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不同粒径纳米氧化硅改性白水泥水化过程的 ^{1}H 低场核磁弛豫特征

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摘 要：采用 ^{1}H 低场核磁共振仪连续监测不同粒径(15，50 nm 和 100 nm)纳米氧化硅对白水泥从加水到水化 72 h 横向弛豫时间的变化，研究不同粒径氧化硅对水泥水化过程的影响程度，最后结合维卡仪测定水泥浆的凝结时间。结果表明：纳米氧化硅的晶核作用会影响水泥的早期水化过程，还可以通过物理吸附和火山灰反应打破早期水泥浆体的絮凝结构，减少大孔隙的数量，提高水泥浆体的均质性。此外，纳米氧化硅粒径越小，水化过程中自由水含量消耗越快，表现出的凝结时间越短。

关键词：纳米氧化硅；白水泥；低场核磁共振；横向弛豫时间；水化过程
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^{1}H Low-Field NMR Relaxation Characteristics of Hydration Process of White Cement Modified with Silica Nanoparticles

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Abstract: ^{1}H low-field nuclear magnetic resonance instrument was used to continuously monitor the changes in the transverse relaxation time of white cement with silica nanoparticles with different sizes (*i.e.*, 15 nm, 50 nm and 100 nm) from adding water to hydration for 72 h. The effect of silica nanoparticles with different sizes on the hydration process of cement was investigated. The setting time of cement paste was measured using the Vicat apparatus. The results show that the crystal nucleation of silica nanoparticles can affect the early hydration process of cement, thus breaking the flocculation structure of cement paste due to the physical adsorption and pozzolanic reaction, reducing the number of macropores, and improving the uniformity of cement paste. In addition, the smaller the silica nano particles is, the less the free water content in hydration process and the shorter the setting time will be.

Keywords: nano-silica; white cement; low-field nuclear magnetic resonance; transverse relaxation; hydration

1 Introduction

Nano-materials have a broad application prospect in cement-based materials. The introduction of nano-materials into cement-based materials can improve the microstructure, mechanical and durability properties[1–4]. Among many inorganic nano oxides, nano silica (NS)[5–7] was often added to cement-based materials for the performance modification. The interfacial transition zone of cement-based materials modified by NS is greatly improved, and the impermeability is enhanced[8–10]. This is mainly due to the nucleation effect of nano silica[11] and secondary hydration reaction, which consumes calcium hydroxide in the system and generates additional calcium silicate hydrate (C–S–H), thus increasing the compressive strength, refining the pore structure, and finally improving the durability[6–7]. However, the effect

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of nano silica with different particle sizes on the cement performance could be different.

Nano silica affects the hydration process of cement. The cement hydration is determined by various methods (*i.e.*, setting time measurement, ultrasonic testing, electrical conductivity testing, and calorimetry). However, the setting time of cement can only obtain two points of initial setting and final setting times. The parameters given by ultrasonic testing method and electrical conductivity method reflect the change in the paste compactness, and the relationships between these parameters and hydration process are quite fuzzy[12]. Nuclear magnetic resonance (NMR) is widely used as an effective method for analyzing porous media. In particular, NMR is noninvasive and nondestructive in analyzing the behavior of water in porous media, and can provide the microstructure development from fresh state to hardened state without special treatment of specimens, such as pore structure inspection[13], cement hydration mechanism[14], and permeability measurement[15]. The signal intensity of NMR is related to water content when measuring porous materials. Poli *et al*[16]. pointed out that the transverse relaxation time (T_2) depended on the degree of water confinement in the porous structure, and the signal of water in the small pores decayed rapidly while the water in the large pores decayed slowly, *i.e.*, the relaxation time of small pores was shorter and that of macropores was longer. In general, the pores in cement-based materials are divided into gel pores (2–10 nm), capillary pores (10–200 nm), and microcracks or air voids (>1 μm)[17]. The water in the gel pore was subjected to the greatest restriction, indicating that the transverse relaxation time was usually less than 0.28 ms. The water in the pores at the transverse relaxation time between 0.28 ms and 3 ms was capillary water. The water in the pores at the transverse relaxation time greater than 3 ms was the least constrained, and belonged to the water existing in the micro cracks or air voids[17]. Other researchers noted that T_2 spectrum of the NMR showed a multi-peak distribution characteristic, but the division of the gel pore, interlayer pore, and capillary pore in the relaxation spectrum were still unclear[18–19]. This could be related to the selected sequence parameters and inversion sequence.

Cement hydration is an exothermic process, and a process of continuous water binding. However, the effect of nano silica on the pore structure of cement paste during hydration, drying and moisture absorption process are rarely reported. In this paper, ^{1}H low-field NMR instrument was used to continuously monitor the change in the transverse relaxation time of cement paste with nano silica with different sizes (*i.e.*, 15, 50 nm and 100 nm) from adding water to hydration for 72 h. The effect of nano silica with different sizes on the cement hydration process was investigated. The setting time of cement paste was measured by a Vicat apparatus.

2 Experimental

2.1 Materials and mix proportions

Common building materials, such as cement and concrete, contain a large number of magnetic materials including iron, which can shorten the measured relaxation time and widen the relaxation line width[20]. Therefore, white Portland cement (WPC) with little iron was used. The chemical composition and the X-ray diffraction (XRD) pattern of the white cement are shown in Table 1 and Fig. 1, respectively. Nano silica with the particle sizes of (15±3), (50±3) nm and (100±3) nm were used. The content of nano silica in the specimen is 1.0% of the mass fraction of the cementitious material. Table 2 shows the proportions of the materials.

Table 1　Chemical compositions of WPC　　*w*/%

SiO_2	Al_2O_3	Fe_2O_3	CaO	Na_2O	MgO	K_2O	SO_3	Loss
10.63	1.24	0.27	50.29	0.2	11.04	0.37	1.07	24.89

w is mass fraction.

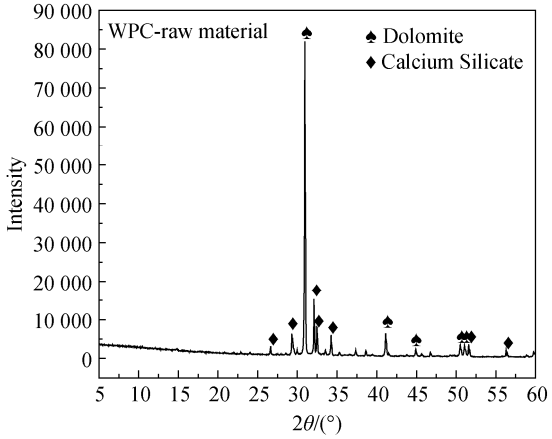


Fig. 1　XRD pattern of white cement

Table 2　Mix proportions of different systems

Label	Size of NS/nm	Mass ratio		
		Cement	Water	NS
WPC (Control group)		100	50	0
PNS15	15±3	99	50	1
PNS50	50±3	99	50	1
PNS100	100±3	99	50	1

2.2 Mixing and molding

Nano silica easily aggregate when directly mixed with cement due to the large specific surface area, thus affecting the microstructure. Therefore, nano silica was

dispersed in 80% of the weighed water, and the suspension was obtained by ultrasonic dispersion for 30 min. Afterwards, the suspension and remaining 20% water were mixed with cement at a low rotational speed (140±5) r/min for 120 s and at a high rotational speed (285±5) r/min for 120 s, respectively. After stirring, the obtained paste specimens were mounted in the specimen bottles (*Φ*21.9 × 50 mm) for continuous measurement from 0.25 h to 72 h. The specimen bottles were sealed with cling film to prevent water evaporation.

2.3 Characterization

The transverse relaxation time was measured using a model pq-001 nuclear magnetic resonance (NMR) instrument (Shanghai Newman Analytical Instrument Co., Ltd., China). During the measurement, a cylindrical specimen was put into a probe coil of the instrument, and the relaxation signal of cement paste was collected *via* Carr–Purcell–Meiboom–Gill (CPMG) pulse sequences. The inversion curve was obtained by simultaneous iterative reconstruction technique (SIRT) and inversion algorithm based on a correlation analysis software. The number of iterations and relaxation time points are 10 000 and 200, respectively. The number of selected data is 200. T_{2min} and T_{2max} are 0.001 ms and 10 000 ms, respectively. The test parameters were set according to a literature[21]. The echo time used in this experiment is 0.3 ms. Table 3 shows the NMR parameters.

The setting time of cement paste was determined in accordance with the Chinese Standard GB/T 1346–2011. The initial time was recorded when water was added to cement. After the specimens were molded for 30 min, the value of Vicat needle drop into the specimens was measured every 5 min until the initial and final settings. During the measurement, the specimens were cured at a relative humidity of 95% and room temperature.

3 Results and discussion

3.1 Relaxation characteristics of hydration process

Cement paste as a porous material is mainly affected by the surface relaxation mechanism. The environment of water molecule can be judged from the length of relaxation time[18]. The cement hydration system contains different forms of structural water, such as capillary water, gel water and interlayer water, and Fig. 2 shows their relationships[15].

Table 3 NMR parameters

Instrument parameters		Sequence parameters	
Spectrometer Frequency (SF)	12 MHz	Magnetic field strength	0.53 T
Receiver Bandwidth (SW)	125 kHz	Resonant frequency	22.6 MHz
Frequency Offset 1 (O_1)	698 833.74 Hz	Magnetic field uniformity	40 ×10^{-6}
90° Pulse Length (P_1)	7.52 μm	Temperature-controlled	32 °C
180° Pulse Length (P_2)	15.04 μm	RF field pulse frequency range	1–30 mHz
Waiting time for repeated (TW)	1 000.0 ms	Linear distortion	<0.5%

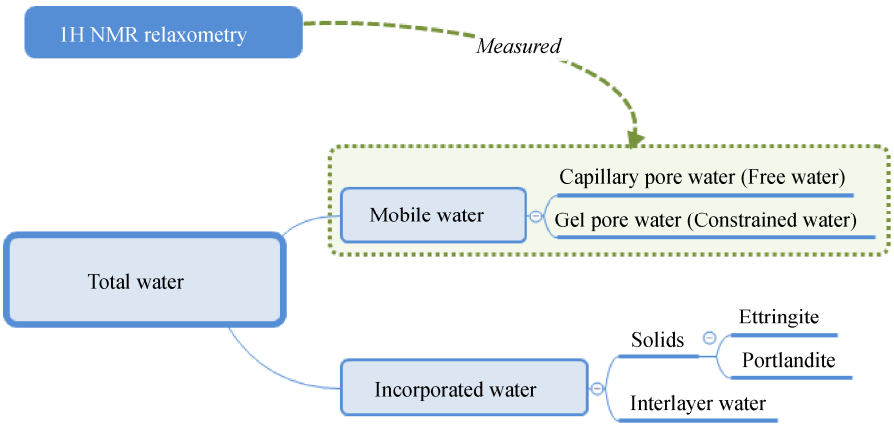


Fig. 2 Classification and relationship of water in hardened cement paste[15]

In Fig. 2, there are the mobile water in the specimen, namely capillary pore water and gel pore water. Fig. 3 shows the T_2 spectra of hydration at different time (*i.e.*, 15 min, 2 h, 3.5 h, 5 h, 24 h and 72 h). In Fig. 3, the T_2 spectra mainly consist of three peaks at the early stage of hydration, and the peaks at different positions present the water in different states. The peaks shift to the decreasing direction with increasing hydration time, indicating that the free water in the capillary pores decreases, and the water molecules enter the C–S–H gel

pore, the constraint of water molecules enhance, thus shortening the relaxation time[21]. In addition, there is a small peak in the range 300–1 100 ms in the specimen without nano silica (WPC or control group) during the whole hydration process. The relaxation time of this part of structure water is longer (300–1 100 ms), which may belong to the large capillary pores or flocculation structure water of cement paste. However, there is no obvious peak in the range 300–1 100 ms in the specimens mixed with nano silica (*i.e.*, PNS15, PNS50 and PNS100), showing that the presence of nano silica accelerates the hydration of cement and reduces the number of larger pores.

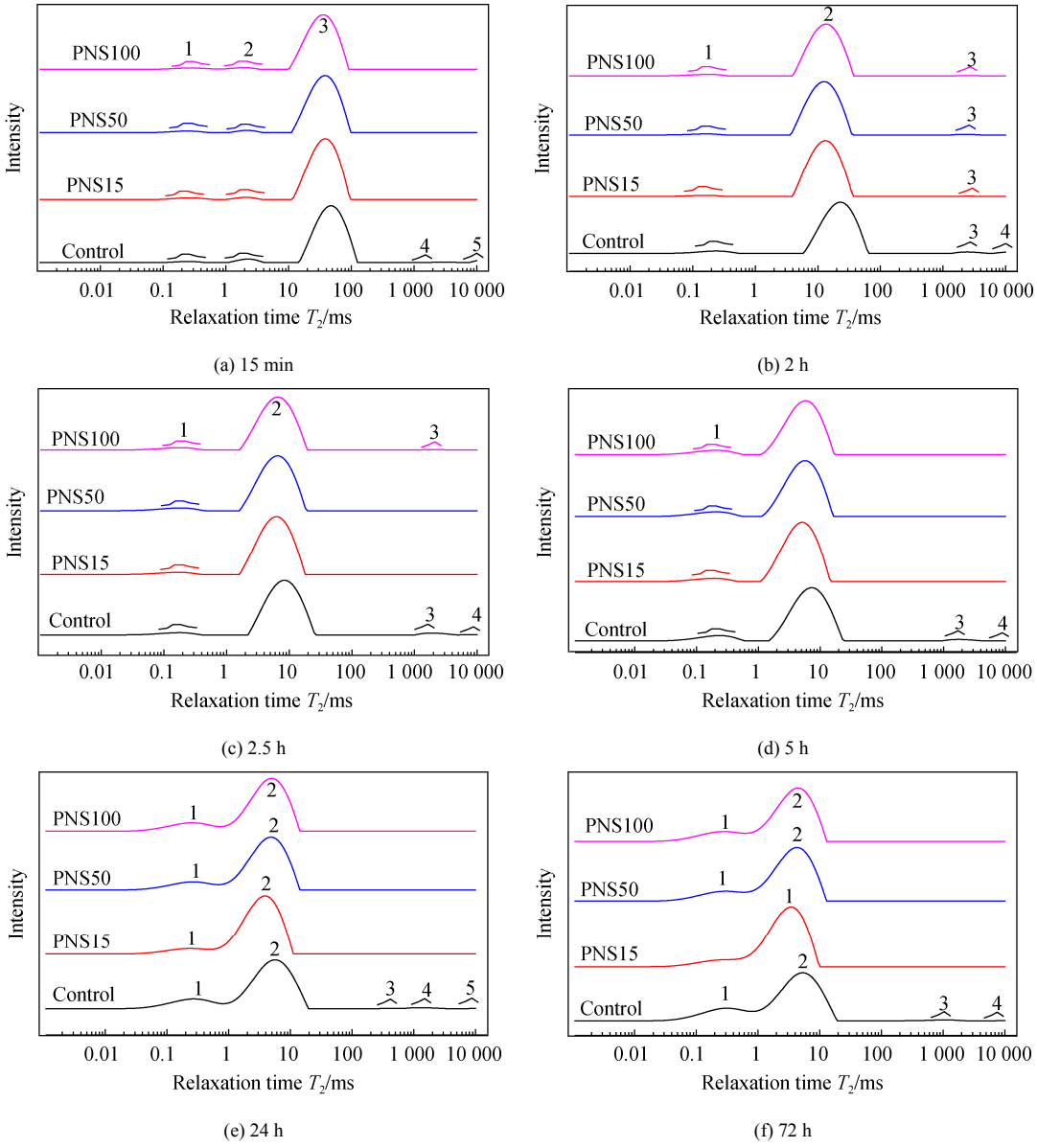


Fig. 3　T_2 spectra of hydration at different time

In Fig. 3, cement paste after hydration for 15 min is in a plastic flow state, and the paste can be regarded as a suspension system composed of water and cement particles. Cement micron-sized particles and nano silica is easy to aggregate and condense into a group network structure in the whole system when cement micron-sized particles to the system are mixed with silica nanoparticles. The free water is wrapped in the system, and the degree of hydration is rather low. The relaxation time of this part of the water greatly shortens as confined to the structure of the aggregation due to the limited structure of the solid phase surface. In addition, most of the water in the paste is filled in the gap between the non-aggregated cement particles. The specific surface area of solid phase does not increase significantly, restricting the relaxation effect on this part of water due to the low hydration degree of the paste. Therefore, in the T_2 distribution of the early paste, the main peak with a longer relaxation time represents more free water distributed in cement particles, while the shorter

relaxation time indicates the water in the aggregation structure in the paste. The spectra of the control group show four peaks before the hydration for 15 min, while the spectra of the specimens PNS15 and PNS50 with nano silica except the specimen PNS100 have only two peaks located as T_2 < 30 ms. The hydration products formed at the initial stage are wrapped on the surface of the unhydrated particles when cement hydration is carried out for 2 h, thus hindering the dissolution of the clinker mineral phase and slowing down the time when Ca^{2+} ions concentration becomes the supersaturation value[22]. Therefore, at this stage, the amount of hydration products and the specific surface area of the paste increase slightly. In this case, the spectra of the specimens with nano silica have a small peak (peak-3) as T_2>1 000 ms (Note: the number of peaks is only the order of peaks, and does not represent any structural water). This process can be considered as the water releasing of nano silica, compared to the hydration for 15 min. The phenomenon of water releasing is not rather obvious because the nanoparticles content in cement is only 1.0%. The unhydrated cement particles aggregate and wrap a small amount of free water. As the surface of the particles is slowly hydrated to form calcium hydroxide, nano silica react with calcium hydroxide to form C–S–H gel that absorbs the free water in the pores, which is finally converted into gel water or free water releasing into capillary water. Therefore, the relaxation signal at greater than 1 000 ms disappear. This illustrates that nano silica can destroy the aggregation structure of cement and release internal free water or convert it into gel water, thus being conducive to reducing the porosity of hardened specimens.

In fact, the water releasing time of nano silica with different sizes is different. Fig. 4 shows the NMR signal distribution areas. In Fig. 4, the *X* axis represents the hydration time, the *Y* axis represents the NMR signal, and the signal (blue area) means that the water can be detected.

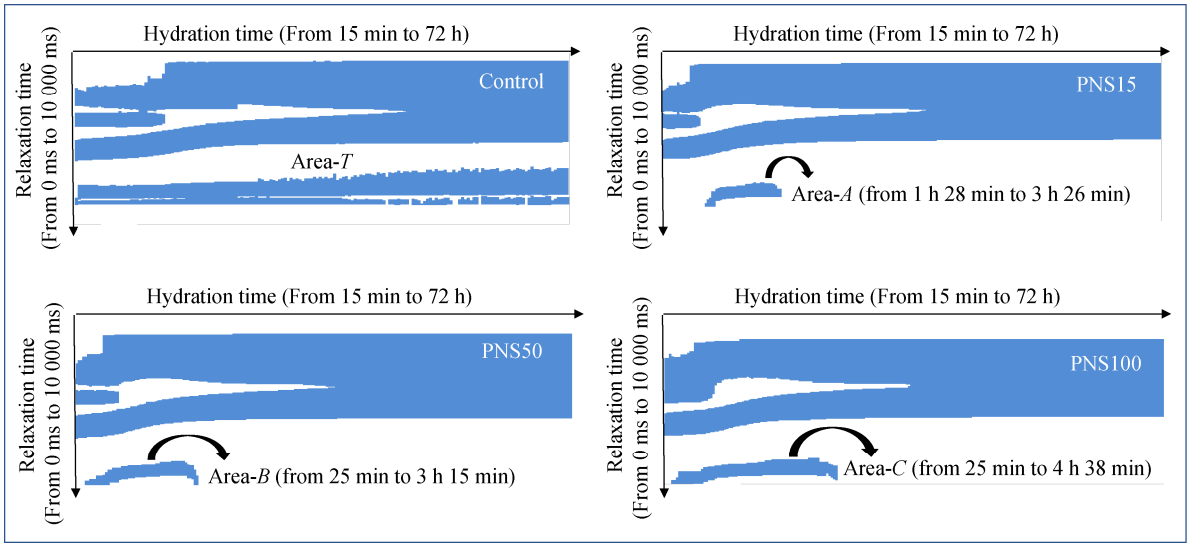


Fig. 4 NMR signal distribution areas

Clearly, the control group specimens always have signals at T_2 greater than 100 ms, *i.e.*, "Area-*T*", while the specimens with nano silica (*i.e.*, PNS15, PNS50 and PNS100) do not have any signals at greater than 100 ms initially. The specimens with nano silica begin to show signal at 88, 25 min and 25 min, respectively, with increasing time, and the signal disappears at 3 h 26 min, 3 h 15 min and 4 h 38 min. Areas '*A*, *B* and *C*' are defined as the water releasing (internal bleeding) time for the specimens with nano silica with different sizes, *i.e.*, the water releasing time for the specimen with nano silica of 15 nm (PNS15) is 88–206 min, the water releasing time for the specimen with nano silica of 50 nm (PNS50) is 25 min–195 min, and the water releasing time for the specimen with nano silica of 100 nm (PNS100) is 25–278 min. Fig. 3 shows the T_2 spectra for 3.5 h and 5 h. In the hydration reaction, the internal bleeding of NS-cement suspensions disappears, the proportion of peak-1 increases and peak-2 decreases, indicating that the capillary pore water in cement paste decreases, the gel pore water increases, and the hydration degree deepens. At the end of the induction period, a new surface reacts with the water as a surface of the cement particle, indicating that nano silica efficiently reduces the amount of bleeding or free water to the extent that bleed water flows back into smaller capillary pores. This indicates that the refinement of the pore structure is enhanced *via* the acceleration of cement hydration, both being triggered by silica nanoparticles. In the reaction, $Ca(OH)_2$ precipitates after supersaturation of Ca^{2+}, promoting the hydration of C_3S, generating a large amount of C–S–H gels, as well as filling and compacting the pore structure of the paste[23]. The specific surface area of the paste increases rapidly, which is affected by the solid surface

due to the presence of the colloidal product. Hence, the relaxation time decreases significantly with increasing hydration time. The activity of the surface of nano silica gradually stimulates in saturated $Ca(OH)_2$, and the particle size is rather small, which makes it easy to become the nucleating point of C–S–H gel or $Ca(OH)_2$ crystal, thus promoting the cement hydration reaction. The relaxation time reduces rapidly. At this time, cement hydration is at a stable stage. In addition to the transfer of water in the paste into chemical binding water, the rest of the physical binding water in the paste become capillary water or gel water. After hydration for 72 h (see Fig. 3), only one peak appears in the specimen with nano silica of 15 nm as T_2 <10 ms, indicating that there are no large pores (T_2 >10 ms) in the system. This is attributed to the pozzolanic activity and nucleation effect of nano silica, promoting the formation of hydration products and increasing the specific surface area of the solid phase. As a result, the relaxation time of specimens with nano silica is shorter than that of the control group.

3.2 Water content

The hydration of cement is a process of continuous water binding. The more the free water is consumed, the deeper the hydration reaction will be. The peaks at different positions in T_2 spectra represent the different forms of structural water[24] and the total peak area represent the total water content in cement. The relative water content (see Fig. 5) is chosen to express the water content change in the specimen.

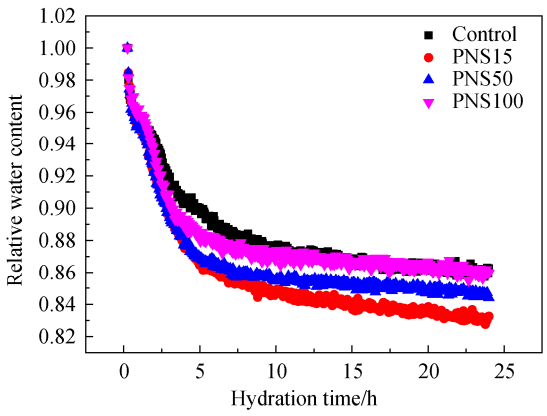
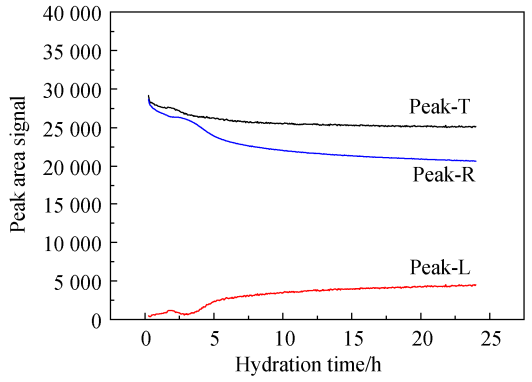


Fig. 5　Water content change during hydration

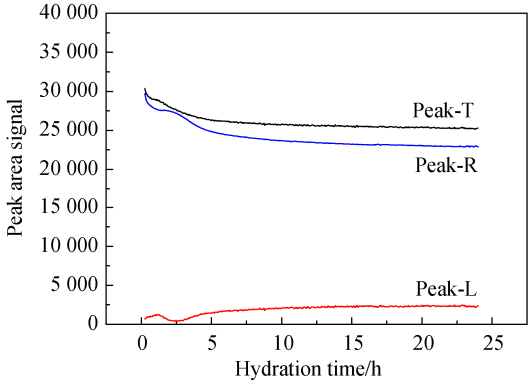
In Fig. 5, the peak area of all specimens decreases rapidly at the beginning of hydration for 5 h. Note that free water rapidly reacts to produce hydration products, which cannot be detected by NMR. After 5 h, the water loss rate decreases and the water content in different specimens is varying. Especially, the specimen with nano silica of 15 nm (PNS15) has the fastest water loss rate, compared to the specimen without nano silica (control group) mainly due to the physical absorption of nano silica and the chemical reaction between $Ca(OH)_2$ and nano silica. Fig. 5 also shows that nano silica promotes the hydration of cement mainly after hydration for 1 h, thus shortening the induction time. After hydration for 5 h, the peak area of the specimen with nano silica of 15 nm (PNS15) further decreases, *i.e.*, the free water decreases, and the total area is the smallest among all the systems, indicating that the degree of cement hydration deepens. After hydration for 24 h, the hydration degree of the specimens with nano silica of 15, 50 nm and 100 nm (*i.e.*, PNS15, PNS50 and PNS100) is increased by 21.9%, 13.9%, and 1.5%, respectively, compared to that of the control group. The reduction in free water can promote a rapid condensation of cement paste, as shown from the test results of the setting time.

The peaks of different positions in relaxation spectra represent different water states in cement paste. Fig. 6 shows the change in the water states of different samples during hydration. The leftmost peak (Peak-L) in T_2 spectra is generally at less than 0.28 ms, representing the gel water[17]. In addition to the Peak-L, other peaks are described as peak-R and Peak-T that represent the total peaks. In Fig. 6, in the hydration reaction, the total water and capillary water in the system decrease, the gel water increases continuously, and finally gradually stabilizes.

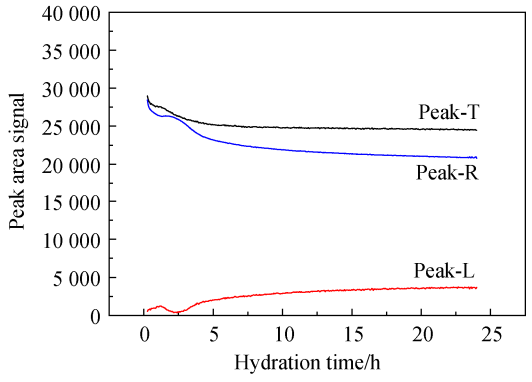
Fig. 7 shows the peak-L area change in different specimens during hydration. Before the hydration for 1 h, the specimens with nano silica (*i.e.*, PNS15, PNS50 and PNS100) contain a large amount of gel water, thus proving that nano silica accelerate the cement hydration and shorten the induction time. The decrease in the peak area at 1–2.5 h is related to the induction period experienced in cement hydration. The induction period usually occurs 2–4 h after hydration. There are some explanations for the initiation and termination of induction period, such as protective film hypothesis, lattice defect hypothesis, delayed nucleation hypothesis and comprehensive hypothesis. Regardless of the hypothesis, the induction period occurs because the dissolution of C_3S is blocked. The hindrance of C_3S dissolution shows that the exothermic rate and the dissolution rate of Ca^{2+} ions into the solution slow down, and the formation of C_3S product, *i.e.*, calcium silicate hydrate gel, is inhibited. The formed gel adheres onto the unhydrated C_3S surface, and the gel absorbs water to a certain extent. When the relaxation signal of the gel is similar to that of the small capillary pores, this part of the gel water is regarded as a capillary pore, exhibiting that the gel water reduces, and the corresponding capillary water increases (the blue and red lines in Fig. 6). After hydration for 2.5 h, the Peak-L proportion of the specimens with nano silica increases obviously mainly because of the pozzolanic activity of silica nanoparticles, producing more C–S–H gel, and the gel absorptivity leads to the formation of gel water. Moreover, the smaller the size of NS is, the higher the pozzolanic activity is, thus producing the more C–S–H gel. Also, the paste with NS generates more hydration products and improves the hydration degree of cement.



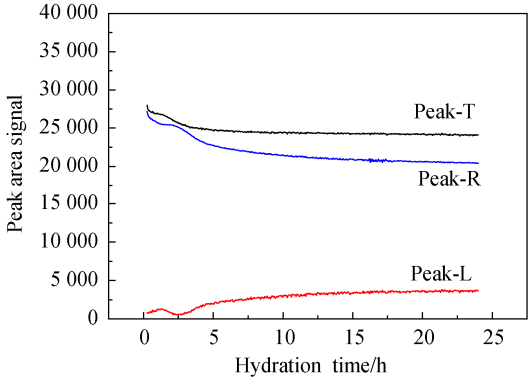
(a) Control



(b) PNS15



(c) PNS50



(d) PNS100

Fig. 6 Variation of peak areas in hydration process

3.3 Setting time

In order to analyze the effect of nano silica on the cement hydration process, the penetration depth of Vicat needle was evaluated. Fig. 8 shows the results. In Fig. 8, the penetration depth of Vicat needle decreases with the hydration reaction, indicating that the free water content in the specimen decreases and the hydration products increases. Usually, the setting process invloves the following steps[19], (1) dissolution from casting to transverse relaxation begins to decrease; (2) dormant period, from the transverse relaxation begins to decrease, for the initial setting time measured by Vicat needle; (3) setting process, from the initial setting time measured by Vicat needle to the fitting slope change; and (4) hardening, after final setting time. From the result of Vicat needle falling depth, the addition of nano silica into cement obviously shortens the setting time of the specimen. The initial setting time of the control group, the specimens with nano silica of 15, 50 nm and 100 nm is 158, 108, 118 min and 123 min, respectively. The corresponding final setting time is 243, 173, 178 min and 203 min, respectively. The smaller the size of NS is, the shorter the setting time will be. In addition to the nanoparticles increases the viscosity of cement paste, the nucleation effect and pozzolanic activity of nano silica consume free water and generate additional calcium silicate hydrate to accelerate the setting of cement.

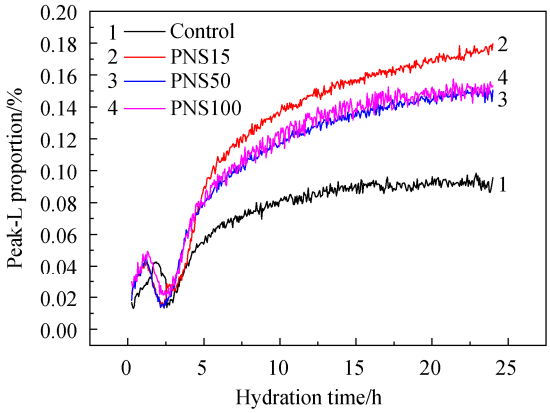


Fig. 7 Peak-L area change during hydration

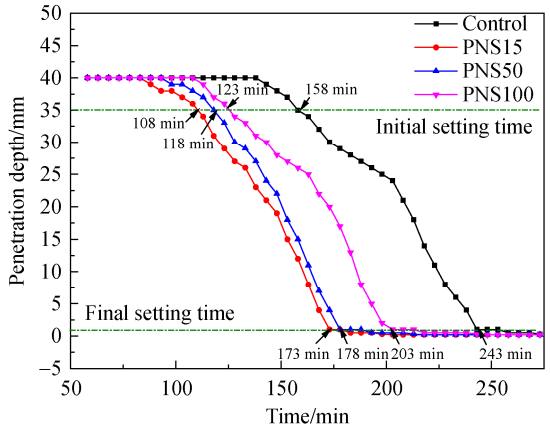


Fig. 8 Evolution of the penetration depth of Vicat needle

4 Conclusions

Nano silica with different particle sizes is able to promote cement hydration, i.e., mainly in shortening the induction period time and reducing the number of larger pores during hydration. After hydration for 24 h, the hydration degree of the specimens with nano silica of 15, 50 nm and 100 nm (i.e., PNS15, PNS50 and PNS100) is enhanced by 21.9%, 13.9% and 1.5%, respectively, compared to that of the control group (WPC). Furthermore, the paste with 15 nm nano silica (PNS15) has the shortest setting time and the fastest water binding rate during the hydration. In addition, the addition of nano silica into cement can break the aggregation structure of early cement paste through physical adsorption and chemical reaction, reduce the bleeding and the amount of free water, and improve the uniformity of cement paste as well.

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