Relationship between early-age autogenous shrinkage and cement hydration of concrete

L. Xie & S.X. Wu
College of Civil Engineering, Hohai University, Nanjing, China

ABSTRACT: When cement mixes with water, hydration immediately takes place. The cement hydration leads to the arising of chemical shrinkage and the decreasing of internal relative humidity, and further induces self-desiccation of concrete, which is the direct reason of autogenous shrinkage, so it is necessary to study the relationship between early-age autogenous shrinkage and cement hydration of concrete. In this paper, the relationship between early-age autogenous shrinkage and chemical shrinkage, degree of hydration, and internal relative humidity related to cement hydration are discussed. The results indicate that during the very early hours autogenous shrinkage can be fully attributed to the chemical changes due to cement hydration, but it is not equal to chemical shrinkage because of different shrinkage mechanisms; the point when autogenous shrinkage changes from being a function of chemical shrinkage versus self-desiccation is degree of cement hydration; and there is obvious linear correlation between autogenous shrinkage and internal relative humidity.

1 INTRODUCTION

Autogenous shrinkage of cement paste or concrete is defined as the macroscopic volume change occurring with no moisture transferred to the exterior surrounding environment. As we know, autogenous shrinkage is the result of self-desiccation or internal desiccation (Tazawa et al. 1999). For lacking of external water, further hydration will begin to consume the capillary water and thus will induce the hydrating cement paste dried. The type of drying is called as self-desiccation, which is the intrinsic attribute of concrete. Self-desiccation leads to shrinkage and the mechanics of autogenous shrinkage is identical with that of traditional drying shrinkage. The volume change induced by self-desiccation is firstly affirmed by Lyman in 1934 (Lyman 1934). But it is then neglected by engineers because autogenous shrinkage of ordinary concrete can be ignored when compared with drying shrinkage. However, with the popularization of high performance concrete and the use of special cements and water reducing agents in recent years, autogenous shrinkage is again payed attention to. Recent research indicates that autogenous shrinkage greatly contributes to early age cracking when the water-cement ration is lower than 0.4, even if it is normal strength concrete (Tazawa et al. 1993).

Hydration immediately occurs as soon as cement mixes with water. Hydration leads to cement stone shrinking and internal relative humidity decreasing, and thus induces self-desiccation of concrete which is the direct cause of autogenous shrinkage. So it is necessary to study the relationship between early-age autogenous shrinkage and cement hydration of concrete.

2 RELATIONSHIP BETWEEN EARLY-AGE AUTOGENOUS SHRINKAGE AND CHEMICAL SHRINKAGE

Chemical shrinkage, which is also called as hydration shrinkage, results from the difference between the average density of reactants and that of reaction products. The negative effect of chemical shrinkage is to result in autogenous shrinkage of concrete and even lead to concrete cracking. The basic reactions of cement clinker are generally defined by the following equations of the clinker phases (Erika 2001):

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \quad (1)$$

$$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \quad (2)$$

$$C_3A + 6H \rightarrow C_3AH_6 \quad (3)$$

$$C_4AF + 2CH + 10H \rightarrow C_3AH_6 + C_3FH_6 \quad (4)$$

The cement chemistry will affect the autogenous shrinkage due to the varying chemical shrinkage in the very early ages. If a cement has a high C_3A content, it is expected that there will be greater shrinkage than a comparable cement with lower C_3A. Some compounds also work together, such as C_2S and C_3S. Cement with high C_2S content usually has a corresponding lower C_3S content. This combination of a higher C_2S and lower C_3S would result in an overall lower shrinkage than the reference cement. The final magnitude of the shrinkage will only be influenced by the chemical composition of the cement as the degree of hydration approaches 100%.

Figure 1 gives the relationship between autogenous shrinkage and chemical shrinkage with no moisture evaporation and external water source. As figure 1 shows, autogenous shrinkage is fully attributed to chemical shrinkage during the very first hours after mixing. Immediately after mixing water and cement, a chemical shrinkage change will occur due to the reduction in volume of the reaction products. In this early phase while the concrete is still liquid, autogenous shrinkage is due only to chemical shrinkage and equivalent to it (Erika 2001).

At the point when a skeleton is formed due to the stiffening of the paste, concrete can resist some of the chemical shrinkage stresses. Soon after this initial skeleton formation, concrete will set. During this stage the capillary under-pressure will start to develop and may cause shrinkage. As water is lost from subsequently smaller pores, the water meniscus will continue to be pulled into the capillary pores and will generate more stress on the capillary pore walls, and it can cause a contraction in the cement paste. Once the skeleton has formed, chemical shrinkage becomes more and more restrained. At this time, the material is rigid and autogenous shrinkage is comprised of less and less chemical shrinkage. The further volume reductions are only due to self-desiccation (Boivin et al., Hammer & Justnes et al. 1999). Once concrete has hardened with age (> 1+ day), autogenous shrinkage may no longer be the result of only chemical shrinkage. During the later ages, autogenous shrinkage can also result from self-desiccation since rigid skeleton is formed to resist chemical shrinkage. Self-desiccation occurs over a longer time period than chemical shrinkage and does not begin immediately after casting. It is only a risk when there is not enough localized water in the paste for cement to hydrate; thus water is drawn out of the capillary pore spaces between solid particles. This would typically begin after many hours or days in high strength concretes with low *w/c* ratio.

As earlier described, autogenous shrinkage is a portion of chemical shrinkage. Although chemical shrinkage is the key cause of autogenous shrinkage, there is no direct relationship between them. As the hardened cement stone is considered as the compound of solid phase, gas phase and liquid phase, chemical shrinkage is the reduction in absolute volume of reactant, while autogenous shrinkage is the reduction in the external volume after solid phase has formed. So autogenous shrinkage is far from chemical shrinkage (Yue LI et al. 2000).

3 RELATIONSHIP BETWEEN AUTOGENOUS SHRINKAGE AND DEGREE OF HYDRATION

The development of early-age concrete properties can be described dependent on the degree of hydration (Gutsch 2001). The progress of a cement reacting until it reaches its full potential is referred to as the degree of hydration α. For normal strength concrete, the ultimate hydration of α approaching 1, or 100%, is reached after many years. In high strength concrete, with developing of hydration, there will be more and more thick hydrated products film around big particles, and this will lead to the reaction speed slowing and even may stop the shuttle transfer of

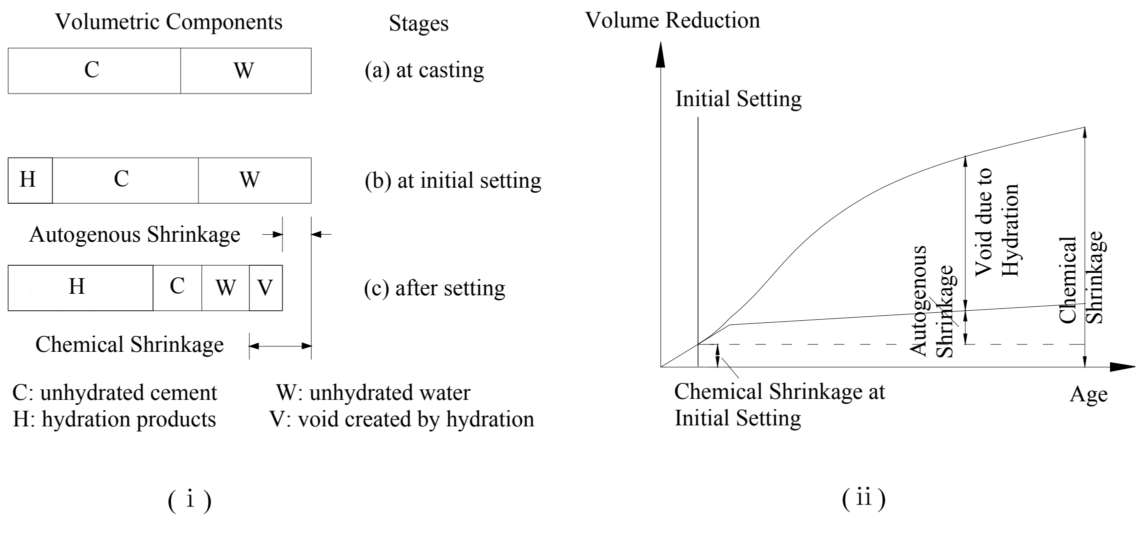

Figure 1. Relationship between autogenous shrinkage and chemical shrinkage

ions on the surface of water-free cement particles. In such a case, cement hydration may stop and the degree of hydration α is far from 1.

Powers (1999) gives the degree of hydration in Eq.(5):

$$\alpha(\%) = \frac{W_{ne}(t)}{W_{ne}(t_\infty)} \times 100 \tag{5}$$

Where $W_{ne}(t)$ = the bound water content at time t ; and $W_{ne}(t_\infty)$ = the water quantity necessary for complete cement hydration.

Physically absorbed layers do not contribute to the progress of hydration, and only free capillary water is available for further hydration. Therefore, when modelling the degree of hydration concrete, not only the temperature rate factor but also *w/c* and water distributions should be taken into account. The following expression has been used to describe the degree of reaction of cement α (Byung 2003):

$$\alpha = \exp\left(-a_c \left(\ln\left(1 + \frac{t_{eq}}{b_c} \right) \right)^{-c_c} \right) \tag{6}$$

where t_{eq} = the equivalent maturity age; and a_c, b_c, c_c = empirical constants that can be obtained by relating Eq.(6) ~ (8). The degree of hydration of each compound in Portland cement is related to α and can be taken as a weighted average (Byung 2003 & Tazawa et al. 1995):

$$\alpha = \sum_{i=1}^{4} \alpha_i W_i = \alpha_{C_3S} W_{C_3S} + \alpha_{C_2S} W_{C_2S} + \alpha_{C_3A} W_{C_3A} + \alpha_{C_4AF} W_{C_4AF} \tag{7}$$

Where α_i = the individual degree of reaction for each compound; and W_i = the initial percentage weight for each compound. A set of the same-type equations as Eq.(6) is used here to approximate the degree of hydration for each compound.

$$\alpha_i = \exp\left(-a_i \left(\ln\left(1 + \frac{t_{eq}}{b_i} \right) \right)^{-c_i} \right) \tag{8}$$

The constants a_i, b_i, c_i can be determined empirically by nonlinear regressions of test data. The term t_{eq} in Eq.(8) is assumed to be real time t in the test, that is, the environmental temperature is 20℃ and the required water to react each compound completely is sufficient. The three-parameter models of Eq.(6) and (8) can adequately express the realistic hydration processes, especially at very early ages.

The equivalent maturity time for cement t_{eq} in Eq.(6) can be considered as a function of temperature, *w/c* and water distribution as follows:

$$t_{eq} = \int_0^t \beta_T \beta_{w/c} \beta_w dt \tag{9}$$

The rate factors β_T , $\beta_{w/c}$ and β_w take into account a curing temperature, water shortage, and water distribution, respectively.

There is not the direct mathematic representation of the relationship between autogenous shrinkage and the degree of hydration, but it was shown that the point when autogenous shrinkage changes from being a function of chemical shrinkage versus self-desiccation is a function of the degree of cement hydration (Erika 2001). When concrete is still liquid immediately after mixing, autogenous shrinkage is due only to chemical shrinkage and proportional to the degree of hydration. With developing of hydration, once a skeleton has formed, the material is rigid and autogenous shrinkage is comprised of less and less chemical shrinkage.

4 RELATIONSHIP BETWEEN AUTOGENOUS SHRINKAGE AND INTERNAL RELATIVELY HUMIDITY

Autogenous shrinkage occurs in sealed ambient in which the relative humidity change is only in certain range. Experimental results indicate: eigen relative humidity caused by self-desiccation in concrete is no less than 75%, while the actual internal relative humidity in concrete should be higher than it.

The result of self-desiccation is that the saturation state of capillary water changes to be unsaturation and the water meniscus has formed in capillary pores, and thus results in autogenous shrinkage when hydrated cement stone is affected by capillary under-pressure. The mechanics of autogenous shrinkage is similar to that of drying shrinkage. There are many theories about drying shrinkage of concrete, such as capillary pressure theory, gel particle surface energy change theory and repulsion force theory. But according to the research of Fisher and Crassous (Tazawa et al. 1999), the above capillary pressure theory of drying shrinkage can well explain autogenous shrinkage as the relative humidity is greater than 80%.

Because gel water and hydration water can not take part in the cement hydration, the phenomenon of self-desiccation only occurs in capillary pores and the mechanics of shrinkage caused by it agrees with capillary tension theory. The useful relation for interpretation of the effect of the pore sizes is given by Kelvin's equation, which correlates the relative humidity existing within concrete to the size of the capillary pore. As the pore size decreases, the internal relative humidity quickly drops, which in-turn induces stress and shrinkage (Guoxing HUANG et al. 1990).

$$\ln \phi = -\frac{2\sigma M}{\rho R T r} \tag{10}$$

where Φ = internal relative humidity; M = molecular weight of water (18kg/Kmol); ρ = density of water (998kg/m^2); R = gas constant (8214J/(Kmol° K)); T = temperature (° K); and r = pore radius (m).

According to the effect mechanics of self-desiccation, it is self-desiccation that causes the autogenous relative humidity of cement paste decreasing and the decrease of internal relative humidity directly leads to autogenous shrinkage of cement paste. Zhengwu JIANG (2003) & Seungwook (2002) point out that for cement paste with different water-cement ratios, the magnitude of autogenous shrinkage at different ages is in dramatically linear proportion to the change of autologous relative humidity. Zhengwu Jiang (2003) gives the relationship between the magnitude of autogenous shrinkage and the autologous relative humidity:

$$\varepsilon_s(h_s) = mh_s + n \tag{11}$$

where ε_s = the magnitude of autogenous shrinkage of cement paste; h_s = the change of autologous relative humidity caused by self-desiccation of cement paste; and m, n = constants which depend chiefly on water-cement ratio, the types and amounts of mineral admixture, and so on. According to the mathematical model, autogenous shrinkage increases greatly with the decreasing of autologous relative humidity. The lower of water-cement ratio, the larger of the ultimate autogenous shrinkage when the autologous relative humidity of cement paste reduces to zero, which is consistent with the experimental results. Based on the linear correlation between the magnitude of autogenous shrinkage and the autologous relative humidity change of cement paste, the autogenous shrinkage can be well predicted and decreased by testing, adjusting and controlling the magnitude of internal relative humidity of cement paste, and thus the cracking risk of high performance concrete at very early ages is reduced to the minimum degree.

According to the chemical agent of self-desiccation from the thermodynamic angle, the continuation of cement minerals hydration will lead to the evaporable water content reducing in capillary pores, which is the direct cause of autologous relative humidity decreasing of concrete. The hydration characteristic and speed rate of minerals are important to affect the degree of reduction of autologous relative humidity, while the hydration dynamic force of cement minerals is affected directly by the magnitude of autologous relative humidity. As autologous relative humidity decreases, the hydration process of cement will be inhibited, which becomes very obvious when the relative humidity is lower than 75% (Zhengwu JIANG et al. 2003).

For the decrease of pore humidity is the physical cause of autogenous shrinkage, and self-desiccation is a result of hydration process, it is also assumed that the degree of self-desiccation or the loss of pore humidity can be expressed as a function of the degree of hydration (Seungwook 2002):

$$\varepsilon_{AS} = \alpha_{AS} \cdot \Delta h_{AS} \tag{12}$$

$$\Delta h_{AS} = \frac{a+\alpha}{b} \tag{13}$$

Where ε_{AS} = autogenous shrinkage; Δh_{AS} = humidity reduction due to self-desiccation or autogenous drying; α_{AS} = autogenous shrinkage coefficient, determined by experiments; α = degree of hydration; and a, b = experimental coefficient (a=0.1, b=10 for the cylinder specimen).

Eq.(12) again verifies the linear correlation between the magnitude of autogenous shrinkage and the change of autologous relative humidity, which is consistent with the conclusion of other researchers (Guoxing HUANG et al. 1990 & Zhengwu JIANG et al. 2003).

5 CONCLUSIONS

The relationships between early-age autogenous shrinkage and chemical shrinkage, degree of hydration and internal relative humidity caused by cement hydration are mainly discussed in this paper. However, there are many factors influencing autogenous shrinkage of concrete at early ages, such as types of cement, water-cement ratio, mineral admixtures and aggregate. These factors interact, and it is necessary to further study the action of them on autogenous shrinkage at early ages.

REFERENCES

Ahmed Loukili, Abdelhafid Khelidj, Pierre Richard. 1999. Hydration kinetics, change of relative humidity, and autogenous shrinkage of ultra-high-strength concrete. *Cement and Concrete Reaearch* 29: 577-584.

Boivin, S., Acker, P., Rigaud, S., and B. Clavaud. 1999. Experimental Assessment of Chemicak Shrinkage of Hydrating Cement Paste. In Ei-ichi Tazawa, E&FN Spon(eds), *Autogenous Shrinkage of Concrete*. London: 81-92.

Byung Hean Oh & Soo Won Cha. 2003. Nonlinear Analysis of Temperature and Moisture Distributions in Early-Age Concrete Structures Based on Degree of Hydration. *ACI Materials Journal* 100(5): 361-370.

Ei-ichi Tazawa & Shingo Miyazawa. 1995. INFLUENCE OF CEMENT AND ADMIXTURE ON AUTOGENOUD SHRINKAGE OF CEMENT PASTE. *Cement and Concrete Reaearch* 25(2): 281-287.

Erika E. Holt. EARLY AGE AUTOGENOUS SHRINKAGE OF CONCRETE[D]. Doctor of Philosophy of University of Washington, 2001.

Gange, R., Aouad, I., Shen, J. and C. Poulin. 1999. Development of a New Experimental Technique for the Study of the Autogenous Shrinkage of Cement Paste. *Materials and Structures* 32: 635-642.

Guoxing HUANG & Rongyan HUI. 1990. *Shrinkage of Concrete*. Beijing: Railway Publisher of China.

Gutsch, A.-W. 2001. Properties of Early Age Concrete – Experiments and Modelling. *RILEM-Conference "Early age Cracking in Cementitious Systems – EAC'01"*. Haifa, Israel.

Hammer, Tor Arne. 1999. Test Methods of Linear Measurement of Autogenous Shrinkage before Setting. In Ei-ichi Tazawa, E&FN Spon (eds), *Autogenous Shrinkage of Concrete*. London: 143-154.

Justnes, H., Sellevold, E.J., Reyniers. B., Van Loo, D., Van Gemert, and A., Verbovern, F. 1999. The Influence of Cement Characteristics on Chemical Shrinkage. In Ei-ichi Tazawa, E&FN Spon (eds), *Autogenous Shrinkage of Concrete*. London: 71-80.

Lyman C G. 1934. *Growth and movement in Portland cement concrete*: 1-139. London: Oxford University Press.

Seungwook Lim. 2002. *Viscoelastic age-dependent analysis of restrained shrinkage stress development in early-age concrete*. Doctor of Philosophy in Civil Engineering in the Graduate College of Texas A&M University.

Tazawa. E, E&FN Spon. 1999. *Autogenous Shrinkage of Concrete*. New York.

Tazawa, E. & Miyazawa, S. 1993. Autogenous shrinkage of concrete and its importance in concrete technology. In Bazant, Z.P. & Carol, I.(eds), Creept and Shrinkage of Concrete:159-168. Proceedings of the 5th International RILEM Symposium, E&FN Spon, London.

Yue LI, Muhua TAN, Xiong ZHANG, Keru WU. 2000. Autogenous Shrinkage of Concrete and Its Research Progress. *Journal of Building Materials* 3: 252-257.

Zhengwu JIANG, Zhenping SUN, Peiming WANG. 2003. Study on Autogenous Relative Humidity Change and Autogenous Shrinkage of Cement Pastes. *Journal of Building Materials* 4: 345-349.

Zhengwu JIANG, Zhenping SUN, Peiming WANG. 2003. Study on Autogenous Relative Humidity Change in High Performance Concrete. *Journal of the Chinese Ceramic Society* 8: 770-773.