TENSILE CREEP MODEL BASED ON CORROSIVE
ATTACK OF WATER VAPOR ON C-S-H GEL AFFECTED BY
SELF-DESICCATION AND APPLIED STRESS

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Abstract

With experimental result that the amount of chemically bound water of low water cement paste under restraint condition increase as against the same cement paste without restraint, hypothesis is presented that afford to explain this phenomena is proposed and the relation between tensile creep behavior and internal moisture content of cement paste. Based on this hypothesis, it is attempted to develop a tensile creep model.

1. Introduction

High-Performance Concrete, characterized by low water-binder ratio, are particularly sensitive to self-desiccation of the cement paste during the hydration process, which is a principal cause of autogenous shrinkage. If an external restraint is present, autogenous shrinkage, added to temperature-induced deformations, may lead to high self-induced stresses, possibly causing surface and even through cracks. In order to estimate the cracking risk, it is of vital importance to accurately calculate the self-induced stresses. In this calculation the early-age creep behavior of the concrete plays a prominent role, since the self-induced stresses will be substantially reduced due to relaxation.

A number of mechanisms of creep/relaxation, especially concerned with compressive creeping behavior, have been proposed and discussed over the years [1-5]. Concerning the cracking problem, it is the tensile creep that plays important and main role. The tensile creep mechanism is not discussed as much. In this contribution, chemically bound water of cement paste under 2 different conditions, i.e. restraint condition and non-restraint condition, was measured. Hypothesis that afford to explain the phenomena of
this experiment is proposed and based on this hypothesis the simple tensile creep model
is developed.

2. Experiment

Amount of chemically bound water of cement paste under different restraint
condition, i.e. non-restraint condition and restraint condition by embedded screw bar, was
measured. The cement used in this simple experiment is Ordinary Portland Cement,
which chemical and physical property is shown in detail in Table 1. And the
water-to-cement ratio of cement paste is 30% in weight. In addition, for smooth stirring
and uniformity of cement paste, chemical admixture (salt of polycarboxylic acid) is used
by 0.3% of cement in weight.

Table 1 - Properties of cement paste

<table>
<thead>
<tr>
<th>Speciﬁc mass (g/cm³)</th>
<th>Speciﬁc surface area (cm²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.16</td>
<td>3260</td>
</tr>
<tr>
<td>SiO₂ (% )</td>
<td>20.5</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
<td>5.31</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
<td>2.73</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>64.3</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>0.93</td>
</tr>
<tr>
<td>SO₃ (%)</td>
<td>2</td>
</tr>
<tr>
<td>Na₂O (%)</td>
<td>0.23</td>
</tr>
<tr>
<td>K₂O (%)</td>
<td>0.37</td>
</tr>
<tr>
<td>Cl⁻ (%)</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Specimen size is 40mm x 40 mm x 160 mm and curing conditions are sealed with
polyester ﬁlm or 100% RH after 1 day sealed condition. Both specimens are placed in 20
°C constant chamber. Screw bar of 8 mm in diameter and 140mm in length is embedded
in the center of paste specimen as restraint on deformation of paste. (see Figure 1)

On 1, 3, 7 day after placing, chemically bound water of cement paste are measured.
Specimens are crushed and immersed in acetone for 1 day, and then D-dried 2weeks in
each. After D-drying the specimens were grinded and sieved. The grinded powder of
cement paste, under 88 μm in diameter, is oven-heated up to 1000 °C. And the loss of
weight is measured.
3. Experimental Result

In Figure 2, the result of experiments is shown. The notation “w” and “s” represent the curing condition of 100% RH and sealed respectively. And “non” and “screw” stand for the restraint condition of free and screw bar restraint respectively.

Figure 2 - Difference of chemically bound water of cement paste under free and screw-bar restraint with sealed and 100% RH curing.
As is shown in Figure 2, the amount of the chemically bound water under restraint condition is slightly increased compared with the one under non-restrained condition. The increase can be seen in both sealed and 100% RH curing. The difference is rather big in the cement paste with sealed curing than that of 100% RH curing.

4. Discussion

Amount of chemically bound water should be differentiated by the difference of condition in the cement paste specimen, i.e. different stress condition. With the restraint of autogenous shrinkage stress must be induced in the cement paste specimen especially around the screw bar. Thus the most likely explanation is that the stress induced by the autogenous shrinkage yields the increase of chemically bound water.

Kumano [6] investigated a relationship between the pore structure and the creep phenomena and he found that the amount of small pores of which diameter is around 1 µm in cement paste increase with tensile stress (see Fig. 3). According to his conclusion, micro-cracks are responsible for this increase of porosity [6].

![Figure 3 - Pore size distribution under different tensile stress [6]](image)

Experimental results by Wiederhorn [7] may account for fundamental doubt about the feasibility of micro-crack under such a low stress/strength ratio. The double cantilever cleavage specimen made by soda-lime glass was used for crack propagation test. This test
was conducted with different constant force applied to the ends of specimen and different environmental condition of relative humidity. It is shown that even in a low strength/stress ratio the crack of soda-lime glass propagated slowly, especially in the condition of high relative humidity. In Figure 4 the crack velocity depending on the relative humidity is presented.

Figure 4 - Dependence of crack velocity on applied force. The percent relative humidity for each set of runs is given on the right-hand side of the diagram. [7]

Mould [8] proposed a mechanism of this slow crack propagation under low stress/strength ratio. According to his hypothesis, water is the most effective agent for
this process and the rate of crack growth is governed primarily by the localized stress at the crack tip and by the concentration of water or water vapor at that point. And the reaction generally appears to involve only water and the silica network of the glass and may be thought of as a simple hydrolysis of the surfaces formed during crack growth. The schematic of Si-O-Si and H$_2$O reaction is shown in Figure 5.

![Figure 5 - Schematic of hydration under stress between Si-O bonds and water at the crack tip](image)

It follows from the hypothesis and the experimental results introduced above that the Si-O bonds, which exist in C-S-H gel as well, are activated with stress and become easy to hydrate. And based on this assumption, the increase of chemically bounds water can be explained.

### 5. Summary

To sum up the argument above, under stress condition, Si-O bonds are activated and easy to hydrate. And at low stress/strength ratio micro-crack propagation is mainly governed by this chemical reaction of Si-O hydration and its speed is very slow.

Many Si-O bonds can be found in C-S-H gel. The C-S-H gel of cement paste at ordinary temperature has many crystal defects and it is highly possible that stress is localized around these crystal defects and Si-O bonds hydrate with water at these points if the cement paste is restrained from autogenous shrinkage. Thereby chemically bound water increase.

### 6. Modeling of tensile creep phenomena

As is discussed above, the tensile creep-relaxation phenomenon can be explained by
the microcrack that is dominated by the chemical reaction between Si-O bond and H$_2$O. Based on this assumption, model of tensile creep phenomena is developed.

### 6.1 Nucleation of crack

The theory of crack nucleation in amorphous material under stressed condition is suggested by Fisher [9]. Reversible formation of the two surfaces of a semicircular crack requires work equal to $\pi r^2 \gamma$ where $\gamma$ is the solid surface tension and $r$ is the radius of the crack. The work required for the reversible relaxation of strain energy in the neighborhood of the crack is $-4(1-\nu^2)r^3\sigma^2/3E$ where $\sigma$ (in tension) is the stress in the direction normal to the plane of the crack, $\nu$ is the Poisson’s ratio and $E$ is the Young’s modulus of material. The net work associated with the reversible formation of a circular crack of radius $r$ is,

$$ W = \pi r^2 \gamma - 4(1-\nu^2)r^3\sigma^2/3E \quad (1) $$

The curve of $W$ versus $r$ has a maximum.

$$ W_{\text{max}} = \pi \gamma E^2 /12(1-\nu^2)\sigma^4 \quad \text{at} \quad r_{\text{ini}} = \pi \gamma E /2(1-\nu^2)\sigma^2 \quad (2) $$

![Figure 6](image)

**Figure 6**: Work required for reversible formation of a crack of radius $r$ in a amorphous under tensile stress [9]
This maximum of reversible work depends on the surface tension of newly created surface and applied stress. Assuming that body of cement paste is composed of a uniform C-S-H gel and it has capillary pores filled with water vapor, many molecules of water are adsorbed on the internal surface of cement paste and it decreases the energy of surface tension of cement paste[10]. In respect that the surface energy of internal pore is low, it is highly possible that the nucleation of crack appear on the surface of capillary pore and the possibility of nucleation of crack depends on relative humidity in the capillary pore through the surface energy of C-S-H gel.

![Diagram of cement paste and capillary pore]

Fig. 7 Schematic structure of cement paste and capillary pore

Using the equation of the theory of nucleation [11], which is based on the theory of absolute reaction rates, the equation (3) shows the rate of nucleation of circular crack under stressed condition is derived.

\[
\frac{dn}{dt} = \frac{NS_kT}{h} \exp\left[-\left(\frac{E_s + W_{ma}}{kT}\right)\right]
\]

\[ (3) \]

where

- \( E_s \) denotes the free energy of activation for separating a pair of atoms
- \( N \) denotes the number of bonds on capillary pores in stressed material
- \( T \) denotes the absolute temperature
- \( k \) denotes the Boltzmann constant
- \( h \) denotes the Planck constant
Sf denotes the shape factor determined from pore structure of cement paste
n denotes the number of crack nucleation

According to the equation (3) and using the assumption that the total number of molecules that are able to fracture is constant, the following equation that shows the number of nucleation at time t is obtained.

$$C_{nucleation}(t) = N_0 e^{-\alpha t}$$

where $C_{nucleation}$ denotes the number of nucleated crack per unit time at time t
$N_0$ denotes the number of bonds on the surface of capillary pore which is able to crack under stressed condition.
$\alpha$ denotes the

$$\frac{S_f kT}{h} \exp\left[-\frac{(E_s + W_{min})}{kT}\right]$$

6.2 Crack propagation

Once a crack is nucleated, the crack propagates according to the rate of chemical reaction. Charles and Hillig [12] suggested following equation for the velocity of a moving crack under the influence of a corrosive environment and a crack tip stress $\sigma'$:

$$v = v_0 \exp\left[-\left(E^* - V'\sigma' + c\sigma'^2 + \Gamma V_m/2p\right)/RT\right]$$

where $E^*$ denotes the activation energy for surface corrosion at a stress-free surface.
$V'$ denotes the activation volume for the process
$c\sigma'^2$ denotes the combined effect of the disappearance of strain energy due to corrosion and a second order term in the expansion of the activation energy
$\Gamma V_m/2p$ denotes the effect of curvature of the reaction surface
$\Gamma$ denotes the surface free energy of the Si-O bonds of surface corrosion product interface
$V_m$ denotes the molar volume of the C-S-H
$p$ denotes the radius of curvature of the crack tip
\( \sigma' \) denotes the crack tip stress

Using this equation (4), the \( \sigma^2 \) term is small compared to the other terms in the exponential of equation (5) and can be neglected to a good approximation [7] and the surface energy term is assumed to be constant, the following equation is obtained:

\[
v = v_0 \exp[-(E' + \mu_s - \beta' \sigma')/RT]
\]

where \( \beta' \) denotes the constant
\( \mu_s \) denotes the energy required for new surface
\( E' \) denotes the activation energy for surface corrosion at a stress-free surface and surface energy required for new surface

Equation (6) describes the crack propagation velocity according to rate of chemical reaction.

Based on 1 mole of reacting Si-O-Si bonds, the equation for chemical reaction at a free surface is

\[
\text{H}_2\text{O} + \text{B} \rightarrow \text{B}'^*
\]

\( E' \) should be expressed as the difference in chemical potential between the reactants and product.

\[
E'=\mu'_{\text{B}'}-\mu'_{\text{B}}-\mu_{\text{H}_2\text{O}}
\]

where \( \mu'_{\text{B}'} \) denotes the chemical potential of activated bond
\( \mu'_{\text{B}} \) denotes the chemical potential of bond
\( \mu_{\text{H}_2\text{O}} \) denotes the chemical potential of water

\[
\mu_{\text{H}_2\text{O}} = RT \ln\left(\frac{2\pi m_{\text{H}_2\text{O}} kT}{h^2}\right)^{-3/2} \cdot \frac{P_{\text{H}_2\text{O}}}{kT}
\]

where \( P_{\text{H}_2\text{O}} \) denotes the partial pressure of \( \text{H}_2\text{O} \)
\( m_{\text{H}_2\text{O}} \) denotes mass of \( \text{H}_2\text{O} \) molecule

Assuming that \( \mu'_{\text{B}'} \) and \( \mu'_{\text{B}} \) are independent of environment, \( \mu_s \) is constant under constant relative humidity atmosphere and the crack tip stress \( \sigma' \) is proportional to the applied stress \( \sigma \) the following equation is obtained:

\[
v = c \exp[-(RT \ln(\frac{2\pi m_{\text{H}_2\text{O}} kT}{h^2})^{-3/2} \cdot \frac{P_{\text{H}_2\text{O}}}{kT} - \beta \sigma)/RT]
\]
where \( c \) denotes material parameter effected by RH and C-S-H gel properties
\[
\beta \quad \text{denotes material parameter effected by pore structure}
\]

If it is now assumed that the crack velocity is proportional to the rate of chemical reaction at the crack tip, the following equation (10) is obtained:
\[
N_{\text{propagation}} = \beta_1 \exp[\beta_2 \sigma / RT]
\]  
(11)

where \( \beta_1 \) denotes \( \frac{2 \pi m_{H_2} kT}{h^2} \cdot \frac{P_{H_2}}{kT} \) :constant parameters affected by temperature and C-S-H gel properties
\( \beta_2 \) denotes constant parameter effected by pore structure
\( N_{\text{propagation}} \) denotes the number of moles of bonds reacting at crack tip per unit area per unit time.

In former section the crack is assumed as circular crack. The increase ratio of radius of crack is obtained as follows.
\[
r(t) = \sqrt{2A_B N_{\text{propagation}} (t + \frac{r_{\text{ini}}^2}{2A_B N_{\text{propagation}}})}
\]  
(12)

where \( N_{\text{propagation}} \) denotes the number of moles of bonds reacting at crack tip per unit area per unit time (see equation (11))
\( A_B \) denotes Area per bonds
\( t \) denotes span under load
\( r_{\text{ini}} \) denotes the radius \( r \) with \( W_{\text{max}} \) (see equation (2))

### 6.3 Time dependent deformation based on the linear elastic fracture mechanics

In this section time dependent deformation under constant tensile stress is discussed with crack nucleation concept and crack propagation concept. The creep tensile creep phenomena can be expressed by the rate of crack nucleation and the rate of crack propagation with the linear elastic fracture mechanics. For expression of creep phenomena with linear elastic fracture mechanics, several assumptions that are taken into account are detailed below:
- C-S-H gel is elastic even after cracks are nucleated.
- Nucleated crack has semicircular shape.
- Crack propagation keeps its shape.
- Stress intensity factor is the same in each crack and expressed in equation (13).

\[ K_i = \sigma p \sqrt{\pi r} \]  \hspace{1cm} (13)

where \( p \) denotes the shape parameter

- Strain energy release rate is expressed in equation (14)

\[ G_i = \frac{1}{E'} K_i^2 \]  \hspace{1cm} (14)

- Each crack does not affect applied stress of the others.
- On this tentative formulation, cylindrical specimen is assumed.
- The specimen has base in \( A[\text{m}^2] \) and height in \( L[\text{m}] \)

Released work of nucleated cracks:

The release energy of each nucleation of crack is given in the form:

\[ \int_0^r \frac{(\sigma p \sqrt{\pi r})^2}{E'} dA = \frac{\pi p^2 \sigma^2}{E'} \left( \frac{\pi r}{E'} \right) dr = \frac{\pi^2 p^2 \sigma^2}{3E'} r_{n_i} \]  \hspace{1cm} (15)

And the number of nucleated crack at time \( t \) is derived from equation (4):

\[ N_{\text{crack}} = \frac{N_0}{\alpha} [1 - \text{Exp}(-\alpha t)] \]  \hspace{1cm} (16)

Then the total strain energy release owing to the nucleation of cracks \( W_n \) at time \( t \) is given by:

\[ W_n = \frac{\pi^2 \sigma^2}{3E'} r_{n_i}^3 \times \frac{N_0}{\alpha} [1 - \text{Exp}(-\alpha t)] \]  \hspace{1cm} (17)

Released work by crack propagation:

The radius of crack at time \( t \) with the time of nucleation \( t_i \) is \( r(t-t_i) \). Therefore released work \( W_c(t-t_i) \) by crack propagation of each crack is:
\[
W_p(t - t_i) = \int_{t_i}^{r(t - t_i)} \frac{K^2}{E'} dr = \frac{\sigma\pi r^2(t)}{E'} = \frac{\sigma\pi}{E'} A_b N(t - t_i)
\] (18)

And the released work per unit time is determined:
\[
\frac{dW_p}{dt} = \frac{\sigma\pi}{E'} A_b N
\] (19)

The rate of release work by crack propagation of each crack is constant. This means that the rate of energy for crack propagation is independent of time of load and span under load. Therefore the total energy for crack propagation, \(W_p\), per unit time is expressed as:
\[
\frac{dW_p}{dt} = \frac{N_b}{\alpha} \left[ 1 - \text{Exp}(-\alpha t) \right] \times \frac{\sigma\pi}{E'} A_b N
\] (20)

Then accumulated total release work by crack propagation is:
\[
W_p = \int_0^t \frac{N_b}{\alpha} \left[ 1 - \text{Exp}(-\alpha t) \right] \times \frac{\sigma\pi}{E'} A_b N dt
\]
\[
= \left[ \frac{\sigma\pi}{E'} A_b N \frac{N_b}{\alpha} t + \frac{\sigma\pi}{E'} A_b N \frac{N_b}{\alpha} \text{Exp}(-\alpha t) \right]_0^t
\]
\[
= \frac{\sigma\pi}{E'} A_b N \frac{N_b}{\alpha} \left( t + \frac{1}{\alpha} \text{Exp}(-\alpha t) - 1 \right)
\] (21)

Time dependent deformation:
The total released work by crack nucleation and crack propagation is:
\[
W_{total} = W_n + W_p
\] (22)

The time dependent strain is determined by using \(W_{total}\) shown above:
\[
\varepsilon = \frac{1}{A\sigma - L} W_{total}
\]
\[
= \frac{1}{A\sigma - L} \left( \frac{\pi^2\sigma^2}{3E'} \varepsilon_i \left( 1 - \frac{N_b}{\alpha} \text{Exp}(-\alpha t) \right) \right)
\]
\[
+ \frac{\sigma\pi}{E'} A_b N \frac{N_b}{\alpha} \left( t + \frac{1}{\alpha} \text{Exp}(-\alpha t) - \frac{1}{\alpha} \right)
\] (23)
In engineering expression, assuming that the $\alpha$ is less than 1, the term \( \frac{1}{\alpha} \text{Exp}(\alpha t) - \frac{1}{\alpha} \) can be ignored compared to time span.

Therefore, the convenient expression of tensile creep stress is:

\[
\varepsilon = A[1-\text{Exp}(-Bt)] + Ct
\]  

where $A$ denotes the parameter for nucleation of crack

$B$ denotes the parameter representing the magnitude of cracking tendency

$C$ denotes the parameter for crack propagation

Validation of model:

Using the formulated engineering model of creep phenomena, comparison with experimental data is attempted. The result of this comparison is shown in figure 8. Experimental results that are represented as dots in fig.8 are shown in the reference of Illston [13]. Normal Portland cement is used, the water to cement ratio is 40% and aggregate/cement ratio is 1.5. Age of applied stress is 7 day after casting and the specimens are stored in the average condition of 18.3°C and 63% R.H.

Results of fitted parameters are listed in Table 2. The parameter $A$ is concerning with the crack nucleation phenomenon. According to equation (17), as the applied stress increase or the surface tension in capillary pores decrease, this parameter $A$ increase. Regarding parameter $B$, which represents the rate of crack nucleation, become smaller as the applied stress increase of the surface tension decrease (see equation (2) and (4)). The parameter $C$, which is the parameter of crack propagation, is affected by the applied stress and the surface tension as in the previous parameters (see equation (6)). These tendencies of parameters agree with the results of fitted parameters shown in Table 2.
Figure 8 - Validation of engineering tensile creep model (doted data is the result of Illston [15])

Table 2 - Result of curve fitted parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curve I</td>
<td>0.00007</td>
<td>0.45</td>
<td>1.26–6</td>
</tr>
<tr>
<td>Curve II</td>
<td>0.00006</td>
<td>0.1</td>
<td>1.8–8</td>
</tr>
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</table>

7. Conclusion

The chemically bound water under stressed condition increases. This phenomenon can be evidence of microcrack under low tensile stress by corrosive attack of water vapor. Based on this hypothesis with using absolute reaction rate theory and linear elastic fracture mechanics the tensile creep phenomena is formulated as the process of cracking and engineering model is suggested. The results of fitted curve parameters show correspondence with theories that are used in formulating.
References
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13) Illston, J. M., The creep of concrete under uniaxial tension, Magazine of Concrete Research, Vol.17, No.51, June 1965, pp.77-84