HYDRATION AND PORE STRUCTURE EVOLUTION OF WHITE CEMENT PASTE AT EARLY AGE BASED ON ^{1}H LOW-FIELD NUCLEAR MAGNETIC RESONANCE

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In order to investigate the hydration and pore structure evolution of wet white cement paste at early age, the transverse relaxation time (T_2) spectrum signals of wet white cement paste were tested by ^{1}H low-field nuclear magnetic resonance (NMR). The effects of water to cement (W/C) ratio on the T_2 spectrum, T_2 geometric average values, hydration degree and pore structure of the cement paste samples hydrated within 168 h were studied. The results show that the T_2 can characterize the hydration process and pore structure of wet white cement paste. With the increase of hydration time, the T_2 peak area and T_2 geometric average values decrease gradually. The hydration degree of cement increases rapidly within the first 24 h, and then slows down gradually after 24 h. For the cement pastes hydrated from 0 h to 7 h, most of the evaporable water is filled in the capillary pores in the range of 10 nm ~1000 nm. With the continuous hydration of cement, the water in these pores is consumed and the peak pore radius decreases constantly. The increase of W/C ratio can improve the hydration degree, but results an increase in the porosity and the proportions of larger pores.

Keywords:*^{1}H low-field NMR; hydration; pore structure; white cement*

1. Introduction

Hydration and microstructure formation of cement paste are the combinations of many chemical and physical processes taking place after contact of the dry cement with water [1,2]. The processes are very complicated and hard to comprehend completely. Furthermore, the simultaneous observing of hydration and microstructure formation in fresh cement pastes is also an significant issue for assessing the performance of cement-based materials and adjusting their compositions [3,4].

Nowadays, many traditional characterization methods including the hydration calorimeter, scanning electron microscopy (SEM), mercury intrusion porosimetry (MIP) and nitrogen adsorption methods have been widely used to analyze the hydration and pore structure evolution of cement pastes [5-8]. However, these methods still have many disadvantages. The hydration heat measurement requires thermal insulation, and is not appropriate for heat-cured cement-based materials. Most other characterization methods including SEM and MIP, etc., require drying of the sample prior to measurement. The exposure of cement-based materials in drying environment may vary the hydration process and the pore structure [2,9]. Therefore, it is significant to develop new characterization methods that can be applied to the wet fresh cement paste.

^{1}H low-field nuclear magnetic resonance (NMR) may be a fast and potential non-invasive technology for the measurement of the hydration and pore structure of wet cement paste[10-12]. The basic principle of ^{1}H NMR is based on the spin of hydrogen proton and precession at a certain frequency under the action of external magnetic field. By applying a radiofrequency pulse to the hydrogen proton, the low-energy proton obtains the energy and converts into high-energy state. When the radiofrequency pulse turned off, the spin nuclear returns from the high-energy state to the low-energy equilibrium state and the macro magnetization vector relaxes to the equilibrium state [13,14]. Hence, the amounts of water molecules in different states can be measured by ^{1}H NMR based on different times of recovery from the excited state to the ground state, which are called the relaxation times.

Previous studies [15,16] have documented the relationship of the transverse relaxation time (T_2) distribution with the hydration process of cement paste. Ji et al. [16] has qualitatively studied the relevance of the T_2 distribution to the curing age, hydration process, bleeding ratio and pore structure of cement pastes. Hu et al. [17] used ^{1}H NMR to gain the cumulative pore volume and predict the internal humidity of the cement paste.

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Table 1

Chemical compositions of white cement (wt %)

	SiO_2	Fe_2O_3	Al_2O_3	CaO	MgO	K_2O	Na_2O	Loss on ignition
Cement	25.18	0.20	2.98	63.54	1.87	0.76	0.25	2.14

Fischer et al. [18] observed that the peak at 0.25 ms in the T_2 spectrum represented water in gel pores and 1.25 ms for interlayer water. Heijden et al. [19] also pointed out that T_2 spectrums of less than 0.28 ms, range from 0.28 ms to 3 ms, and greater than 3 ms, represented to water in the gel pores, the capillary pores and micro cracks or air voids, respectively. In addition, many studies [20-22] have investigated the variation trends of the T_2 distribution with the different water to cement (W/C) ratios, curing temperatures and ages of the cement pastes. The results implied that there is an obvious correlation between the T_2 distribution and W/C ratio as well as curing age. However, the present studies of cement hydration based on ^1H NMR were still less and mainly performed qualitative analyses, and the T_2 distributions were rarely used for the further analysis of the early hydration and pore structure evolution.

In this study, ^1H NMR was used to investigate the hydration process of white cement pastes hydrated within 168 h. Through the noninvasive and nondestructive method, more detailed information in respect to the hydration and pore structure of cement pastes with different W/C ratios were achieved.

2. Experimental

2.1 Raw materials

There is a certain amount of paramagnetic ion such as Fe in Portland cement that may result in some certain errors in the measurement of ^1H NMR [23]. Therefore, white cement containing small amount of Fe_2O_3, was used in this experiment. Table 1 shows the chemical compositions of white cement. The specific surface area and density of white cement are 335 m^2/kg and 3.15 g/cm^3, respectively. The water used in this study is deionized water.

2.2 Preparation of specimens

Cement pastes with W/C ratios of 0.3, 0.4 and 0.5 were prepared, respectively. Before the NMR tests, about 100 g of the fresh cement pastes with different W/C ratios were mixed quickly, then approximate 10 g of them were poured into cylindrical glass bottles, as is shown in Figure 1. Thereafter, the corresponding glass bottles were put in a curing room at 20 °C. At the different ages of curing, the corresponding glass bottles were firstly weighed and then put into the sample tube of NMR instrument for T_2 signal tests.

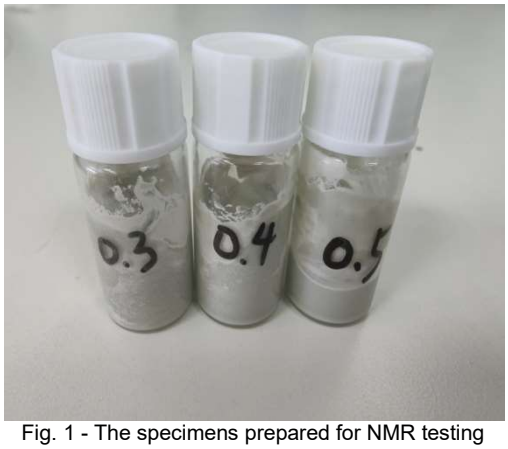


Fig. 1 - The specimens prepared for NMR testing

2.3 ^1H NMR

A ^1H NMR instrument with a model of MesoMR23-060H was provided by Niumag Analytical Instrument Corporation, Suzhou, China. Figure 2 presents the NMR instrument used in this experiment. The measurements of ^1H NMR were conducted by applying a low-field NMR spectrum with a constant magnetic field of 0.5 T and a 60 mm coil operating at 23 MHz. In this study, the Carr-Purcell-Meiboom-Gill (CPMG) measurements were applied in the experiments to obtain the T_2 curve. Two hundred relaxation time points were collected and the time range was 0.01-10,000 ms. The T_2 of less than 0.01 ms corresponds to chemically bound water (also known as solid water) [17] that cannot be detected by the instrument.

Fig. 2 - The ^1H NMR instrument used for testing

In cement-based materials, the interaction between water molecules and pore surface is the main mechanism affecting relaxation. The total transverse magnetization of the cement-based material $M_2(t)$ (a.u.) is a multi-exponential function gradual decayed over time t(s) [12]:

$$M_2(t) = M_0 \sum_i f_i \exp\left(-\frac{t}{T_{2i}}\right) \quad (1)$$

where M_0 is the initial magnetization at time t=0, f_i and $T_{2i}$are the relative intensity and the transverse relaxation time of the component i, respectively. Due to the fast exchange between surface layer and bulk water, the transverse relaxation rate $1/T_{2i}$ of the ith pore volume with surface S_i and volume V_i is represented as the sum of surface and bulk relaxation terms:

$$\frac{1}{T_{2i}} = \frac{S_i}{V_i} \cdot \frac{\lambda}{T_{2S}} + \frac{1}{T_{2B}} \quad (2)$$

where λ denotes the thickness of surface water layer, and T_{2S}, T_{2B} denote the relaxation time of surface water layer and bulk water, respectively. Based on two fundamental assumptions (i) $T_{2B} >> T_{2S}$ and (ii) micro-pore in cement-based materials has a cylindrical geometry, the transverse relaxation time can be directly converted to equivalent radius of pore based on Eq. (3) [24]:

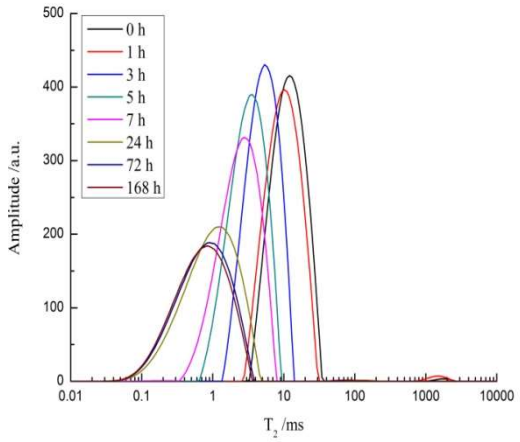
$$\frac{1}{T_{2i}} = \rho_2 \frac{S_i}{V_i} = \frac{2\rho_2}{r_i} \text{ and } \rho_2 = \frac{\lambda}{T_{2S}} \quad (3)$$

where $\rho_2$is the surface relaxivity and r_i is the equivalent radius of micro-pore. According to Eq. (3), the equivalent pore radius is related to the surface relaxivity and T_2time. Bhattacharja et al. [25] have concluded that the magnetization relaxation of protons in white cement pastes complies with the fast diffusion model, in which the surface relaxivityρ_2= 1.6×10^{-6} cm/ms. Therefore, the distribution curve of free water in different pores of cement paste can be obtained by Eq. (3) with mathematical inversion technique.

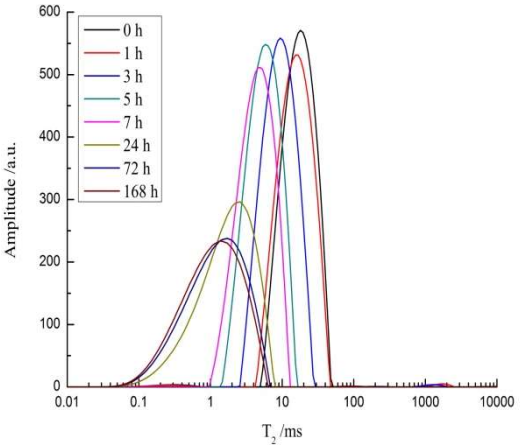
3. Results and discussion

3.1. T_2 distributions

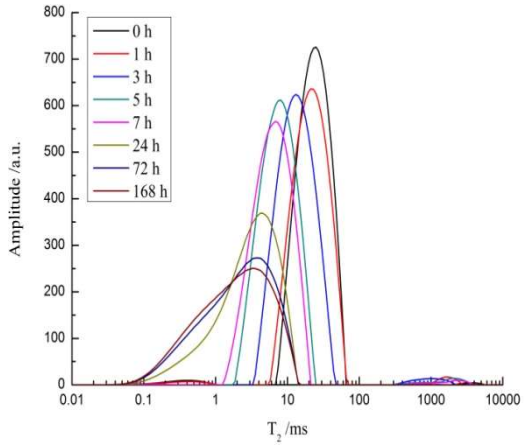
As is well known, the hydration process of cement is not only an exothermic process, but also a process of free water decreasing. Therefore, the transformation of different state water can be monitored by ^{1}H NMR continuously in the hydration process. Figure 3 presents the T_2 distributions of cement pastes with different W/C ratios. The T_2 distributions were measured from the time of the water addition until 168 h later. As is shown in Figure 3, at the beginning of cement hydration, the increase of W/C ratio increases the T_2 distribution obviously, and the main T_2 relaxation curves of cement pastes with W/C ratio of 0.3, 0.4 and 0.5 are in the range of 3 ~ 40 ms, 4.5 ~ 50 ms and 7 ~70 ms, respectively. With the increase of hydration time, the peak value of T_2 signal moves to the left and the main peak area decreases gradually. It indicates that the changes of the T_2 distributions are affected obviously by the W/C ratio and curing time.



(a) W/C=0.3



(b) W/C=0.4



(c) W/C=0.5

Fig. 3 - T_2 distributions of cement pastes with different W/C ratios at different curing time

Figure 4 shows the changes of T_2 geometric mean values of cement pastes at different curing time. It can be clearly seen from Figure 4 that the T_2 geometric average values of cement pastes exhibit the rapid decline within the first 24 h, and slowdown in the later period. The change trend of T_2 geometric mean values corresponds to that of left-ward shift of the T_2 peak value. In addition, the T_2 geometric

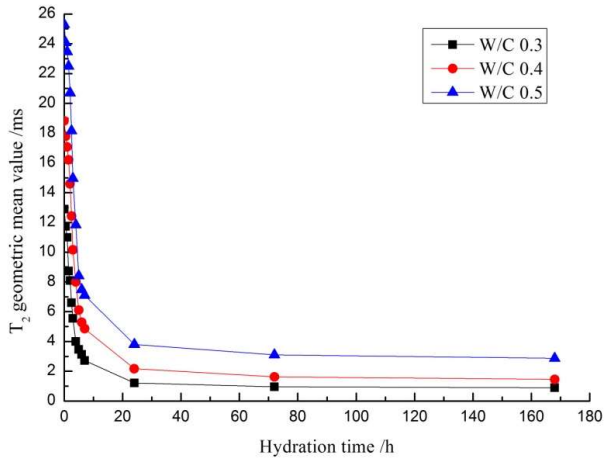


Fig. 4 - Changes of T_2 geometric mean value during hydration

in the whole hydration process.

3.2 Analysis of the hydration process

According to previous studies [12,14,26], the peak area of T_2 represents the content of evaporable water in the cement paste. In this study, the weights of cement pastes with different W/C ratios were uniformed to approximate 10 g. However, there still exists non-negligible difference. Therefore, it is necessary to calculate firstly the T_2 signal intensity of unit mass paste during hydration. Then, assuming that there is no free water consumption for each paste in mixing process, the initial evaporable water content is 30%, 40% and 50% for the cement paste samples with W/C of 0.3, 0.4 and 0.5, respectively. Based on the T_2 signal intensity of unit mass paste during hydration, the evaporable water content of paste samples with different W/C ratios can be calculated due to the linear relationship between the peak area of T_2 and number of mobile water molecule [12].

Through normalizing, the evaporable water contents of cement pastes during hydration were calculated, as is shown in Figure 5. It is observed that the evaporable water shows a continuous decrease with the prolonging of curing time, in which the reduction rate is the fastest within the first 24 h. This is mainly attributed to that the hydration reaction of cement is very fast in the early period especially in the first 24 h, and thus the evaporable water is consumed rapidly at that time. After 24 h, the reduction rate of evaporable water begins to slow, which indicates that the cement clinker particles have been wrapped around by a large number of hydration products and the contact between free water in the pores and unhydrated clinker particles becomes difficult.

As mentioned above, the consumption of evaporable water in cement paste is caused due to the hydration reaction of cement. Therefore, the content of non-evaporable water in cement pastes can be obtained. Hansen [27] and Powers et al. [28] average values of cement pastes decrease with decreasing the W/C ratio

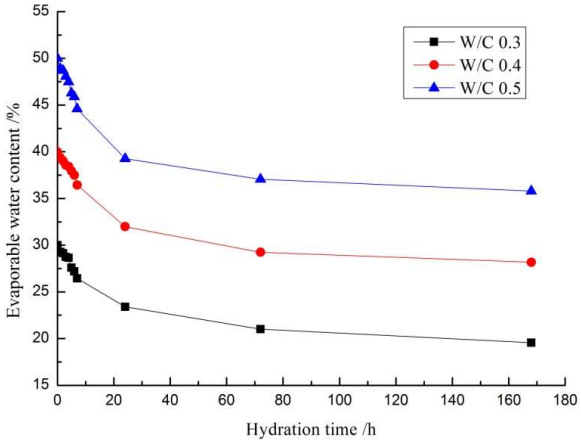


Fig. 5 - The evaporable water contents of cement pastes during hydration

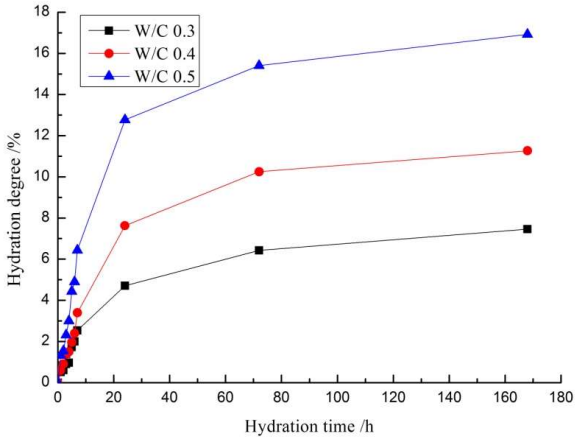


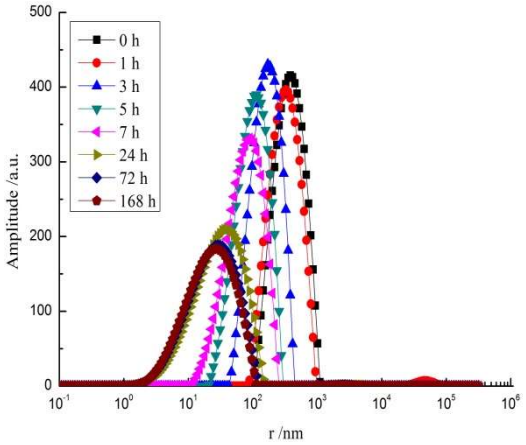
Fig. 6 - Hydration degree of cement pastes with W/C ratios of 0.3, 0.4 and 0.5

have reported the proportional relationship between the hydration degree and non-evaporable water in neat cement paste, and obtained Eq.(4):

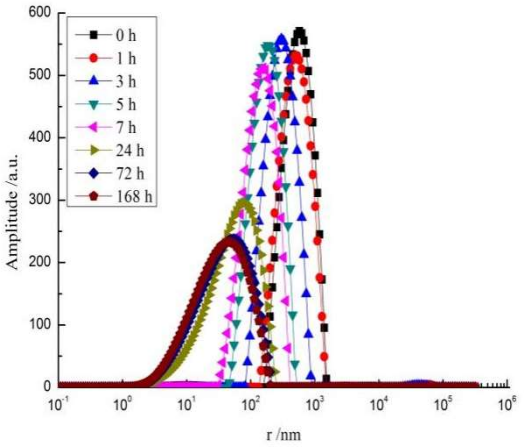
$$\alpha = \frac{W_{\text{non-e}}}{W_{\text{non}-e}^{0}} = \frac{W_{\text{non-e}}}{\gamma \cdot M_C} \qquad (4)$$

Where α is the hydration degree of cement, $W_{non\text{-}e}$is the non-evaporable water content in cement paste,$W_{non\text{-}e}^{0}$is the non-evaporable water content in completely hydrated paste, M_c is the weight of cement and γ is the minimum W/C ratio required for complete hydration of cement, in which γ=0.42 [28].

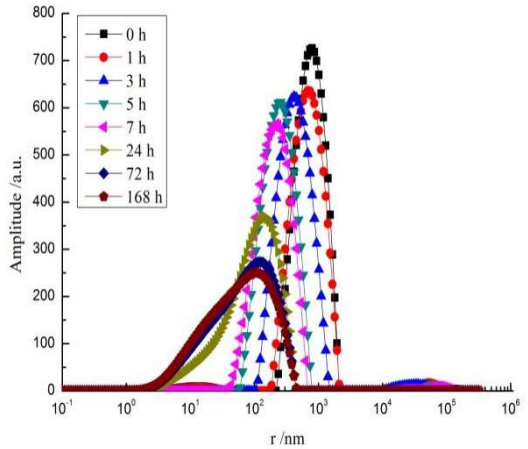
Based on Eq. (4), the hydration degree of cement paste is calculated, as is shown in Figure 6. It can be found obviously that the hydration degree of cement paste increases rapidly within the first 24 h. After 24 h, the hydration of cement slows down gradually. For the cement paste samples with various W/C ratios, the hydration degree increases with increasing the W/C ratio. It indicates that the



(a) W/C=0.3



(b) W/C=0.4



(c) W/C=0.5

Fig. 7 - The distribution curves of free water in different pores of cement pastes during hydration

3.3 Pore structure evolution of cement pastes during hydration

Figure 7 presents the inversed T_2 signal amplitude in different pore ranges of cement pastes with different W/C ratios during hydration. It should be noted that two preconditions must be satisfied those pores contain free hydrogen protons, namely, mobile waters. For the cement paste with W/C ratio of 0.3 hydrated from 0 h to 7 h, most of the evaporable water is filled in the capillary pores in the range of 10 nm ~1000 nm, and while only a small amount of free water is constrained in the bigger air voids with a size of 10 μm ~ 100 μm. With the continuous hydration of cement, the water in those pores is constantly consumed accompanied by the migration from bigger pores to smaller pores, and resulting in the continuous decline of the peak pore radius. For instance, the peak pore radius decreases from 380 nm to 26 nm for hydrated from 0 h to 168 h.

Similar variation trend of proton relaxation signals is found in cement pastes with W/C of 0.4 and 0.5, as is shown in Figure 7(b) and (c). The difference is that the W/C ratio is the larger, the relaxation signal in the pores with pore size of larger than 10 nm is the stronger. Moreover, at the same time for hydration, the peak pore radius is also obvious larger than that of the cement pastes with low W/C ratio. It indicates that the increase of W/C ratio can result an increase in the proportions of larger pores in cement pastes.

The total porosity (the volume of evaporable water) of cement paste during hydration is shown in Figure 8. With the extension of hydration age, the hydration products continuously generate and the porosity decreases. In the first 24 h of hydration, the porosity decrease significantly, and then slow down gradually. In addition, at the same time for hydration, the porosity increases with increasing the W/C ratio.

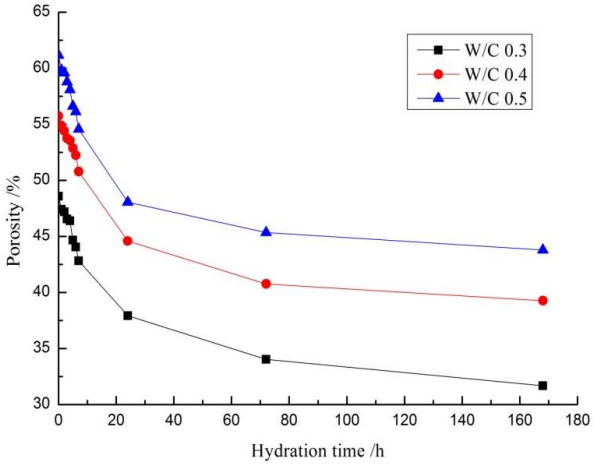


Fig. 8 - The porosity of cement pastes during hydration

4. Conclusions

Through ^{1}H NMR transverse relaxation tests, the hydration and pore structure evolution of white cement pastes at early age was experimentally investigated in this study. The following conclusions

synchronously for observing the relaxation signal in a certain pore size range: i) the hydrating cement paste contains pores in such range, and ii)

structure of wet white cement paste with advantages of rapid and nondestructive. With the increase of hydration time, the main T_2 peak area of cement pastes decrease gradually. The T_2 geometric average values of cement pastes exhibit the rapid decline within hydration for 24 h, and slow down after 24 h. Additionally, the increase of W/C ratio increases the T_2 distribution and T_2 geometric average values obviously.

(2) The evaporable water content of cement pastes can be calculated based on the T_2 signal intensity during hydration, and then the hydration degree of cement paste can be obtained based on the non-evaporable water content. The hydration degree of cement increases rapidly within the first 24 h, and slows down gradually after 24 h. With the increase of W/C ratio, the hydration degree also increases obviously.

(3) For the cement pastes hydrated from 0 h to 7 h, most of the evaporable water is filled in the capillary pores in the range of 10 nm ~1000 nm. With the continuous hydration of cement, the water in those pores is constantly consumed and meanwhile migrated from bigger pores to smaller pores, and then leading to the continuous decline of the peak pore radius. The increase of W/C ratio can result an increase in the porosity and the proportions of larger pores.

Acknowledgments

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could be drawn from the obtained experimental data:

(1) It is proved that the T_2 can be used to characterize the hydration process and pore

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