC mortar, most of the cement hydrates during the initial curing period and the temperature mainly influences the sulfate reaction to hydrates other than the continuing hydration of cement during the mortar's immersion in sulfate solution. According to Santhanam [14], an increase in temperature of the attacking solution results in the increasing rate of deleterious ions diffusion into mortar. Hence, the formation of gypsum, ettringite and brucite, the depletion of CH and the decalcification and decomposition of C-S-H would be accelerated when the temperature is increased. As a result, Mortar C0 showed more badly deterioration at 20^0C than at 5^0C after 1 year immersion in sulfate solution. However, much mineral admixture, which has a much slower reactivity than cement, is used in the blended cement mortar and its pozzolanic reaction induces the continuing increase of mortar's strength after the initial curing. Ma's research [15] shows that the pozzolanic reaction of mineral admixture is obviously activated and reinforced by a high temperature. The positive influence of high temperature on the pozzolanic reaction maybe exceed its negative influence on the sulfate attack deterioration of mortar, therefore the overall deterioration of the blended cement mortar is reduced with the increasing temperature and such influence of temperature becomes greater when the used mineral admixture has a slower reactivity.

Most researchers [16,17] believe that thaumasite forms below 15^0C, especially at about 10^0C or less, ideally within the range 0-5^0C under cold damp conditions. This viewpoint has also been supported by many thaumasite form of sulfate attacks occurred in field concretes in UK, Italy, Germany, and Canada. Bensted [18] even suggested that thaumastie formation reaction does not occur to any perceptible extent at about 20□ or above. In the report from the Thaumasite Expert Group (TEG), it is advised that 'Fairly low temperatures, generally less than 15^0C, are needed for vigorous formation of thaumasite'[19]. Thus, 15^0C has been often regarded as the upper threshold for determining the thaumasite sulfate attack in practice. However, Diamond [9] reported that significant contents of thaumasite have been found in a building located in Southern California, a region with mild temperatures. Irassar [10] found that thaumasite occurred, near the surface of OPC+ 20% limestone filler mortars, as the final stage of sulfate attack at (20±2^0C). XRD and FTIR analyses presented here on samples from Mortar C0 confirm the formation of thaumasite after 1 year exposure to sulfate solutions at three different temperatures. In this experiment, it is not easy to determine the effect of temperatures on the amount of thaumasite formed in the attacked mortars. In any case, it reveals that the formation of thaumasite does not be limited to low temperature, and it may affect a broader range of structures than expected.

4. Conclusions

● The influence of temperature on the resistance to sulfate attack of cement mortar is related to the binder compositions. On the one hand, a higher temperature leads to a quicker deterioration (due to more ettringite, gypsum and brrcite formation) of the mortar without mineral admixture after a long exposure to sulfate; on the other hand, a high temperature is favorable for the pozzolanic reaction of mineral admixture and the overall deterioration of blended cement mortar is alleviated with the increasing temperature. When the used mineral admixture has a lower reactivity, such influence of temperature on resistance to sulfate attack of blended cement mortar becomes greater.

● At the three different temperatures, the addition of either SF plus GGBS or GGBS plus FA effectively improves the resistance of mortar to sulfate attack. According to the temperature's influence on sulfate attack, it is necessary to execute a long enough initial curing on the concrete when a high addition of mineral admixture with a slow reactivity is used to improve the resistance to sulfate attack.

● After 1 year of exposure to sulfate solutions, the formation of thaumasite was checked in all the OPC mortars at three different temperatures. It is concluded that the thaumasite formation does not be limited to structures at low temperature (less than 15^0C).

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MANIFESTĂRI ŞTIINȚIFICE / SCIENTIFIC EVENTS

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- Polymer admixture for concrete
- Fiber reinforcement of concrete-polymer composites
- Polymer fiber reinforced concrete
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- Others

Contact: icpic2013@tongji.edu.cn

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