Fracture Mechanics of Concrete and Concrete Structures -
Assessment, Durability, Monitoring and Retrofitting of Concrete Structures- B. H. Oh, et al. (eds)

Effect of heat curing at early age on drying shrinkage and microstructure of hardened cement pastes

Z.J. Kang
Chongqing University, Chongqing, China
Dalian Research Institute of Building Sciences, Dalian, China

C.J. Wan*, Q.Y. Yin & L.J. Liu
Chongqing University, Chongqing, China

W. Zhang & Y.S. Wang
Dalian Research Institute of Building Sciences, Dalian, China

ABSTRACT: Disc-shaped specimen, drying plus rewetting procedure were designed to get better investigation of effect of heat curing at early age on drying shrinkage of hardened cement pastes. The experimental results show that the drying shrinkage as well as its irreversible and reversible components of the hardened cement pastes is decreased by heat curing, even only curing at 60℃ for the first 24 hours after mixing. The results of pore structure analysis show that the gel pore structure is optimized, that is, the volume of smaller gel pores with radius from 1.5 to 7 nm was increased and the volume of larger gel pores with radius from 7 to 100 nm was decreased, while the total volume of gel pores is little changed. The results of TG-DSC thermal analysis show that the microstructure of both calcium silicate hydrate (C-S-H) gel and $Ca(OH)_2$ phase in hardened cement pastes is possibly changed by the heat curing.

1 INSTRUCTION

As is well known, when a hardened cement paste or concrete specimen is exposed to environmental humidity, which is normally lower than 100% relative humidity (RH), the material begins to lose water and the drying shrinkage occurs associated with the loss of water. When rewetting, some of the contraction is regained, which is called reversible or recoverable shrinkage. Correspondingly, some of the deformation of total drying shrinkage is permanent, called irreversible or irrecoverable shrinkage. Cracking and warping induced by drying shrinkage in concrete is widely acknowledged as one of the fundamental flaws for concrete and reinforced concrete structures, it leads to premature deterioration and shortening the service life.

Heat curing is generally applied to accelerate the early strength of concrete, and is needed for high production capacity in precast production. However, it's known to reduce the long-term strength and durability of concrete. The effects of heat curing and drying shrinkage on the mechanical properties of hardened cement pastes have been studied and modeled respectively. (Helmuth & Turk 1967, Jennings 2000, Juenger & Jennings 2002, Wan et al. 2006a, b, 2007) However, there is still no full understanding of the effects of heat curing at early age on the shrinkage behavior of the cement pastes. This work aims to experimentally measure the drying shrinkage of cement pastes in relation to heat curing at early age and the change of microstructure, thus could give further insights and better understanding on the effect of heat curing at early age on drying shrinkage and microstructure of hardened cement pastes.

2 EXPERIMENTAL PROCEDURES

2.1 *Preparation of the cement pastes*

The cement pastes used in this study were prepared by deionized water and ordinary Portland cement named P.O.42.5 according to China standard GB175-2007 (so called CN P.O.42.5 Cement hereafter). The chemical analysis result of the cement is given in Table 1.

Table 1. Composition of CN P.O.42.5 Cement.

Composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O
Content (percent by weight, %)	63.8	21.1	6.6	2.8	2.1	0.2	0.4

The water to cement ratio of the cement pastes was determined at 0.50 by mass. The pastes were mixed by hand, cast in the plastic vials with diameter of 25 mm, and shaped into cylinders.

Three groups of pastes were prepared for three different curing conditions. The first one was cured at room temperature, that is, 20±1℃, which is called room temperature curing. The second one was cured at higher temperature, that is, placed in the 60±1℃ waterbath immediately after being cast until demoulding, which is called heat treatment. The third one was cured just like the second one before demoulding for the first 24 hours. When 24 hours after mixing, both of the first and second groups were demoulded and immersed in the saturated lime water which was filled in the plastic cups in room condition and cured for other 27 days at 20±1℃ until drying, while the third group was immersed in the saturated lime water which was filled in the plastic cups at 60±1℃waterbath immediately after being demoulded until drying.

As a matter of convenience, the curing condition of cured at 60℃ for the first day followed by 20℃ for the other 27 days is simply named as "cured at 60℃+20℃" or "heat treatment", the curing condition of cured at 20℃ for 28 days is simply named as "cured at 20℃" or "normal curing" or "control", and the continuously cured at 60℃ is simply named as "cured at 60℃" or "heat cured" hereafter.

2.2 *Preparation of sample discs*

When the pastes were ready for drying and other measurements, thin discs, which were 0.8 mm thick and 25 mm in diameter, were cut from the hardened cement pastes by precision saw. In order to precisely get the radial length change of the discs, three lines were drawn slightly and crisscrossed on each disc surface separated by approximately 120 degree angles as shown in Figure 1. The final radial length change of the disc is the average of the three.

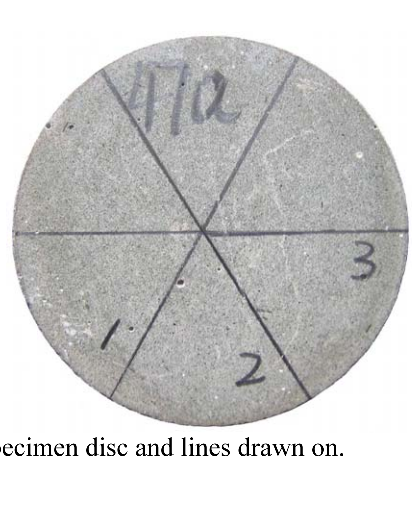

Figure 1. Specimen disc and lines drawn on.

2.3 *Measurements of weight and diameters of sample discs*

Fine digital balance with a resolution of 0.1 mg was used to measure the weight of discs. A satisfactory level of accuracy was achieved by this balance as indicated by the relatively small scatter in the data. Digital caliper with a resolution of 0.01 mm was used to measure the changes in diameters of the discs. During the measurements of diameters, the caliper was mounted on a fixed surface. For each measurement, the length readings for three marked diameters were recorded. Exposure of cement paste discs to carbon dioxide was minimized by flushing the desiccator with nitrogen after each open of the desiccator.

In each measurement, in order to increase the accuracy, three same discs were used.

2.4 *Drying and rewetting*

The pastes were dried in the desiccator over saturated $Ca(NO_3)_2$ solution when drying is needed. The relative humidity (RH) and temperature in the desiccator were recorded by thermo-hygrometer. According to the record, the relative humidity kept constantly at 43%±2%, and the temperature at 20±1℃. In order to distinguish the reversible and irreversible components of drying shrinkage, after drying, rewetting followed. The dried discs were quickly immersed in the saturated lime water, which was filled in a plastic cup, after the last measurement of drying. The weight loss and shrinkage during drying and rewetting were determined in reference to the weight and diameters of the saturated discs before drying.

3 RESULTS ANALYSIS

3.1 *Reversible and irreversible drying shrinkage*

The radial length changes with drying and rewetting time of heat cured cement pastes and the control were measured and shown in Figure 2. In Figure 2, point O to point A is the drying process and after point A, that is, A to B, is the rewetting process. According to the results in Figure 2, the corresponding reversible drying shrinkage and irreversible drying shrinkage of cement pastes were calculated and plotted, as shown in Figure 3. From Figure 2 and Figure 3, the effect of heat curing on drying shrinkage is revealed. The total drying shrinkage as well as its irreversible and reversible components of heat treated and heat cured cement pastes are both lower than the control, particularly, the drying shrinkage of heat cured cement paste is much lower than that of the other two.

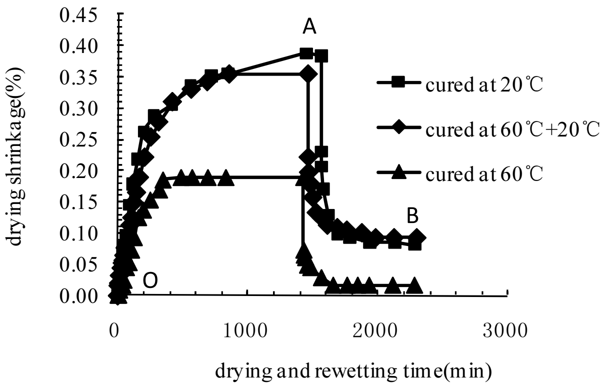

Figure 2. Drying shrinkage of normal, heat treated and heat cured cement pastes with drying and rewetting time when dried at 43%RH and subsequently rewetted.

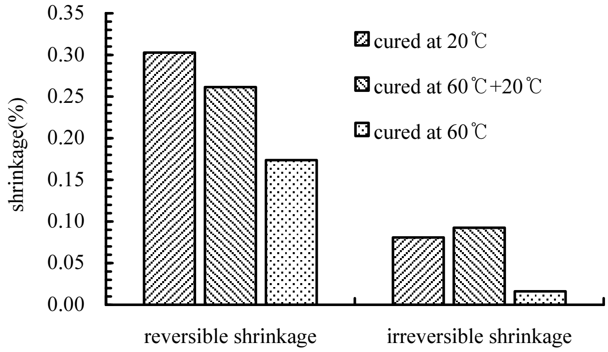

Figure 3. Reversible and irreversible drying shrinkage of normal, heat treated and heat cured cement pastes when dried at 43%RH.

It has been reported that high curing temperatures decrease drying shrinkage (Bentur 1980a, Parrott 1976, Parrott 1977a,b, Bergstrom 1993). Bentur et al. (1980b) showed that increasing the temperature (65℃) decreased both reversible and irreversible shrinkage. In this study, heat curing at early age had the similar effect on drying shrinkage. It is known that the primary driving force for shrinkage at relative humidity (RH) levels from 100% down to 43% is capillary tension in the pores, and disjoining pressure between the particles of cement. Both of these processes are intrinsically reversible, so irreversible shrinkage strains must result from physical or chemical changes of the paste. These changes are generally considered to be a rearrangement of the C-S-H gel particles due to drying, and possibly associated with permanent changes in the packing density. Thus, the weight losses during drying and subsequent rewetting and the pore micro-structure were measured. The results were plotted in Figure 4 and Figure 5 respectively.

3.2 *Weight loss during drying and subsequent rewetting*

Based on the method described in this study, the weight loss during drying and subsequent rewetting is very easy and accurate to obtain, which is shown in Figure 4. It is obviously shown that heat curing at early age has also effect on the weight loss. The heat treated and heat cured cement pastes have more weight loss than the normal cured, when dried at 43% RH. As known, free water in capillary pores is removed during drying at 43% RH. So it can be concluded that heat curing made the capillary pore water more easy to be removed when drying, which gives a support to the most agreement of that heat curing can coarsen the capillary pores and lower the surface area of cement paste (Bentur 1980a).

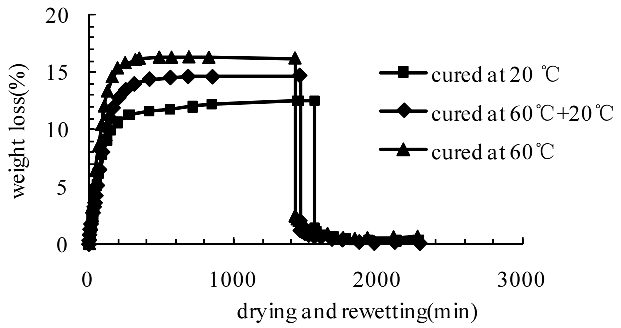

Figure 4. Weight loss of normal, heat treated and heat cured cement pastes with drying and rewetting time when dried at 43%RH and subsequently rewetted.

3.3 *Pore structure*

Nitrogen adsorption and desorption of hardened cement pastes were carried out on an instrument named Micromertics ASAP 2010. Surface area was calculated using the Brunauer, Emmett and Teller (BET) method, and pore size distribution were calculated by the Barrett, Joyner and Hallenda (BJH) method using data from the desorption isotherm. This technique only measured the pores of cement pastes with radii between 1 and 100 nm approximately, as known, which should be pores in C-S-H gel , thus, named gel pores. Pore size distribution results for samples with 0.50 of water to cement ratio are shown in Figure 5. In order to get information of the pores with radii more than 100 nm, the pore size distribution of the cement paste cured at 20℃ was measured by Mercury Intrusion Porosimetry (MIP), which is also shown in Figure 5 as a reference.

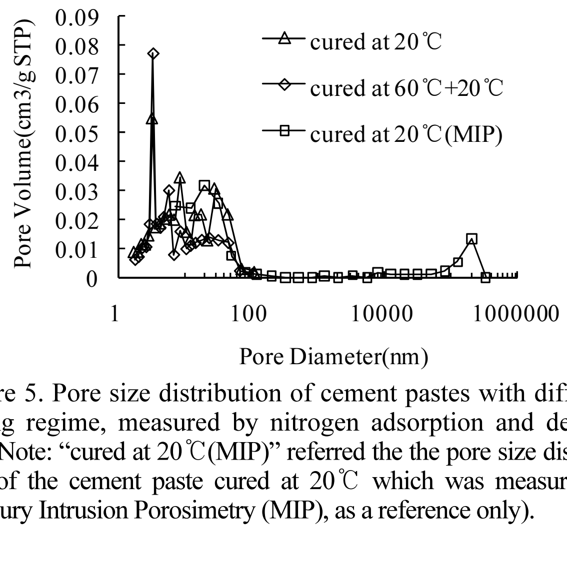

Figure 5. Pore size distribution of cement pastes with different curing regime, measured by nitrogen adsorption and desorption(Note: "cured at 20℃(MIP)" referred the the pore size distribution of the cement paste cured at 20℃ which was measured by Mercury Intrusion Porosimetry (MIP), as a reference only).

As for the effect of heat curing on the pore structure of cement paste, the most agreement is that heat curing can coarsen the capillary pores and lower the surface area of cement paste (Bentur 1980a). In this study, according to the measured BET surface area data, the cement paste which was heat cured at early age has a little lower surface area (184.90m^2/g) than that of the normal cured (198.19m^2/g), which is consistent with the most agreement. As shown in Figure 5, it is clear that heat curing at early age increases the volume of smaller gel pores (1.5-7 nm radius range) and decreases the volume of larger gel pores (7-100 nm radius range). It means that heat curing fined (not coarsened) the gel pores of cement paste. That is, heat curing affects the capillary pores and gel pores with opposite way.

When drying at 43% RH, that is, the capillary pores are dried up as known, since heat treated and heat cured pastes lose more weight of water than the normal cured paste (Fig. 4), more and larger pores of heat treated and heat cured pastes are dried up, which caused less capillary tension and thus less shrinkage, while less and smaller pores of normal cured paste are dried up, which caused more capillary tension and thus more shrinkage, as shown in Figure 2.

3.4 *Thermal analysis results*

Thermal analysis of cement pastes were carried out on an instrument named NETZSCH STA 449 C Jupiter. The thermal analysis results of cement pastes with normal curing, heat treatment and heat curing at early age are shown in Table 2.

Table 2. Thermal analysis results of cement pastes.

Curing type	Result type	Temperature range(℃)		
		30-350	350-575	575-1000
20℃	TG,%	-26.32	-4.30	-0.66
	DSC,J/g	-746.9	-118.9	----
60℃+20℃	TG,%	-29.19	-4.36	-1.01
	DSC,J/g	-822.1	-95.78	----
60℃	TG,%	-25.47	-4.77	-1.32
	DSC,J/g	-664.6	-103.9	----

Concerning the thermogravimetric analysis(TG) and differential thermal analysis(DSC) results in Table 2, the endothermic peaks from 30℃ to 350℃ is approximately considered as the loss of free water; the endothermic peaks from 350℃ to 575℃ is approximately considered as the destruction of $Ca(OH)_2$ phase; and the exothermic peaks from 575℃ to 800℃ is approximately considered as decomposition of C-S-H gel. Therefore, according to the result data shown in Table 2, the free water of heat treated cement paste was measured as 29.19%, while that of normal cured one was 26.32%, lower than that of heat treated one, that possibly means the capillary pores volume of heat treated cement paste is more than that of normal cured one, thus, heat curing coarsened the capillary pores, which is consistent with the most agreement as mentioned above. Although the free water of heat cured cement paste was measured as only 25.47%, its DSC was measured as 664.6 J/g, much lower than that of normal cured one(746.9J/g), that means the free water of heat cured cement paste is possibly easier to be removed when drying.

The weight loss caused by the destruction of $Ca(OH)_2$ of heat treated cement paste was measured as 4.36%, that of heat cured one was 4.77%, while that of normal cured one was 4.30%, a little bit lower than that of heat treated and heat cured ones, that possibly means the hydration degree of heat treated and heat cured cement paste is a little bit more than that of normal cured one. The total weight loss from the begin(30℃ in this study) to 1000℃ of heat treated cement paste was measure as 34.56%, that of heat cured one was 31.56%, while that of normal cured one was 31.28%. For the paste with water to cement ratio 0.5, the original water is 0.5/(1+0.5), that is, 33.33%. So it can be concluded that when curing, the heat treated cement paste can absorb some water from the environment, while the heat cured cement paste and the normal cured one lose their water.

Thus, heat curing at early age possibly affect the micro-structure of both $Ca(OH)_2$ crystal and C-S-H gel.

4 CONCLUSIONS

(1) The drying shrinkage as well as its irreversible and reversible components of the cement paste is decreased by curing at 60℃ for the first 24 hours after mixing or for 28 days.
(2) Heat curing at early age optimizes the C-S-H gel pores distribution, that is, increases the volume of smaller gel pores with radius from 1.5 to 7 nm and decreases the volume of larger gel pores with radius from 7 to 100 nm, while the total volume of gel pores is little changed.
(3) Heat curing at early age possibly influences the micro-structure of both C-S-H gel and $Ca(OH)_2$ phase in cement paste.

ACKNOWLEDGEMENT

We gratefully acknowledge the financial support provided by the National Natural Science Foundation of China, Grant No. 50772136, named as Disc Method Used to Study the Drying Shrinkage of Hydrated Cement Pastes and Its Micro Mechanism.

REFERENCES

Bentur, A. 1980a. Effect of curing temperature on the pore structure of tricalcium silicate pastes, J. Colloid Interface Sci. 74 (2) (1980): 549-560.

Bentur, A., Kung, J.H., Berger, R.L., Young, J.F., Milestone, N.B., Mindess, S., Lawrence, F.V. 1980b. Influence of microstructure on creep and drying shrinkage of calcium silicate pastes, Proceedings of the 7th International Congress on the Chemistry of Cement, III (VI): 26-31.

Bergstrom, T. 1993. An environmental scanning electron microscope investigation of drying cement paste: drying shrinkage, image analysis, and modeling, PhD dissertation, Northwestern University.

Helmuth, R.A. & Turk, D.H. 1967. The reversible and irreversible drying shrinkage of hardened Portland cement and tricalcium silicate pastes, J. Port. Cem. Assoc. Res. Dev. Lab. 1967. 9 (2): 8–21.

Jennings, H.M. 2000. A model for the microstructure of calcium silicate hydrate in cement paste. Cement and Concrete Research. 2000. 30 (1): 101-116.

Juenger, Maria C. Garci & Jennings, H.M. 2002. Examining the relationship between the microstructure of calcium silicate hydrate and drying shrinkage of cement paste. Cement and Concrete Research. 2002. 32: 289-296

Parrott, L.J. 1976. Effect of a heat cycle during moist curing upon the deformation of hardened cement paste, Hydraulic Cement Pastes, Cem. Concr. Assoc., Slough, UK: 189_204.

Parrott, L.J. 1977a. Recoverable and irrecoverable deformation of heat-cured cement paste, Mag. Concr. Res. 29 (98) (1977): 26-30.

Parrott, L.J. 1977b. Basic creep, drying creep and shrinkage of a mature cement paste after a heat cycle, Cement and Concrete Research. 1977 (7): 597-604.

Wan, C.J., Kang, Z.J. et al. 2006a. Dimensional stability of hardened cement pastes during and after accelerated leaching process. Proceedings of the sixth international symposium on cement & concrete, CANMET/ACI international symposium on concrete technology for sustainable development. Xi'an, China. September 19~22. 2006. Foreign languages press. 2006. Volume 3: 1709~1715.

Wan, C.J., Kang, Z.J. et al. 2006b. Effect of heat cure and decalcification on the drying shrinkage behavior of hydrated cement pastes. Proceedings of 1st international workshop on service life design for underground structures, Serviceability of underground structures. Shanghai, China. 2006.10. Tongji University press. 2006.10: 170~177.

Wan, C.J., Jennings, H.M., Thomas, J., Chen, J., Kang, Z.J. et al. 2007. The shrinkage behavior of decalcified cement paste. 12th international congress on the chemistry of cement. Montreal, Canada. July 8-13.