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Enhanced Shrinkage Model Based on Early Age Hydration and Moisture Status in Pore Structure

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Abstract

In this research, an existing multi-scale model for shrinkage behavior is enhanced to improve its applicability and precision. The enhancement work focuses on the initial autogenous shrinkage and intrinsic driving forces of the shrinkage at the microscale. The existing model underestimates the rapid development of the autogenous shrinkage of cement with a low water/cement (w/c) ratio. Hence, combined with self-desiccation, the autogenous shrinkage at an early age is first discussed. As an approximation, a portion of the autogenous shrinkage at an early age is quantitatively calculated using the chemical volume change and distance between cement particles, and that portion is added to compensate for the underestimation in the existing model. Furthermore, in the existing model, capillary tension is assumed to be the principal driving force in all of the pores with various sizes, which would cause an overestimation of the long-term shrinkage in the analysis. Therefore in the enhanced model, the driving forces are discussed and modified. The capillary tension is assumed to only be active in relatively coarse pores, whereas the disjoining pressure dominates in fine pores on the nanoscale. These two driving forces are quantified by the water status in the pores using the proposed formulas. With the above enhancements, the autogenous and drying shrinkage behaviors with various w/c ratios and relative humidity can be simulated reasonably.

1. Introduction

Drying shrinkage, which has been studied for a long time, occurs when concrete is exposed to a low relative humidity (RH). Moreover, concrete with a low water/cement (w/c) ratio is now being widely used. Although a low w/c results in high strength and low permeability, it has been found that autogenous shrinkage becomes non-negligible (Tazawa and Miyazawa 1994, 1995). Tensile stress would be induced by shrinkage, which would cause cracking and undermine the long-term performance of structures. To evaluate and predict the influence of shrinkage, empirical formulas have been suggested in previous studies (Sakata and Ayano 1989; JSCE 2007; CEB 1993; Bazant and Baweja 1995). From another standpoint, shrinkage behavior is associated with microscale thermodynamic properties such as the hydration, pore-structure formation, and water status in micropores. These properties vary according to the raw materials, mix proportion, age, and ambient conditions. Without substantially grasping their relationship, it is difficult to provide an appropriate evaluation of the shrinkage under arbitrary conditions. Therefore, it is important to establish a model that couples the shrinkage behavior and microscale properties.

In order to explain the microscale aspects of the drying shrinkage principle, theories concerning the water status in micropores have been proposed, such as those involving the capillary tension caused by the water meniscus (Powers 1968; Bazant and Rafshol 1982; Mindess et al. 2003; Shimomura and Maekawa 1997), the disjoining pressure caused by water films in narrow pores (Powers 1968; Ferraris and Wittmann 1987; Beltzung and Wittmann 2005; Maruyama 2010), the surface energy change caused by water desorption (Powers 1968; Feldman 1969; Wittmann 1968), and so on. Because the micropores in a cement matrix vary widely in size, the water status values are quite different, and such theories are usually combined to explain the shrinkage under various RHs. For instance, capillary tension is considered to act at comparably high RHs, whereas the disjoining pressure or surface energy change dominates at lower RHs. The mechanisms of autogenous shrinkage are regarded as similar to that for drying shrinkage (Kovler and Zhutovsky 2006; Lura et al. 2003; Hua 1995), with the difference that the water is consumed by self-desiccation rather than loss to the environment. The relationship between chemical shrinkage and autogenous shrinkage has also been investigated and discussed (Tazawa et al. 1995; Holt 2005).

With respect to the simulation of the shrinkage behaviors of concrete, a multi-scale constitutive model (Zhu et al. 2004; Maekawa et al. 2009) was developed in the Concrete Laboratory of the University of Tokyo based on the thermodynamics. In this model, the hydration process, pore-structure formation, moisture equilibrium and transport are simultaneously coupled to attain the water status in the micropores. Accordingly, the driving

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forces of the shrinkage are quantified and applied to the cement matrix. In addition, a two-phase stiffness model is established to describe the deformation response. As long as the mix proportion, specimen dimensions, and ambient conditions are input, the multi-scale constitutive model is theoretically capable of simulating autogenous or drying shrinkage simply by altering the boundary condition to a sealed or exposed condition. This methodology has been proven to be effective, and the shrinkage trends can be approximately traced. Nonetheless, for practical application, an improvement in the precision is requisite, especially for low w/c concrete. Therefore, in this study, the authors conduct a further investigation of shrinkage on the basis of microscale phenomena. Accordingly, the model is refined and improved. Before that, the existing model is briefly introduced in Section 2.

2. Scheme of multi-scale constitutive model

2.1 Water equilibrium and transport in micropores

The bases of the model are the pore structure and internal water status, which are simulated by a computational system called DuCOM (Durability CONcrete Model) (Maekawa et al. 2003, 2009). In this system, the hydration reaction, pore-structure formation, and moisture equilibrium and transport in a cement matrix are coupled and simulated comprehensively. Figure 1 shows the scheme of the pore-structure model. The micropore information essentially consists of two parts: the porosity and pore size distribution. The micropores in the model are categorized into three types according to the size and formation mode: capillary pores, gel pores, and interlayer pores. During the hydration, gel grains are generated inside and outside the cement particles. The gel grains precipitating outside fill in large voids, while the remaining voids are categorized as capillary pores. An individual gel grain is considered to contain much smaller voids, called gel pores. Moreover, gel grains consist of numerous layers, with extremely tiny spaces between these layers, called interlayer pores (the size is assumed to be 0.28 nm), each of which is accessible only by a single water molecule. The porosities are calculated according to the hydration degree, chemically bound water, intrinsic porosity of the gel grains, and surface area. The size distributions of the capillary and gel pores are described by a Raleigh-Ritz distribution function.

The water retaining capacity of the pore structure at a given RH is calculated by considering the thermodynamic equilibrium of the liquid and vapor. First, as a result of the surface tension, a capillary meniscus is formed and a pressure difference is generated across the vapor-liquid interface. Assuming the micropores are cylinder-shaped, the pressure difference $P_l$ (Pa) is described as

$$P_l = \frac{2\gamma}{r_c}$$  \hspace{1cm} (1)

where $\gamma$ is the surface tension of water (N/m) and $r_c$ is the pore radius (m) where the interface is present. In addition, the pressure difference can also be written as the Kelvin equation

$$P_l = \frac{\rho RT}{M} \ln \frac{p_{\text{vap}}}{p}$$  \hspace{1cm} (2)

where $\rho$ is the density of liquid water (kg/m$^3$), $R$ is the gas constant (J/mol · K), $T$ is the absolute temperature (K), $M$ is the molecular mass of the water (kg/mol), $p_{\text{vap}}$ is the actual vapor pressure, and $p^*$ is the saturated vapor pressure (Pa). The ratio $p^*/p_{\text{vap}}$ is the relative humidity with the mark $h$. Combining Eq. 1 and Eq. 2, the relationship between $h$ and $r_c$ is obtained as

$$\ln h = -\frac{2\gamma M}{RT\rho} \frac{1}{r_c}$$  \hspace{1cm} (3)

It is assumed that pores smaller than $r_c$ are totally filled by water. Pores larger than $r_c$ are partially filled because of the ink-bottle effect. Moreover, physically adsorbed water exists in the pores that are not filled by condensed water. According to the modified BET adsorption theory by Hillerborg (1985), the thickness of adsorbed layer, $t_a$, is calculated by the equation

$$t_a = \frac{0.525 \times 10^{-8} h}{(1-h/h_m)(1-h/h_m+15h)}$$  \hspace{1cm} (4)

where $h_m$ is the relative humidity at which the pore is fully saturated. $h_m$ can be obtained based on Eq. 3 using the equation

$$h_m = \exp \left( -\frac{\gamma M}{\rho RT} \right)$$  \hspace{1cm} (5)

where $r_1 = r_c - t_a$ is the residual value of the radius $r_c$ minus the thickness of the adsorbed water layer. By combining this with the pore size distribution, the saturation of the gel or capillary pores $S$ can be calculated using the three portions of water as follows (Fig. 2)
Mechanism of surface energy
Absorbed water

Therefore, the driving force from the capillary tension is quite small and set to zero, which is the derivation of negative pressure in the liquid water (the vapor pressure indicated by Eq. 2, the formation of a meniscus causes a negative pressure caused by the desorption of the absorbed water. As the condensed water, whereas the surface energy change is non-negligible and the surface energy increases. Accordingly, the distance between the gel grains decreases and shrinkage occurs. The driving force from the surface energy changes is expressed as stress \( \sigma_{\text{sib}} \) and calculated as follows:

\[
\sigma_{\text{sib}} = S_{\text{sib}} \cdot \gamma_{\text{gl}}
\]

where \( \gamma_{\text{gl}} \) is the surface tension of the gel grains, which is assumed to be 350 mN/m, according to Hori (1962). \( S_{\text{sib}} \) is the distribution density function (1/m). \( S_{\text{sib}} \) is related to the total surface area of the gel pores and the thermodynamic status of the absorbed water. It is quantified using the equation

\[
S_{\text{sib}} = f(h)S_{\text{pore}}
\]

where \( S_{\text{pore}} \) is the specific surface area of the gel pores (1/m). \( h \) is the internal RH, and \( f(h) \) is the thermodynamic function of the absorbed layer. Without the adsorbed water, the surface energy reaches its maximum value, and \( f(h) \) is equal to 1.0. When the absorbed water is saturated, \( f(h) \) is assumed to be 0.0. Essentially, the thermodynamic status falls between these two cases. Referring to the BET theory, \( f(h) \) is quantified using the equation

\[
f(h) = \frac{V_{m} - V_{w}}{V_{m}} = \frac{1 - h / h_{s}}{1 - h / h_{s} + 15h}
\]

where \( V_{m} \) is the water volume of the first adsorbed layer nearest to the gel pore surface and \( V_{w} \) is the water volume when the first adsorbed layer is fully occupied by water molecules.

2.3 Time-dependent deformation response under shrinkage stress

When the stress obtained by Eq. 7 and Eq. 8 is applied to a cement matrix, the strain deformation can be calculated using a time-dependent response law (Zhu et al. 2004; Asamoto et al. 2006, 2008). Concrete is idealized as a two-phase composite, which consists of a cement matrix and aggregate (sand and gravel). The aggregate is assumed to be rigid and to exhibit an elastic deformation with a linear law. The shrinkage caused by aggregates is also taken into account (Asamoto et al. 2008). A cement matrix is assumed to be an assembly of fictitious clusters, referring to the solidification theory by Bazant.
and Prasannan (1989). As the hydration proceeds, the amount of clusters increases. The load capacity of a cement matrix is the summation of the capacities of all of the clusters. An individual cluster exhibits a time-dependent deformation relevant to the history. This time-dependent deformation consists of elastic, viscoelastic, viscoplastic, and plastic components, which are simulated based on the water status in the simulated capillary, gel, and interlayer pores. The details are omitted here. Herein, it needs to be emphasized that the response law can treat creep as well as shrinkage deformation, because the load applied to the clusters can be external or shrinkage stress. Attempts to modify the response law will influence both the shrinkage and the creep deformation. The creep behavior has been verified in previous studies, and reasonable results have been obtained. Therefore, this study essentially focuses on the driving forces of shrinkage (see Section 2.2). The response law is not considered at all.

3. Discussion and modification of existing model

3.1 Simulation of autogenous shrinkage using existing model

As introduced, the pore structure and internal water status are quantified at the microscale level, and the driving forces of shrinkage are explicitly derived from the pore pressure difference, saturation degrees, and water volume of the absorbed layer, for any self-desiccation or ambient exchange. This implies that given the initial material and ambient temperature, by setting the moisture exchange condition as isolation or exposed, it is possible to freely simulate autogenous or drying shrinkage. In previous studies, this methodology has proved to be effective, and the shrinkage trends have been roughly verified. Here, the authors focus on the precision. First, an analysis of autogenous shrinkage with a low w/c is conducted and compared with a test from Tazawa and Miyazawa (1997) (Fig. 4). The shrinkage value before the initial setting is deduced, as was done in this test. An obvious difference can be observed. In the test, the shrinkage increased rapidly in the initial days, after which the slopes tended to be gentle. Conversely, the analysis shows a continuous increase for a long period. Therefore, a great underestimation occurs at the early age. For low w/c concrete, extensive previous studies (Yang et al. 1998; Miyazawa et al. 1999; Nawa and Horita 2004; Jiang et al. 2005) found the distinct feature that the autogenous shrinkage develops rapidly and drastically at an early age. As for the analysis, the water consumption and internal RH decline produced by the self-desiccation are both automatically calculated by the coupled hydration and pore-structure formation models. Then, the shrinkage stress is calculated using the water status, after which the shrinkage strain is obtained. For low w/c concrete, this calculated self-desiccation is a gradual process rather than a drastic development. This is the reason that the shrinkage in the analysis increases gradually. In the existing model, factors relevant to self-desiccation, such as the hydration degree, porosity, and internal RH, have been extensively investigated and verified (Maekawa et al. 2003, 2009; Ishida et al. 2007; Nakarai et al. 2007). Therefore, the overall self-desiccation process in the simulation could be regarded as reasonable, and it is infeasible and inefficient to tackle it. The drastic increase in shrinkage is often encountered in reality, and so it is necessary to clarify the reason for it on the basis of the current self-desiccation simulation and driving forces, and provide an appropriate modification.

3.2 Portion of autogenous shrinkage quantified by chemical shrinkage

According to the JCI Autogenous Shrinkage Committee (Tazawa, 1996), chemical shrinkage is defined as the absolute volume change in hydrates from unhydrated cement and water. In contrast, autogenous shrinkage is defined as the macro-dimension or volume changes. When concrete is fluid, the chemical shrinkage can be completely converted to a macro-volume change. After the skeleton is completely formed, the matrix becomes rigid and the macro-volume change can be resisted. Therefore, nearly all of the chemical shrinkage is converted into internal pores. Actually, just after the initial setting, a significant portion of the chemical shrinkage is converted to a macro-volume change. This conversion is a result of the combination of the self-desiccation and uncompleted skeleton. A meniscus is formed by self-desiccation in the forming skeleton, and the driving force of capillary tension is generated. Furthermore, just after the initial setting, the cement matrix is in the process of transforming from a liquid to a solid. Thus, the skeleton is far from completion. It could not resist even a small driving force, and a relatively large deformation occurs, resulting in the observed drastic shrinkage increase. Theoretically, this drastic increase could be described quantitatively by means of the shrinkage stress and constitutive law at an early stage. However, in the analysis, although the self-desiccation and shrinkage stress can be simulated, it is very difficult to precisely
quantify the stiffness of concrete just after the initial setting, because the pore structure is still unstable and the cement paste is soft. On the other hand, chemical shrinkage is easier to measure and calculate. Hence, a possible approach is to evaluate a portion of the autogenous shrinkage at an early stage using chemical shrinkage. This portion of the autogenous shrinkage can be applied as the initial strain to compensate for the underestimated portion in the existing model. In this study, the authors adopt this approach as an approximation.

Hence, the authors evaluate the underestimated portion in Fig. 4 by means of chemical shrinkage. This portion from chemical shrinkage depends on the w/c, because lower w/c concrete usually exhibits a higher autogenous shrinkage. The authors attempt to explain the influence of the w/c based on a hypothesis at the microscale (Fig. 5). At the beginning, the cement particles are dispersed in water, and the average distance depends on the w/c. After the initial setting, a portion of the chemical shrinkage induces micropores, while the residual amount causes autogenous shrinkage. For a high w/c, the average distance between the cement particles is relatively large. Thus, the particles hydrate independently. For a low w/c, the distance decreases and some particles even contact each other. With the existence of self-desiccation, they may tend to move toward each other more significantly by means of the connection or accumulation of local deformations, resulting in a significant macro-volume change.

Thus, the portion of autogenous shrinkage $\varepsilon_{ch}$ quantified by chemical shrinkage can be described by the equation

$$\varepsilon_{ch} = v_{ch} \cdot f(\delta_m)$$  \hspace{1cm} (11)$$

where $v_{ch}$ is the chemical shrinkage. $\delta_m$ is the maximum thickness of the precipitation layer outside a single cement particle (m), which is calculated using a stereological model (Maekawa et al. 2009). $\delta_m$ has the physical meaning of the average distance between cement particles. $f(\delta_m)$ is the influence function. Following the

\[ f(\delta_m) = \frac{W_{ch}}{(1/\rho_l - 1/\rho_{ch})} \]  \hspace{1cm} (12)$$

where $W_{ch}$ is the weight of the chemically bound water in a unit volume of concrete (kg/m$^3$). $\rho_l$ and $\rho_{ch}$ are the densities of the liquid water and chemically bound water (kg/m$^3$), respectively. The value of $\rho_{ch}$ is assumed to be $1.25 \times 10^3$ kg/m$^3$. $f(\delta_m)$ is given by the empirical equation

$$f(\delta_m) = 0.045 \cdot \exp(-a \cdot \delta_m^b)$$  \hspace{1cm} (13)$$

where $a$ and $b$ are constants with values of $1.2 \times 10^{-4}$ and 6.0, respectively. For a normal w/c, $f(\delta_m)$ is extremely small (Fig. 6). As the w/c falls into a low range, the particle distance $\delta_m$ decreases greatly. Thus, $f(\delta_m)$ increases, and the contribution of chemical shrinkage becomes non-negligible. In the extreme case where $\delta_m$ is zero, $f(\delta_m)$ reaches a maximum. Although it does not occur in reality, the physical meaning is that 4.5% of the chemical shrinkage is converted to autogenous shrinkage.

With this portion of autogenous shrinkage added as
an initial strain to the existing model, the analysis in Fig. 4 is carried out again (Fig. 7). As anticipated, the shrinkage strains increase rapidly and agree with the test results until 20 days. However, another feature in the test is that the shrinkage strains after the initial days tend to be gentle or even stagnate. In contrast, the analysis strains continue to increase, with large slopes, overestimating the long-term values. The low w/c matrix has a relatively large Young’s modulus and high deformation resistance, which may be one reason for the stagnation of shrinkage in the test. Moreover, from the viewpoint of porosity, for a low w/c, most of the capillary pores are filled in reality. It is rational to consider that in reality, the water in the capillary pores is inadequate to provide sufficient driving forces after this. However, the analysis implies that the driving force increases continuously. Thus, some discrepancy still seems to exist.

3.3 Simulation of shrinkage under drying conditions with existing model
The results in Fig. 7 reveal that the long-term autogenous shrinkage is overestimated. In this section, the shrinkage under drying conditions is simulated for extensive investigation. The test conducted by Kiyohara et al. (2002) is used as a comparison. It followed JIS A-1129 (Method of Test for Length Change of Mortar and Concrete). The mix proportions are shown in Table 1. Prism specimens of 10 × 10 × 40 cm were prepared, and sealed-curing at 20 ± 0.5°C was applied for 7 days. Subsequently, they were exposed to RH 60% and measured using contact gauges. In the analysis, the same mix proportion, specimen size, and ambient conditions are provided. The meshing is shown in Fig. 8.

Fig. 9 shows the comparison. In the test, the shrinkage strain tended to be smaller for a lower w/c case. This trend is supported by test results obtained by other researchers (Hansen 1987; Neubauer et al. 1997; Maruyama et al. 2010; Yurtdas et al. 2006; García Juenger and Jennings 2002). It can be partially attributed to a higher Young’s modulus. In the analysis, no clear relationship with w/c is found, and for a low w/c case, the shrinkage is greatly overestimated as well. Combined with Fig. 7, it is suspected that a common point exists for the autogenous and drying shrinkages with low w/c ratios. Although it declines as a result of self-desiccation, RH still lies in a relatively high-level field, whereas during the above drying, the internal RH is higher than 60% before the equilibrium. A natural guess is that the driving force may be overestimated in the mid-high RH field for cases of low w/c. In general, the driving forces in the existing model need to be specifically discussed.

3.4 Discussion of mechanisms concerning driving forces
According to Eq. 7, the driving force from capillary tension is computed by multiplying the negative pressure by the effective factor β. The negative pressure dominates the water movement and is solved using the governing equation of moisture transport. Past verifications (Maekawa et al. 2003, 2009; Ishida et al. 2007) have already proven that the negative pressure is reliable. Therefore, the discussion focuses on β, which is the average saturation of the capillary and gel pores. In other words, the water in both the simulated gel and the capillary pores is assumed to contribute to the capillary tension. However, the capillary pores are usually on the

![Table 1 Mix proportion of concrete with various w/c ratios (Kiyohara et al. 2002).](https://example.com/table1)

<table>
<thead>
<tr>
<th>W/C (%)</th>
<th>Water (kg/m³)</th>
<th>Cement (kg/m³)</th>
<th>Gravel (kg/m³)</th>
<th>Sand (kg/m³)</th>
<th>Air (%)</th>
</tr>
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<td>680</td>
<td>950</td>
<td>536</td>
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<td>170</td>
<td>486</td>
<td>1011</td>
<td>635</td>
<td>3.8</td>
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<td>170</td>
<td>309</td>
<td>969</td>
<td>820</td>
<td>4.6</td>
</tr>
<tr>
<td>65</td>
<td>170</td>
<td>262</td>
<td>936</td>
<td>890</td>
<td>5.7</td>
</tr>
</tbody>
</table>
micro scale, while the gel pores are much finer, and a large portion lies in the nanometer range. It is probable that such a large difference in pore size may induce significant property variation in the internal water. Thus, the capillary tension may only be the principal driving force in a portion of the pores. On the other hand, as mentioned in Sections 3.2 and 3.3, the driving force may be overestimated for a low w/c. In these cases, rare capillary pores remain, and the primary portion consists of gel pores. Therefore, a natural inference is that the capillary tension may be inappropriate as the driving force in gel pores at the nanometer scale. In addition, while $\beta$ is expressed by the average saturation, strictly speaking, the absolute water volume seems to be a more appropriate index. With the same negative pressure and saturation, it can be inferred that a matrix containing more water may exhibit larger shrinkage, because the acting field of water increases.

Based on the above discussion, the driving force is re-established. Most of the capillary pores are at the micro scale in reality. Therefore, it is reasonable to assume that capillary tension is active. Conversely, for gel pores at the nanometer scale, capillary tension may not be the dominant mechanism. One proof is that in fine pores, physically absorbed water occupies a larger portion. Thus, there is a decline in the capillary tension, which is related to the decreased portion of condensed water (Hansen 1987; Garci Juenger and Jennings 2002; Bentur et al. 1979). Beltzung and Wittmann (2005) pointed out that in nanopores, the capillary tension is much smaller than the value calculated by the Kelvin equation. Additionally, in fine pores, the water flow may no longer be continuous. Water is confined by the nanospace and becomes a set with only tens of molecules (Bruni et al. 1998; Farrer and Fourkas 2003). Thus, water movement may be discrete and closer to particles. In short, it is more reasonable to treat the driving force in nanopores separately.

The authors assume that disjoining pressure is appropriate as the driving force in nanoscale pores. This theory was originally proposed by Derjaguin (1940; 1974) and defined as the action of the liquid absorbed in a surface toward the surface. When it is applied to a cement matrix, the disjoining pressure is assumed to be generated by the water in the narrow spaces, and acts as the repulsive force toward gel particles (Powers 1968; Bazant and Wittmann 1982). When the internal RH decreases, the water starts to evaporate, and some disjoining pressure disappears. Accordingly, the repulsive force decreases. Thus, the distance between gel particles decreases and shrinkage occurs. For nanopores, because of the tiny size and tremendous surface area, the disjoining pressure can be thought of as the dominant mechanism.

Furthermore, the surface energy change in the existing model and its difference from the disjoining pressure need to be clarified. The two theories both describe the mechanism in nanopores. The surface energy change is non-negligible only when the adsorbed water layer is extremely thin or completely desorbed. Instead, the disjoining pressure is present as long as the water (condensed and absorbed) exists. From the viewpoint of RH, the surface energy change is active at a very low RH, whereas the disjoining pressure can dominate in a wider field. When the water is completely removed, the driving force from the disjoining pressure reaches the maximum. In some sense, it can be regarded as being equivalent to the surface energy change at complete desorption. In the enhanced model in this study, the disjoining pressure is adopted to replace the surface energy change, as well as the capillary tension in nanopores.

3.5 Simulation of driving forces by capillary tension and disjoining pressure

The newly proposed scheme in the simulated pore-structure is shown in Fig. 10. First, the radius $r_c$ introduced in Eq. 3 is used to distinguish the water distribu-
tion at the unsaturated state. According to Fig. 2, in the simulated pore structure, pores smaller than \( r_c \) are totally saturated, whereas larger pores are partially filled by the ink-bottle and physically absorbed water. In order to separate the action fields, a so-called border radius \( r_{br} \) is suggested. In pores larger than \( r_{br} \) (abbreviated as Group S), the disjoining pressure dominates. Because \( r_{br} \) should be on the nanometer scale, it is assumed to be 10 nm. At a high RH, \( r_c \) is larger than \( r_{br} \), and hence, Group S is totally saturated. The repulsive force from the disjoining pressure sustains the equilibrium with the skeleton force. Therefore, the driving force only occurs in Group L by the capillary tension. As RH decreases, the vapor-liquid interface contains the equilibrium with the skeleton force. Therefore, the repulsive force equals the disjoining pressure when Group S is saturated.

In pores larger than \( r_{br} \), Group S starts to lose water, and a portion of the disjoining pressure disappears. Hence, the repulsive force in Group S decreases and cannot sustain the balance with the skeleton force. As a result, the driving force in Group S is activated.

Hence, the shrinkage stresses are re-quantified. The driving force in Group L is given by

\[
\sigma_w = A \cdot V_L \cdot \Pi = A \cdot (V_{cp,L} + V_{gl,L}) \cdot \Pi
\]  

where \( V_L \) is the water volume in Group L in the cement matrix (m\(^3\)/m\(^3\)). \( V_{gl,L} \) and \( V_{cp,L} \) are the water volumes in capillary and gel pores larger than \( r_{br} \) (m\(^3\)/m\(^3\)). Therefore, \( V_{cp,L} \) and \( V_{gl,L} \) are subsets of \( V_L \), and are illustrated in Fig. 11. \( A \) is an influential constant equal to 8.0.

For Group S, the driving force is derived from the skeleton force and repulsive force caused by the disjoining pressure. This is written as follows

\[
\Delta F = F_0 - F_r
\]  

where \( F_0 \) is the skeleton force, which equals the repulsive force when Group S is saturated. \( F_r \) is the repulsive force caused by the disjoining pressure.

According to Derjaguin and Churaev (1986), the disjoining pressure between two parallel surfaces drastically decreases as the internal distance increases, and can be empirically described by the following equation

\[
\Pi(h) = K \exp(-k / \lambda)
\]  

where \( K \) is the intrinsic magnitude of the disjoining pressure and only depends on the material of the solid surfaces and the liquid inside (Pa). \( \lambda \) is the decay length (nm). \( k \) is the distance between the surfaces (nm). Maruyama (2010) derived a \( K \) value of 4500 MPa for the cement matrix from a statistical thickness disjoining model.

Based on Eq. 16, if the pores are assumed to be cylinder-shaped, the disjoining pressure in an individual pore depends only on the radius. The total repulsive force should be a complex of the disjoining pressures in all of the pores. Thus, integration should be performed. The pore size distribution, surface area, and water content are necessary, and they can be simulated as introduced in Section 2.1.

First, when Group S is saturated, the repulsive force maintains the equilibrium with the skeleton force. Therefore, the repulsive force equals \( F_0 \) in Eq. 15, and is quantified as

\[
F_0 = \phi_s \int_{r_{min}}^{r_{max}} \Pi(2r) dr
\]  

where \( \phi_s \) is the volume fraction of Group S, as illustrated in Fig. 11. \( \chi_0 \) is the total surface area of Group S. Following Eq. 16, \( \Pi(2r) \) is the disjoining pressure in pores with an arbitrary radius \( r \). \( dr \) denotes the infinitesimal increment in the pore surface area for radius \( r \). Hence, in Eq. 17, the integral value from \( r_{min} \) to \( r_{max} \) is the resultant force of the disjoining pressure when Group S is saturated. With the normalization by the surface area, the repulsive force \( F_0 \) is calculated and equals the skeleton force.

Next, the repulsive force at the unsaturated state is expressed by the equation

\[
F_r = \phi_s \int_{r_{min}}^{r_{max}} \Pi(2r) dr \chi_0 \cdot F_0
\]  

where, in contrast with \( \Pi(2r) \), \( \Pi(2r) dr \) denotes an infinitesimal increment in the water-filled pore surface area for radius \( r \). The parameters \( K \) and \( \lambda \) in Eq. 16 are necessary to determine \( \Pi(2r) \). \( K \) is assumed to be 3000 MPa, and \( \lambda \) is

\[
\frac{V_{gl,L} + V_{cp,L}}{r_{br}} = \frac{V_{gl,L}}{r_{br}} + \frac{V_{cp,L}}{r_{br}}
\]  

\[
\phi_s \phi_c \frac{V_{cp,L}}{r_{br}} = \phi_s \phi_c \frac{V_{gl,L}}{r_{br}} + \phi_s \phi_c \frac{V_{cp,L}}{r_{br}}
\]  

\[
V_{gl,L} = \frac{V_{gl,L}}{r_{br}} + \frac{V_{cp,L}}{r_{br}}
\]  

Fig. 11 Water distribution in Group L and Group S.
10 nm. These values are different from Maruyama’s data, because the approaches and thermodynamic variables are not completely the same.

For an unsaturated state, the internal water in Group S consists of two portions. All of the pores smaller than $r_c$ are water-filled, whereas larger ones are partially filled by ink-bottle water. Therefore, using the coefficient $f_r$ in Eq. 6, Eq. 18 can be expressed as

$$F_t = \phi_l \cdot \frac{\int_0^r \Pi(2r) dr + \int f_r \cdot \Pi(2r) dr}{\chi_o}$$  \hspace{1cm} (19)

By combining Eq. 15, Eq. 17, and Eq. 19, the driving force can finally be written in relation to the stress $\sigma_{sd}$ as follows:

$$\sigma_{sd} = F_o - F_t = \phi_l \cdot \frac{\int_0^r \Pi(2r) dr + \int f_r \cdot \Pi(2r) dr}{\chi_o} - \phi_l \cdot \frac{\int_0^r \Pi(r) dr}{\chi_o}$$  \hspace{1cm} (20)

By combining this with the capillary tension in Eq. 14, the total driving force $\sigma_t$ is obtained as

$$\sigma_t = \sigma_{sc} + \sigma_{sd}$$  \hspace{1cm} (21)

The relationships between the driving forces and the internal RH are shown in Fig. 12. The total forces increase as RH decreases. The capillary tension already dominates at an RH field higher than 80%. Conversely, the disjoining pressure is activated at around RH 80%, and contributes principally at mid-low RH values. For a low w/c, the capillary tension tends to decline. Thus, the total driving force decreases.

4. Simulation of shrinkage behaviors using enhanced model

4.1 Verification of autogenous and drying shrinkages

With the above enhanced model, the autogenous shrinkage in Fig. 7 is calculated again, and is shown in Fig. 13. After the initial days, the analysis results gradually increase, which agrees better with the test results. In this case, the simulated capillary pores are abundantly filled. Thus, the water in Group L is insufficient to produce adequate capillary tension. On the other hand, the internal RH remains in the high field, and Group S is almost saturated. Therefore, the disjoining pressure is not active. In the enhanced model, these factors are effectively taken into account.

The shrinkages in Fig. 9 are also re-calculated and shown in Fig. 14. Clearly, the results are in better agreement with the test results for various w/c values. The phenomenon that the shrinkage becomes smaller for a lower w/c is grasped. This improvement was caused by the separation of the driving forces. For an RH higher than 60%, the effect of the disjoining pressure is not significant. Thus, the capillary tension dominates, which decreases as the w/c decreases.

Finally, for a normal w/c (50%), the results of analyses using the existing and enhanced models are compared. The test was carried out by Kanda et al. (2008) and also followed JIS A-1129. The shrinkage was measured by the comparator and laser methods simultaneously, and identical results were obtained. As shown in Fig. 15, the analysis with the existing model underestimates the value within tens of days, even though the
final value is satisfactory. In contrast, the analysis with the enhanced model is consistent with the test for the whole process.

4.2 Shrinkage behaviors of cement matrix under various RH values

The above verifications of drying shrinkages were conducted at the standard RH of 60% from JIS A-1129. Here, a wider RH range is investigated. The test results from Maruyama (2010) are used for the verification. Cement paste specimens with w/c values of 55% and 40% were cast. These were 3 × 13 × 300 mm in size to alleviate RH gradients along the depth. The specimens were water-cured for 91 days, and can thus be regarded as matured. Then, they were exposed to various RHs in the range of 95% to 20%. The water loss and length change were measured simultaneously until the equilibrium state. In addition, some specimens were dried at 105°C, and the remaining weight was defined as the dry mass. For the shrinkage, the length before drying was set as the original length. Exactly the same conditions were utilized in the analyses.

The water contents and shrinkages at the equilibrium states are shown in Fig. 16. For the water contents in Fig. 16(a), although a slight deviation occurs for a w/c of 55% with an RH of 80%, in general, they are well simulated. The shrinkages with the existing and enhanced models are shown in Figs. 16(b) and (c), respectively. The results of another analysis with a w/c of 25% are plotted to make it easier to comprehend. With the existing model, almost the same results are obtained regardless of the w/c. In contrast, with the enhanced model, the difference in relation to w/c can be reproduced, which is consistent with the test results. The comparison of the driving forces in Fig. 17 reveals the reason for the improvement. In the existing model, the total driving force increases as w/c decreases. This is because all of the simulated gel and capillary pores are assumed to contribute to the capillary tension, and the driving force is evaluated using pore pressure and their average saturation. For a low w/c, the total simulated porosity decreases greatly as a result of filling the capillary pores, while variation rarely occurs in the fine pores.
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As a result, with the same RH and $r_c$, it shows a higher saturation but lower water contents. Following Eq. 7, a higher driving force is obtained. The Young’s moduli at 91 days in the analysis are shown in Table 2. The increase in the driving force is neutralized by the higher modulus. Thus, similar shrinkages are obtained, as shown in Fig. 16(b). With the enhanced model shown in Fig. 16(c), the discrepancy is effectively amended.

On the whole, it can be concluded that the shrinkage behaviors can be appropriately simulated using the enhanced model. A little further discussion considers a w/c of 55% and RH below 40%, as shown in Fig. 16(c), where a slight overestimation is still observed. The reason is not clearly understood, but it may be related to the microcracks in the drying surface. Even if the specimens are very thin, at a low RH, microcracks may not be completely avoidable in the test (Bazant and Raffshol 1982; Hwang and Young 1984). Yet, microcracks are not considered in the analysis. The internal restraint may be released along the microcracks, which would cause the shrinkage to partially recover. In the future, the influence of such microcracks on the shrinkage needs to be studied further.

4.3 Sensitivity analysis with border radius $r_{br}$

The border radius $r_{br}$ separates the action fields of the driving forces in the enhanced model. Its value is 10 nm. To examine the rationality of this value, a sensitivity analysis is carried out. The case with a w/c of 40% shown in Fig. 16 is chosen, and the results are shown in Fig. 19. $r_{br}$ is alternated in the range of 2–100 nm. For values smaller than 10 nm, the shrinkages are overestimated. On these occasions, more pores are attributed to Group L. Thus, the water content contribution to the capillary tension becomes higher. In contrast, if an $r_{br}$ larger than 10 nm is adopted, the water volume in Group L decreases, whereas the portions in Group S increase. However, according to Eq. 16, the disjoining pressure decreases exponentially as the pore radius increases. Thus, these additional pores larger than 10 nm contribute little to the disjoining pressure, while the capillary tension is greatly alleviated. In particular, when $r_{br}$ is as large as 100 nm, most of the capillary pores are attributed to Group S, and the disjoining pressure is the only dominant mechanism. Consequently, in an RH field higher than 80%, shrinkage seldom occurs, which is far from reality. Clearly, 10 nm is a rational value to use to separate the capillary tension and disjoining pressure from the viewpoints of both quantitation and physical meaning.

Table 2 Young’s modulus at age of 91 days calculated by analysis.

<table>
<thead>
<tr>
<th>W/C (%)</th>
<th>55</th>
<th>40</th>
<th>25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Young’s modulus (GPa)</td>
<td>14.3</td>
<td>21.9</td>
<td>25.8</td>
</tr>
</tbody>
</table>

Fig. 17 Driving force of shrinkage under various RHs.

Fig. 18 Pore distribution at age of 91 days.

Fig. 19 Sensitivity analysis of border radius $r_{br}$ to drying shrinkage behavior under various RHs.
5. Conclusion

In this study, the authors carried out the necessary enhancement of an existing multi-scale model to improve its validity and precision for shrinkage behavior. In the existing model, the water status in micropores during the self-desiccation and drying processes was simulated at the microscale, and the driving forces of the shrinkage were quantified. By combining with a time-dependent response law, the autogenous and drying shrinkages were uniformly simulated. Although the existing model has been proven to be effective in past verifications, discrepancies from test results still exist. A distinct discrepancy is that the drastic increase in autogenous shrinkage at a very early age in reality is largely underestimated, while the increasing trend at a later age is overestimated. In addition, the drying shrinkage at a low w/c ratio is not well simulated either. Therefore, in this paper, the underestimation of the autogenous shrinkage at an early age was first discussed. The reason was that during the early self-desiccation, the large deformation cannot be effectively simulated because the skeleton of the cement paste is not completely formed. Hence, an approximate model was proposed to quantify the autogenous shrinkage at an early age based on its relationship with chemical shrinkage. This portion of autogenous shrinkage was added to compensate for the underestimation in the existing model. As a result, the autogenous shrinkage at an early age was properly simulated. Furthermore, to counter the overestimation of the autogenous shrinkage at a later age and the discrepancy for drying shrinkage, the driving forces were discussed and improved. In the existing model, the water in all of the pores is assumed to contribute to the capillary tension. However, because the water property greatly depends on the pore size, the authors considered the dominant driving force in nanometer-scale pores to be caused by the disjoining pressure rather than the capillary tension. That driving force is only active at low RH values, and does not contribute significantly to the autogenous or drying shrinkage at relatively high RH values. According to the above assumption, the driving forces of the shrinkage caused by the capillary tension and disjoining pressures were separated and quantified in the enhanced model. A border radius was proposed to separate the microscale and nanoscale pores. The capillary tension is only active in the microscale pores, whereas the disjoining pressure dominates in nanoscale pores. The overall simulation is effectively improved by using the enhanced model. Verification using test data with various w/c and drying conditions showed that the shrinkage behaviors of a cement matrix and concrete can be properly simulated.

Reference
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