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Water consumption of the early-age paste and the determination of "time-zero" of self-desiccation shrinkage

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Abstract

Self-desiccation shrinkage (SDS) is closely related to the interior water consumption and the relative humidity (IRH) drop in the cement paste. Substantial self-desiccation shrinkage has been observed at very early-age for high performance concrete. However, it is difficult to investigate the IRH by conventional method of hygrometer at this time because the materials are still in the superhygroscopic range. In this paper, an automatically measuring system of meniscus depression is developed on the base of the mechanism of tensiometer and Laplace formula. The interior water consumption and the IRH changing within the paste could be automatically monitored at the very early-age (here specially refers to the stage from the beginning of casting till several hours after final setting). By using this system, the effects of water to binder ratio and replacement of cement by fly ash and ground granulated blast furnace slag on the self-desiccation were investigated for the very early-age cement paste. Experimental results could potentially explain the mechanism of the SDS at very early-age as well as determine the "time-zero" of SDS corresponding to its definition.

Keywords: D. cement paste; C. self-desiccation shrinkage; "Time-zero"; Tensiometer; Meniscus depression

1. Introduction

Self-desiccation shrinkage is the reduction in the apparent volume of concrete or paste induced by chemical shrinkage with further hydration of binders after the mixture has developed its initial self-supportive skeleton. The further application of HPC causes more and more attention to SDS since the stress induced by SDS plus temperature deformation under the internal or external restraint could bring micro cracking and impair the concrete quality. Experimental results of SDS of HPC manifested a rapid development at the very early-age. The driving force of SDS at this age is still under discussion. While there is a general agreement about the existence of a relationship between SDS and the drop of IRH of concrete [1,2]. It is difficult to measure the moisture changing in very early-age concrete by conventional method of hygrometer because the materials are still in the superhygroscopic range (approximately in the range of 98%–100% of IRH). Wittmann [3] developed for the first time a special set-up to investigate the capillary under pressure in the cement paste. Radocea [4] improved this experimental set-up and proposed a model of plastic shrinkage. Hammer [5] used the similar system to investigate the influence of entrained air voids and silica fume on pore water pressure. All of these results provide a promising method to explore the possible mechanism of the very early-age shrinkage.

Another important problem involved in the research is the determination of "time-zero", i.e., the time for start of SDS measurement. There isn't a uniform standard about the determination of this time yet, which causes great difficulty in comparing the results provided in the existing literatures [6]. Moreover, in terms of crack, measurement of SDS before this time has little mechanical significance and conversely measurement of SDS after this time may substantially underestimate the actual value [6,7]. It is roughly equal to the setting time but is not identical with it [8]. Present available research methods include

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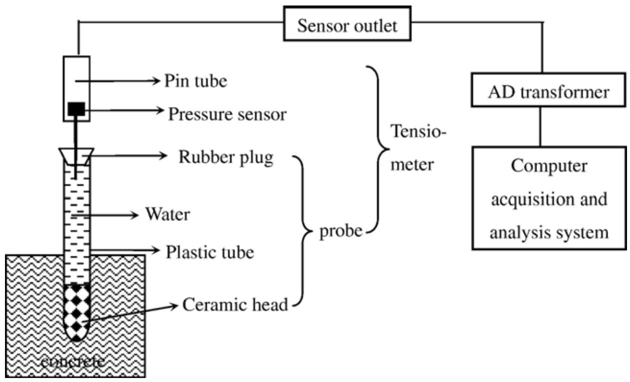


Fig. 1. Sketch of the measuring system of the meniscus depression.

the mechanical penetration test, rate of heat evolution test, shrinkage measurement, electrical conductivity, ultrasonic measurement, active restraint mechanical testing and strength development testing etc. The active restraint systems appear to provide the most direct measure of the age of stress build-up but need an additional research to interpret the actual physical features of the system at this time, while the other methods couldn't provide a direct correlation to the definition of SDS [6].

In this paper, a special automatically measuring system for the meniscus depression within the paste or concrete is developed in virtue of the mechanism of tensiometer in soil research. The "time-zero" corresponding to the definition of SDS can be potentially determined through analyzing the continuous testing results of the capillary depression. Furthermore, combining with Laplace formula it can be realized the quantitative analysis of the development of the critical radius and the water consumption for the paste or concrete at very early-age.

2. Mechanism of the meniscus depression measuring system

Tensiometer is an apparatus used for the measurement of soil water content. The energy level of the water in soil is less than that of free water in natural environment due to the cooperation of capillary tension of meniscus and the attraction of soil granules surface. The movement of the water from the soil to the environment needs to consume energy. At the same time the water does work. Therefore the soil water has potential energy. The water potential is a relative value and depends on the frame of reference. The potential of the pure free water at identical temperature with the research system and normal atmospheric pressure is defined as zero, where "pure" means no solutes and "free" means no restraint [9].

If the temperature is constant and there is no solute, the potential of the soil water

$$\psi_{\mathrm{ws}} = \psi_{\mathrm{ms}} + \psi_{\mathrm{ps}} \tag{1}$$

Where ψ_{ws}, ψ_{ms}, ψ_{ps} is the water potential, matric potential and pressure potential, respectively.

On the other hand, the water potential in a saturated tensiometer

$$\psi_{\mathrm{wD}} = \psi_{\mathrm{mD}} + \psi_{\mathrm{pD}} \tag{2}$$

Where ψ_{wD}, ψ_{mD}, ψ_{pD} is the water potential, matric potential and pressure potential in the tensiometer, respectively.

Once the porous ceramic head is embedded into the soil, the water in them builds hydraulic relation and goes to balance. If the equilibrium is achieved, then

$$\psi_{\mathrm{wD}} = \psi_{\mathrm{ws}} \tag{3}$$

Because the pressure potential of the water in unsaturated soil is zero and there is no solute in the water of tensiometer and thus its matric potential is also zero, so

$$\psi_{\mathrm{pD}} = \psi_{\mathrm{ms}} = V_{\mathrm{w}} \Delta P_{\mathrm{D}} \tag{4}$$

Where V_{w} is the specific volume of water, ΔP_{D} is the difference in water pressure in tensiometer and the atmosphere pressure.

Water fills in the capillary network system of the cement paste due to the cooperation of meniscus depression and the attraction of pore wall in the same way in soil. The automatic measuring system of the meniscus depression is mainly composed of ceramic head, plastic tube, rubber plug, pressure sensor, pin tube and computer acquisition and analysis system (as seen in Fig. 1). The ceramic head has many tiny pores and can be regarded as a piece of rigid porous film, which acts as the inductive component in the system. When the ceramic head is soaked in water, water films form in the tiny pores. The tension in the pore water can ensure water pass through the ceramic head at certain pressure and prevent the movement of air. When the soaked tensiometer is embedded into the concrete, the surface of the ceramic head is fully contacted with concrete directly and builds hydraulic relation between the water in the PVC tube and the water in the concrete. Similar to the drying course of soil, the concrete system will also transfer from saturated state to unsaturated status when the concrete has developed a self-supportive skeleton. So water will transport from the PVC tube into the concrete under the driving force of water potential difference between the tube and the self-desiccated concrete till a new balance is achieved. An under pressure generates in the PVC tube and can be detected by the pressure sensor equipped upon the pinhead of the syringe, which pierces through the rubber bug into the PVC tube, and monitored automatically by the computer acquisition system. The tested value is equal to the meniscus depression of the paste in absolute value but opposite in sign. Because the pore diameter of the ceramic head is large enough for the solute ions passing through without impedance, the results will not be influenced by the dissolved salts in the pore fluid. The modified tensiometer used in this research is provided by Nanjing Soil Institute of China Academy of Sciences. Its measurement range is 0–100 kPa and the resolution is 0.25 kPa.

Under the sealed condition, water consumption in the paste is always from big pores to small pores according to the thermodynamic principles and the meniscus depression increases accordingly with the progressing of the cementitious materials hydration. Using the measured meniscus depression combining with Laplace formula and Kelvin Law the critical radius and the IRH can be calculated directly, which is the main functionary mechanism of the tensiometer in cement-based material and the meniscus depression measuring system. The arising of meniscus

Table 1
Chemical composition and mechanical properties of the powder materials

Symbol	Main chemical composition (%)							Density (kg/m^3)	Specific area (m^2/kg)
	SiO_2	Al_2O_3	CaO	MgO	Fe_2O_3	SO_3	Loss		
C	20.60	5.03	64.11	1.46	4.38	1.72	1.18	3150	450
Fa	49.39	33.36	4.13	0.85	4.92	1.96	2.49	2200	615
Sl	33.12	11.80	34.95	10.75	1.17	0.69	1.23	2890	439

in the paste corresponds to the formation of the solid structure and the beginning of SDS. Therefore, this method may be used to determine the “time-zero” of SDS directly related to its definition and provide specific physical significance of the term.

3. Experimental results and discussions

3.1. Raw materials

3.1.1. Binders

Portland cement(C) with 42.5 grade from Nanjing Jiangnan cement plant was used. The tested compressive strength of the cement at 28 days was 60 MPa according to GB/T 17671-1999. Class I fly ash(Fa) according to JGJ 28-86 came from Nanjing Thermo Electrical Plant. A ground granulated blast furnace slag (Sl) with specific area of 439 m^2/kg was used. The chemical and physical properties of the binders were shown in Table 1 and Fig. 2.

3.1.2. Admixtures

Poly-naphthalene sulfonates superplasticizer, named JM-B, with 20% water reduction at the dosage of 0.5% came from Jiangsu Bote Advanced Materials Co., ltd.

3.2. Experimental program

Totally ten kinds of mixtures were studied in this paper. For pure cement paste five kinds of water/cement ratios were designed: 0.20, 0.30, 0.40, 0.45 and 0.50. For the mixtures with 0.30 water/binder ratio five kinds of mineral admixtures contents (replacing cement by weight) were chosen: 30% and 50% of fly ash and 30%, 50% and 70% of slag respectively. In order to alleviate the effect of bleeding a polysaccharide based viscosity agent (named VA) was added.

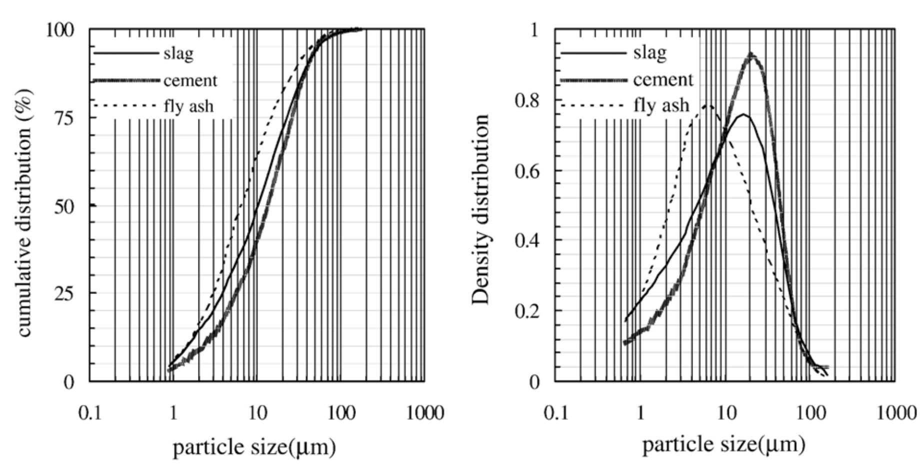
The ceramic heads were immerged into de-aired water for 24 h before testing. After mixing, part of the mixtures were cast into plastic cylinders with size of $\Phi 75 \times 150$ mm for meniscus depression testing. The saturated ceramic head was embedded into the fresh mixture. The top surface of the cylinder was sealed with plastic film and self-adhesion aluminum foil to avoid water evaporation. The meniscus depression data acquisition began from 0.5 h after mixing. The remnant mixtures were used to test the setting time according to GB 8076-2001 under sealed condition.

3.3. Results and discussions

Test results are shown in Figs. 3 and 4. The results are the surplus value by subtracting the initial hydraulic pressure from the measurement values. The corresponding setting time is also shown in the figures represented by the upright line. The shorter upright line represents the initial setting while the higher upright line represents the final setting.

3.3.1. Development of meniscus depression and water consumption at very early-age

From the figures we can see that there is a sensitive transition zone in the meniscus pressure (Δp) development with the hydration process at the very early-age. Before the transition zone the increase of Δp is neglect and very slow. The value of Δp maintains to about zero. After the transition zone, Δp increases rapidly and reaches nearly 100 kPa in a few hours, the corresponding Kelvin radius is about 1–2 μm. The transition zone could be explained from the hydration progress. At the very early beginning immediately after water addition the system is still in a suspending and fluid state. Water enwraps the solid particles and forms successive medium system. The volume reduction resulting from chemical shrinkage will be compensated by the apparent volume decrease. Structural pores can’t form in



(a) cumulative distribution curve **(b) density distribution curve**

Fig. 2. Cumulative and density distribution of powder materials.

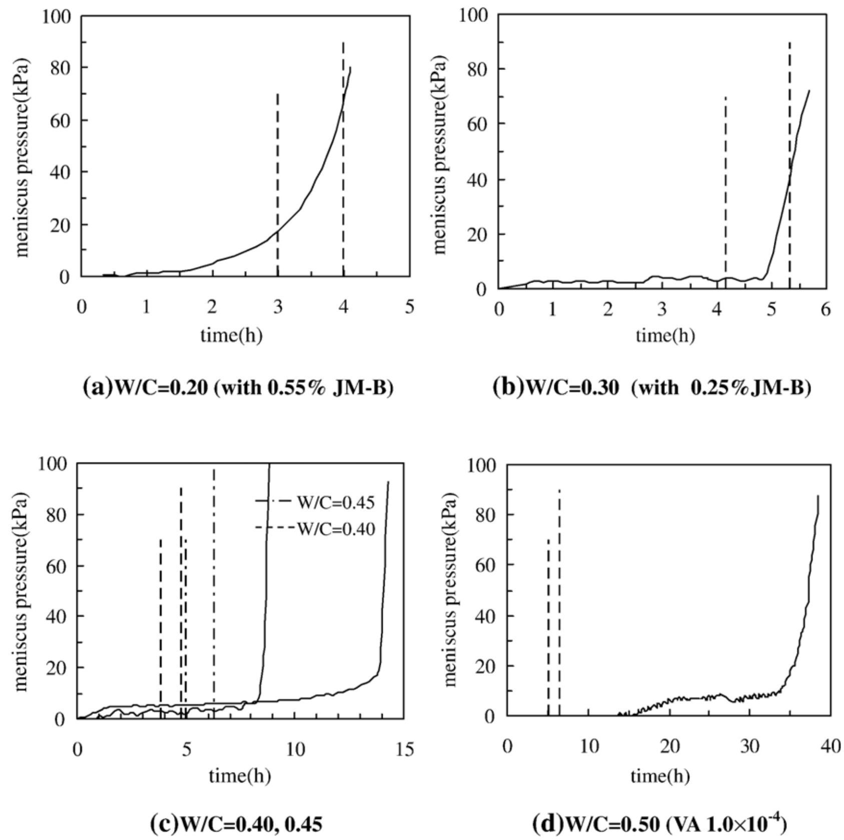


Fig. 3. Effect of W/B on the meniscus depression at initial stage.

the system and so meniscus pressure will not generate at this time. However, once the protective layer breaks open and the anhydrous cement continues to hydrates the system enters into the middle age. The principal components of Portland cement, C_3S and C_2S begin to react and form amorphous calcium silicate hydrate and crystalline calcium hydroxide. These long fibers shaped early-age products interconnect and build bridges between cement particles. Then the solid skeleton is formed and pores can be stably existent. Free water fills within the pore space and the initial saturated capillary network is formed. Further hydration and water consumption leads to partially saturated networks. The depression across menisci generates and builds SDS stress acting upon the viscoelastic system. Since the hydration is speedup once the dormant stage finishes, the middle age is also called accelerating stage [10]. The rapid hydration of cement components at this stage results in the sharp increase of Δp.

3.3.2. *Effect of water to binder ratio on the development of meniscus depression*

From Fig. 3 we can see that the transition time postpones with the increase of water/binder ratio. As for the paste with 0.20 W/B the transition time is about in 2.5–3.5 h. This time is delayed to about 4.5–5.0 h for 0.30W/B, 8.0–9.0 h for 0.35 W/B, 13.0–14.0 h W/B and 34.5–35.5 h for 0.50W/B, respectively. The volume and size of the capillary voids are determined by the original distance between the anhydrous cement particles in the freshly mixed cement paste, i.e., water to binder ratio (W/B) and the hydration degree. The hydration degree is universally about 20% whatever the water to cement ratio is [11]. So the structure of the capillary network at the very early-age should mostly be determined by W/B. A higher water/binder ratio corresponds to a coarser pore structure and higher porosity. In order to achieve thermodynamic equilibrium the consumption of free water is gradually from large pores to small pores. Therefore, due to the increase of the volume of very large pores the water consumption in a higher W/B mixtures results in a much more slowly rising of Δp. However, another possible reasons maybe the bleeding of the paste at higher water to binder ratio. The re-adsorption of the bleeding water into the paste may arrest the increase of Δp.

3.3.3. *Effect of mineral admixtures on the development of meniscus depression*

Fig. 4 demonstrates that the transition time also delays with the increase of the volume of mineral admixtures. At 0.30 W/B, 30% and 50% replacement of cement by fly ash delays the transition time by about 1 h and 5 h, respectively. 30%, 50% and 70% replacement of cement by ground granule blast furnace slag delays the transition time by about 0.5 h, 2 h and 6.5 h, respectively. Keeping the same water/binder ratio the volume and size of the capillary voids is mostly determined by hydration degree. Fly ash is known as a pozzolana which possesses little or no cementitious value and can't react with water in itself. The pozzolanic reaction of fly ash needs to consume calcium hydroxide produced by cement hydration and so in a very slow speed. In the early stages, fly ash mainly acts as space filler and is involved in the formation of ettringite [12]. Although the cement

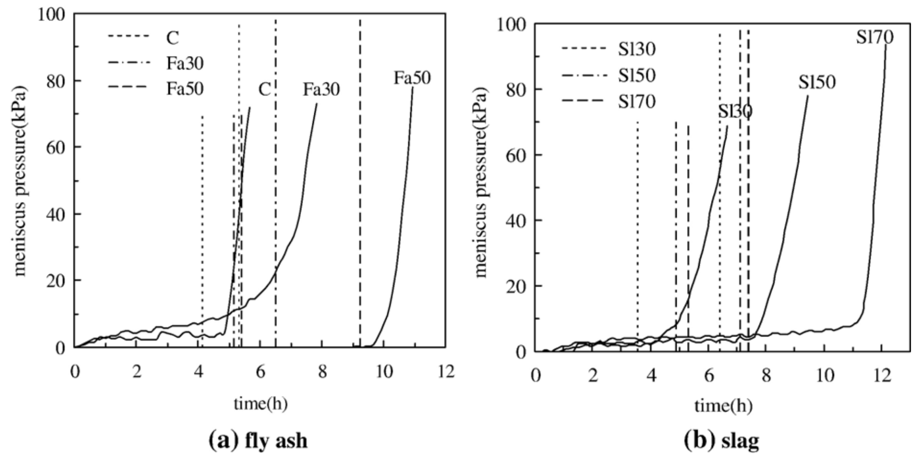


Fig. 4. Effect of the mineral admixtures on the meniscus depression at initial set.

hydration may be enhanced due to a higher w/c ratio [13], the relatively much lower total hydration products at very early-age in fly ash cement paste results in a delayed structure formation and meniscus depression generation. The reaction degree of fly ash also decreases with the increase of fly ash content [14]. Therefore the transition time in the curve of Δp development delays with the increase of fly ash content. Compared to fly ash, fine ground granulated blast furnace slag is self-cementing and need not Ca$(OH)_2$ to form cementitious products. However, the hydration of slag by itself cannot produce sufficient reactants to build the structural network. When used in combination with Portland cement, the hydration of slag is accelerated due to the presence of calcium hydroxide and gypsum. As the slag replacement increases the reactivity of slag reduces due to the reduction of alkaline activating environment provided by the hydration of cement [15]. So the transition time in the curve of Δp development also postpones with slag replacement. But this delaying effect is less distinct compared to fly ash at the same volume due to its relatively higher reactivity.

3.3.4. Discussion about the "time-zero" of SDS

It should also be noted in Figs. 3 and 4 that the transition zone doesn't always match well with the setting time tested by pin-penetration resistance test. When the water/binder ratio is 0.20 the initial setting time takes place in the initial ascending section of the curve while the final setting time takes place in the sharp increasing period, which reveals a well correspondence between Δp development and setting time. However, when the water/binder ratio is 0.30, the initial ascending period is beyond the initial setting time while the final setting time still falls in the sharp increasing period of the curve. Once the water/binder ratio exceeds 0.40 the transition zone of Δp falls beyond the final setting time. This delaying effect is also strengthened by the incorporation of mineral admixtures. When the water/binder ratio is 0.30, the transition zone is beyond initial setting time but still intersects with final setting time curve for the paste with 30% of fly ash or slag replacement. If the replacing percentage is up to 50%, the transition zone is far beyond the final setting time. Therefore, initial setting time obtained by penetration methods doesn't seem to fit well with the real arising time of self-desiccation and thus couldn't provide scientific determination of "time-zero" of SDS in practical testing.

In terms of physical aspects setting refers to the solidifications of the plastic cement paste. The initial set refers to the beginning of solidification and marks the point in time when the paste has become unworkable. The final set corresponds to the time taken to solidify completely. Although the phenomena of set are the physical manifestations of progressive hydration of cement with time, these strength values are considered to be rather arbitrary [6]. From the definition point of view, meniscus depression measurement has more straightforward physical significance and is directly correlative to the definition of "time-zero" of SDS. The experimental results of this test stress the origin of SDS and could potentially be used to explain the effects of water to binder ratio as well as mineral admixtures on SDS at first hand.

3.3.5. Discussion about the mechanism of SDS

Although limited by the measurement range of the tensiometer, the experimental results manifest that the values of Δp are in the level of 100 kPa and the relevant critical radius calculated by Kelvin law are several microns at the very early-age. This result seems to contradict with the traditional theory of shrinkage, according to which water consumption in such size of pores will not result in shrinkage [16]. But substantially rapid SDS development generates at this time if the bleeding effect is avoided, such as for the silica fume modified cement paste with very low water to cement ratios [17]. This could be discussed in terms of the difference between the physical properties of very young paste and hardened paste. It should be noticed that cement pastes are viscoelastic and have large deformation capability at the beginning of structure formation. If the meniscus depression has increased to a substantial value before setting, the paste may exhibit substantial deformation even under minor shrinkage stress. However, if the transition zone takes place after setting due to re-absorption of bleeding water, or the water consumption in large pores at high water/binder ratio or high volume mineral admixtures, the paste has finished the solidification course and turned into the hardening stage. The mechanical properties such as strength, rigidity as well as Young's modulus grow rapidly and then the deformation ability of the paste drops quickly. At this time, a minor shrinkage stress caused by the water consumption in large pores result in a negligible deformation. These might be possible behind the mechanism of the effects of water to binder ratio and mineral admixtures on SDS at very early-age.

4. Conclusions

Preliminary experimental results show that:

1) There is a sensitive transition zone in the meniscus pressure (Δp) development at the very early-age. The transition time is delayed with increase of water/binder ratio and mineral admixtures volume. The presence of bleeding water and its re-adsorption postpone the arising of meniscus depression.
2) At the very early-age water consumed only in large pores in the size of several micros and causes about 100 kPa capillary depressions under sealed condition. Such accordingly minor shrinkage stress may lead to rapid SDS development if the paste still has large deformation capacity while a negligible deformation if the paste has finished the solidification course, which could potentially explain the effects of water to binder ratio and mineral admixtures on SDS at very early-age.
3) It seems that the "time-zero" of SDS determined by penetration methods doesn't have sufficient reliability both for its physical definition and practical testing. The meniscus depression measurement could provide the determination of "time-zero" of SDS directly related to its definition by the adoption of meniscus depression measuring system. However, scientific determination of "time-zero" by this method needs more comprehensive investigations.

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