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# THEORETICAL EXPLANATION OF THE MECHANO-SORPTIVE EFFECT IN WOOD

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## ABSTRACT

It is possible to explain the so called mechano-sorptive effect that occurs in wood by moisture cycling by an earlier derived general deformation kinetics model, as a bond breaking process of secondary bonds, causing internal shifts of adjacent layers with respect to each other, due to sorption.

*Keywords:* Wood, timber, moisture changes, mechano-sorptive effect, visco-hydro-elasticity.

## NOTATIONS

$\epsilon$  is the strain;  $\epsilon_e$ , elastic strain;  $\epsilon_v$ , viscous strain

$\sigma$  is the stress;  $\sigma_i$ , the stress at site  $i$ ;  $\sigma_{im}$ , the mechano-sorptive part,  $\sigma_{ic}$ , the creep part of the stress;  $\sigma_{ui}$ , the flow stress at site  $i$

$K_i$  is the modulus of elasticity at site  $i$ .  $K = K_1 + K_2 + K_3 + \dots$ , is the compound modulus of the matrix and the sites in a cross section

$M$  is proportional to  $K$

$A_i$ ,  $B_i$ ,  $C_i$ ,  $\varphi_i$  are constants at constant temperature

$\omega$  is the moisture concentration;  $\omega_e$ , concentration at the end;  $\omega_s$ , total difference in m.c.

$\rho$  is the concentration of mobile bonds

$k$  is the reaction constant,  $k_f$  for the forward and  $k_b$  for the backward reaction

$a = 23D/d$ , where  $d$  is the diameter of a round specimen and  $D$  is the diffusion coefficient

## INTRODUCTION

In van der Put (1986) the mathematical derivation of a creep and damage model is given, solely based on the chemical reaction equations of plastic deformation at the deformation sites, and the transmission of stresses by the surrounding elastic material. This resulted in the following equations (with an elastic part  $\epsilon_e$  due to the elastic stress redistribution and a viscous part  $\epsilon_v$  due to the stress change by the reacting bonds):

$$\frac{d\epsilon}{dt} = \dot{\epsilon} = \dot{\epsilon}_{ei} + \dot{\epsilon}_{vi} = \frac{\dot{\sigma}_i}{K_i} + (A_i + B_i\epsilon_i)\sinh(\sigma_i\varphi_i(1 - C_i\epsilon_i)) \quad (1)$$

This can be visualized as a parallel system of Maxwell elements (this is a spring with a dashpot on top), where  $\sigma_i$  is the stress on element  $i$ ;  $\epsilon_i$  is the strain of the nonlinear dashpot and  $K_i$  (the modulus of elasticity at the site) is the spring constant.  $A_i$ ,  $B_i$ ,  $C_i$  and  $\varphi_i$  are constants at constant temperature. The terms with  $B_i$  and  $C_i$  give the small structural changes. As discussed in van der Put (1986),  $C_i\epsilon_i$  is very small and can be neglected if an ultimate strain condition is introduced. Hardening, therefore, is due to the influence of the parallel elements and  $\sigma_i$  has

the form of  $\sigma_i = \sigma - M\epsilon$ , where  $M$  is proportional to the spring constants of the parallel elements and  $M \gg C_i$ , during most of the lifetime. The influence of  $C_i$  is only noticeable at the end state of the element by a decrease in the overall stiffness.

In most experiments, one of these processes controls the overall behavior. This means that all dashpots, except one, are frozen and a system of parallel springs with one Maxwell element remains. The parallel springs act as one spring with  $K = K_1 + K_2 + K_3 + \dots$ , and there remain only three elements (one spring  $K$  in parallel with a Maxwell element, being a spring and a dashpot in series) that have to be regarded.

When, in a stress relaxation test, this three-element model is loaded to  $\sigma_0$  at strain  $\epsilon_0$  at time  $t_0$ , then the Maxwell element (spring with dashpot) is loaded to  $\sigma_{v0}$  and the parallel spring receives the stress  $\sigma_0 - \sigma_{v0}$ . This remains unchanged when by relaxation, stress  $\sigma_v$  on the Maxwell element decreases.

For the Maxwell element:  $\dot{\epsilon} = 0$ , or:  $\dot{\sigma}_v = -K_1\dot{\epsilon}_v$  or:

$$-\dot{\sigma}_v = K_1 A \sinh(\varphi\sigma_v) \quad (2)$$

#### CHANGING MOISTURE CONTENT

At changing moisture content conditions, there is an extremely rapid reaction of water with the hydrogen bonds, such that a low activation energy and volume can be expected, and the equation for relaxation, Eq. (2) may be approximated to:

$$\dot{\sigma}_1 + K_1 A \sinh(\varphi\sigma_1) \approx \dot{\sigma}_1 + K_1 A' \omega \varphi \sigma_1 = 0 \quad (3)$$

where  $\sinh(\varphi\sigma_1) \approx \varphi\sigma_1$ ,  $A = A'\omega$ , and  $\omega$  is the change in moisture content. It is assumed that there is no swelling, or that the strain rate is directed in such a way that it follows the free swelling rate in order to achieve true relaxation. For creep, the same equation applies with  $K_1$  replaced by  $K$  ( $1/K = 1/K_1 + 1/K_2$ ). The solution of this equation is:

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -K_1 A \varphi t = -K_1 A' \omega \varphi t \quad (4)$$

if  $\omega$  is the suddenly applied difference (step change) in moisture concentration.

The rate of bond breaking can also be expressed as:

$$\dot{\rho} = -k\rho\omega \quad (5)$$

where  $\rho$  is the concentration of mobile bonds and  $k$  is the reaction constant, having as solution:

$$\ln\left(\frac{\rho}{\rho_0}\right) = -k\omega t \quad (6)$$

and it is seen that this result is identical to Eq. (4). Consequently, the stress supported by the reactive bonds is proportional to the number of bonds and the ratio  $\rho/\rho_0$  can be determined from the stress relaxation test (or from creep tests). This derivation proves the assumption made in Krausz and Eyring (1975) that  $\rho$  is proportional to  $\sigma$  in a relaxation test.

These equations apply for very thin specimens, where the step change of the moisture content is approximately possible. For thicker specimens, the moisture has to diffuse into the specimen. From Fick's second law, the concentration rate for a long, round specimen is:

$$\frac{d\omega}{dt} = D \left( \frac{\partial^2 \omega}{\partial r^2} + \frac{1}{r} \frac{\partial \omega}{\partial r} \right) \quad (7)$$

where  $r$  denotes the radial distances of the points to the center. The solution of this equation is (Krausz and Eyring, 1975):

$$\frac{\omega}{\omega_0} = 1 - \frac{4}{d} \sum_{n=1}^{\infty} \frac{J_0(\psi_n r)}{\psi_n J_1(\psi_n d)} \exp\left(-\frac{4D\psi_n^2}{d^2} t\right) \quad (8)$$

where  $\omega_0$  is the concentration surrounding the specimen,  $D$  is the diffusion coefficient,  $\psi_n$  is the  $n$ -th root of the zero-order Bessel function,  $d$  the diameter of the specimen and  $J_n$  is the Bessel function of the order  $n$ .

Because the mean strain in a specimen depends on the mean stress, it can also be expected that the overall stress relaxation depends on the mean stress in the specimen. Then only the mean concentration is of importance, as also follows from tests. The average concentration is therefore:

$$\bar{\omega} = \frac{4}{d^2 \pi} \int_0^{d/2} 2\pi \omega r dr = \omega_0 \left[ 1 - \sum_{n=1}^{\infty} \frac{4}{\psi_n^2} \exp\left(-\frac{4D\psi_n^2}{d^2} t\right) \right] \quad (9)$$

Substituting  $\bar{\omega}$  in Eq. (3) or Eq. (5) will give the measured mean stress or bond decay. Because only the first term of the summation is of importance, and the other terms may be neglected, the equation becomes:

$$\ln\left(\frac{\rho}{\rho_0}\right) = -k\omega_0 \left[ t + \frac{d^2}{D\psi_1^4} \left\{ \exp\left(-\frac{4D\psi_1^2}{d^2} t\right) + c_1 \right\} \right] \quad (10)$$

or for the stress with  $c_1 = -1$ :

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -K_1 A' \varphi \omega_0 \left[ t + \frac{d^2}{D\psi_1^4} \left\{ \exp\left(-\frac{4D\psi_1^2}{d^2} t\right) - 1 \right\} \right] \quad (11)$$

where  $\psi_1 = 2.405$  is the first root of the Bessel function.

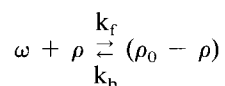
For long times, the exponential function is approximately zero, so this line becomes:

$$\ln\left(\frac{\sigma}{\sigma_0}\right) = -K_1 A' \varphi \omega_0 \left[ t - \frac{d^2}{D\psi_1^4} \right] \quad (12)$$

The intercept of this line with the time axis is thus  $d^2/D\psi_1^4$  showing the time lag due to diffusion. For very thin specimens, this time lag is not noticeable and Eq. (12) is equal to Eq. (4). Equation (12) applies exactly for human hair (Krausz and Eyring, 1975), where there is no swelling or shrinking during wetting and drying. At moistening, the stress quickly dropped to about one third of the applied value. At drying, the stress totally returns to the initial level before wetting in the relaxation tests. This work, therefore, is due to the chemical energy of bond reformation,

and there is no need to search for any other source of energy. This is in contrast to what is assumed for wood, that the energy for the slight restoring of the stress at wetting is delivered by the heat of diffusion.

Tests with alkali solutions on cotton, which has a comparable structure to wood, showed an instantaneous relaxation as rapidly as the solution could be added. After that, a slower process occurred, with the conversion of the crystalline regions into an amorphous structure. The instantaneous stress reduction indicates a very fast reaction where equilibrium is directly reached according to the reaction (with reaction constants  $k_f$  and  $k_b$  for, respectively, the forward and backward reactions):



or:

$$-\dot{\rho} = \rho\omega k_f - k_b(\rho_0 - \rho) = 0 \quad (13)$$

or:

$$\omega = \frac{k_b}{k_f} \cdot \frac{\rho_0 - \rho}{\rho} = \frac{k_b}{k_f} \cdot \frac{\Delta\rho/\rho_0}{1 - \Delta\rho/\rho_0} \quad (14)$$

where  $\Delta\rho/\rho_0 = (\rho_0 - \rho)/\rho_0$ . So  $\Delta\rho/\rho_0$  is about proportional to  $\omega$  ( $\Delta\rho/\rho_0 \ll 1$ ), but this initial linear relation bends off to a limiting value at high values of  $\omega$  according to the measurements (Krausz and Eyring, 1975) and this is explained by Eq. (14). The limiting value of  $\Delta\rho/\rho_0$  for alkali hydroxides at high concentration seems to approach unity according to Eq. (14) (when  $\rho \rightarrow 0$ ), indicating that the structure of cotton may be completely accessible for alkali reagents. This reaction with both the amorphous and crystalline regions followed also from X-ray diffraction experiments. Because  $\Delta\rho$  is not noticeably dependent on the temperature, the enthalpy will be small.

For strong acids  $\Delta\rho/\rho_0$  approaches a limiting value well below 1, being of the same order as the quantity of disordered regions reported from X-ray measurements. The value  $(\Delta\rho/\rho_0)_{lim}$  can be, therefore, expected to be a direct measure of the accessibility of the amorphous regions. The value of  $(\Delta\rho/\rho_0)_{lim}$  increases linearly with the temperature, in concert with a negative entropy increase, which shows the equilibrium between ordered and disordered regions. The equilibrium constant  $K_e$  is:

$$K_e = (k_f\omega/k_b) = \frac{(\Delta\rho/\rho_0)_{lim}}{1 - (\Delta\rho/\rho_0)_{lim}} \quad (15)$$

and the energy of cellulose conversion,  $E_f - E_b = -RT \cdot \ln(K_e)$ , was found to be 4 kcal/mol.

The same can be expected for wood, because acids affect only the amorphous regions and because the limiting value  $(\Delta\rho/\rho_0)_{lim}$  is far below 1, there is no cross section that is totally disordered and the ordered region is the continuous phase.

The nature of the reagents and the rapidity of the reactions indicate an attack of the secondary hydrogen bonds between the cellulose chains. After removal of the reagents, the bonds are unable to return to their original positions, but combine with new neighbors in a relaxed position.

The influence of water on the hydrogen bonds is comparable with the influence of acids because only the amorphous regions are affected, and  $\Delta\rho/\rho_0$  will be proportional to  $\omega$ . Although there is an immediate reaction with water, there is no instantaneous stress drop in a relaxation test because the water must diffuse into the structure, and the rate of diffusion determines the reaction rate with the hydrogen bonds. There is, therefore, an equilibrium, and any change of moisture content gives a reaction close to the equilibrium in the rate of the moisture supply. For the reaction near equilibrium, Eq. (13) is:

$$-\dot{\rho} = \rho\omega k_f - k_b(\rho_0 - \rho) = \rho k_f(\omega - \omega_0) \tag{16}$$

where:  $\omega_0 = k_b(\rho_0 - \rho)/(k_f\rho)$  is the equilibrium moisture content (where  $\rho = 0$ ).

A moisture increase from zero to  $\omega_0$ , is represented by Eq. (9). The first expanded term, with a rounding off to account for the other terms, is approximately:

$$\bar{\omega} = \omega_s(1 - \exp(-at)) \tag{17}$$

where  $a = 4D\psi_1^2/d^2 = 23D/d^2$ , and  $\omega_s$  is the maximal amount of adsorbed water.

For a loaded test specimen, with a moisture content  $\omega_0$  that is placed in a dry environment, causing a moisture content of  $\omega_0 - \omega_s$  after an extended time, Eq. (17) is modified to:

$$\bar{\omega} = \omega_0 - \omega_s + \omega_s \exp(-at) \tag{18}$$

and the solution of Eq. (5) becomes:

$$\ln(\rho/\rho_0) = -k(\omega_0 - \omega_s)t + \frac{k}{a}\omega_s(\exp(-at) - 1) \tag{19}$$

or with Eq. (18):

$$\ln(\rho/\rho_0) = \ln(\rho'/\rho'_0) - \frac{k}{a}(\omega_0 - \omega) \tag{20}$$

where:  $\ln(\rho'/\rho'_0) = -k(\omega_0 - \omega_s)t$  is the relaxation (or creep) at the constant equilibrium moisture content  $\omega_0 - \omega_s$ .

The same solution is obtained from Eq. (3) and the equations can be read by replacing  $\rho$  by  $\sigma$  and with  $k = K_1A'\varphi$  for relaxation and  $k = KA'\varphi$  for creep. So Eq. (20) for desorption is:

$$\ln(\sigma/\sigma_0) = \ln(\sigma'/\sigma'_0) - \frac{k}{a}(\omega_0 - \omega) \tag{21}$$

It is seen that  $\ln\left(\frac{\sigma'}{\sigma'_0} \cdot \frac{\sigma_0}{\sigma}\right) = c \cdot (\omega_0 - \omega)$  is a straight line, that is exactly the same as given in Takemura (1966), and Fig. 1, where  $\omega_0 - \omega =$  the amount of desorbed water.

For adsorption, when a loaded test specimen with a moisture content  $\omega_0$  is placed in a wet environment, causing a moisture content of  $\omega_1$  after a long time, Eq. (17) is modified to:

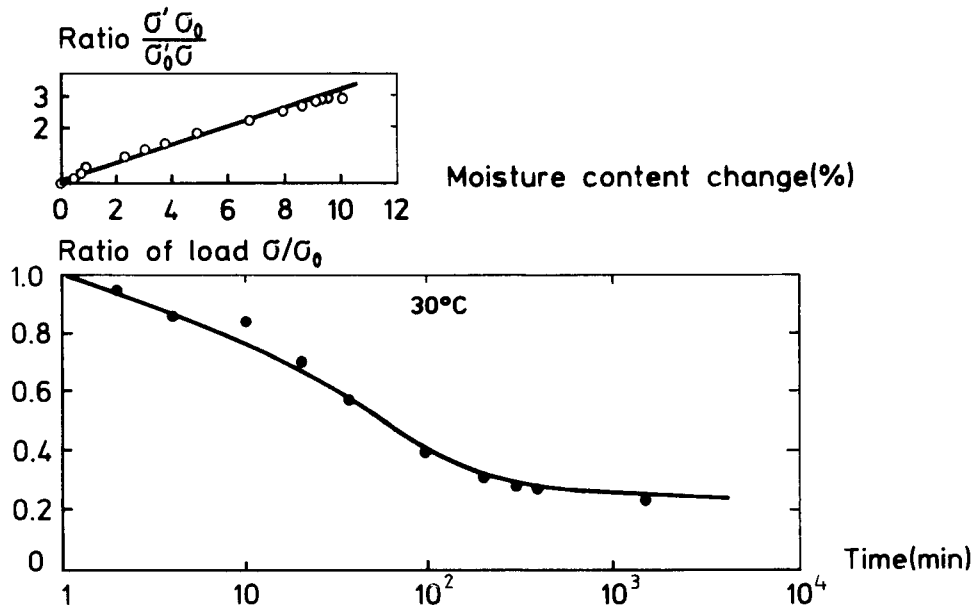


FIG. 1. Comparison of the theoretical Eq. (21) with measurements of [3].

$$\bar{\omega} = \omega_1 - (\omega_1 - \omega_0) \cdot \exp(-at) \quad (22)$$

and the solution of Eq. (5) is:

$$\ln(\rho/\rho_0) = -k\omega_1 t - \frac{k}{a}(\omega_1 - \omega_0) \cdot (\exp(-at) - 1) \quad (23)$$

or:

$$\ln(\rho/\rho_0) = -k\omega_1 t + \frac{k}{a}(\omega - \omega_0) \quad (24)$$

or:

$$\ln(\rho/\rho_0) = \ln(\rho'/\rho'_0) + \frac{k}{a}(\omega - \omega_0) \quad (25)$$

where:  $\ln(\rho'/\rho'_0) = -k\omega_1 t$ , is the relaxation at constant maximum moisture content  $\omega_1$ . This equation is identical to Eq. (20) if the adsorbed amount:  $\omega - \omega_0$  can be regarded as a negative desorption. Eq. (20) shows that there is an increase in deformation on drying, and Eq. (25) shows a restoring of the bond structure on rewetting. These phenomena are caused by the sorption effects and can explain the mechano-sorptive effect.

For the derivation of this effect, a three-element model was used consisting of a Maxwell element and a parallel spring. The nearly total unloading in the relaxation test by a high moisture change as shown in Fig. 1, demonstrates that both springs have dashpots. There may be another very weak parallel spring if there is hardening, but this can be neglected as a first approximation and the behavior

can be described by two parallel Maxwell elements. For large stresses, the derivation is more complicated because the linearization of Eq. (3) is not allowed. Of interest for mechano-sorptive effects, is creep loading at sufficiently high stresses where  $\sinh(x)$  can be approached by  $(\exp(x))/2$ . The strain rate equations for the two nonlinear Maxwell elements 1 and 2 are then:

$$\dot{\epsilon} = \frac{\dot{\sigma}_1}{K_1} + A'_1 \cdot \frac{\omega}{2} \exp(\varphi_1 \sigma_1) \tag{26}$$

$$\dot{\epsilon} = \frac{\dot{\sigma}_2}{K_2} + A'_2 \cdot \frac{\omega}{2} \exp(\varphi_2 \sigma_2) \tag{27}$$

In these equations  $\sigma_2 = \sigma - \sigma_1$  or  $\dot{\sigma}_2 = \dot{\sigma} - \dot{\sigma}_1 = -\dot{\sigma}_1$ , because the total stress  $\sigma$  is constant. Elimination of  $\dot{\epsilon}$  gives:

$$\frac{\dot{\sigma}_1}{K} + A'_1 \cdot \frac{\omega}{2} \exp(\varphi_1 \sigma_1) - A'_2 \cdot \frac{\omega}{2} \exp(\varphi_2 \sigma_2) = 0 \tag{28}$$

where  $1/K = 1/K_1 + 1/K_2$ .

Assuming for simplicity the same sites in the different layers for the mechano-sorptive effect, or  $\varphi_1 = \varphi_2 = \varphi$ , Eq. (28) becomes ( $\sigma_2 = \sigma - \sigma_1$ ):

$$\frac{\dot{\sigma}_1}{K} + \frac{\omega}{2} e^{\varphi \sigma / 2} C (e^{\varphi \sigma_1 - \varphi \sigma / 2 + \ln(\beta)} - e^{-\varphi \sigma_1 + \varphi \sigma / 2 - \ln(\beta)}) = 0$$

where  $C = \sqrt{A'_1 A'_2}$ , and  $\beta = \sqrt{A'_1 / A'_2}$ . So:

$$\frac{\dot{\sigma}_1}{K} + e^{\varphi \sigma / 2} \omega \sqrt{A'_1 A'_2} \cdot \sinh(\varphi \sigma_1 - \varphi \sigma / 2 + \ln(\sqrt{A'_1 / A'_2})) = 0 \tag{29}$$

The integration of this equation has the form:

$$\int \frac{d(x)}{\sinh(x)} = -c \int \omega dt$$

or with:  $\omega = \omega_0 + (\omega_c - \omega_0)(1 - e^{-at})$ , where  $\omega_c$  is the moisture content at the end, this is:

$$\ln(\tanh(x/2)) = -c \left( \omega_c t + \frac{\omega_c - \omega_0}{a} e^{-at} \right) + C_1 \tag{30}$$

or in terms of Eq. (29) becomes:

$$\ln \left( \tanh \left( \frac{\varphi \sigma_1}{2} - \frac{\varphi \sigma}{4} + \frac{1}{4} \ln(A'_1 / A'_2) \right) \right) = C_1 - \varphi K e^{\varphi \sigma / 2} \sqrt{A'_1 A'_2} \cdot \left( \omega_c t + \frac{\omega_c - \omega_0}{a} e^{-at} \right).$$

It can be seen that for very small values of  $a$ , because  $e^{-at} - 1 \approx -at$ , the right-hand term of this equation can be written as:

$$C'_1 - \varphi K e^{\varphi \sigma / 2} \sqrt{A'_1 A'_2} \left( \omega_c t + \frac{\omega_c - \omega_0}{a} (e^{-at} - 1) \right) \approx C'_1 - \varphi K e^{\varphi \sigma / 2} \sqrt{A'_1 A'_2} (\omega_0 t)$$



and the mechano-sorptive effect is not noticeable. Calling:

$$p = \varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot \omega_e t + C_2$$

and

$$q = \varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot (\omega_e - \omega_0) \frac{e^{-at}}{a} + C_3,$$

Eq. (30) is:

$$\frac{\varphi\sigma_1}{2} - \frac{\varphi\sigma}{4} + \frac{1}{4} \ln(A'_1/A'_2) = \operatorname{arctanh}(\exp(-p - q)) \quad (31)$$

and:

$$\operatorname{arctanh}(e^x) = 0.5 \cdot \ln\left(\frac{1 + e^x}{1 - e^x}\right) = 0.5 \cdot \ln(\operatorname{cloth}(-x/2))$$

is:

$$\frac{\varphi\sigma_1}{2} - \frac{\varphi\sigma}{4} + \frac{1}{4} \ln(A'_1/A'_2) = -\frac{1}{2} \ln\left(\tanh\left(\frac{p}{2} + \frac{q}{2}\right)\right). \quad (32)$$

It is seen in this equation that for infinite time,  $x \rightarrow \infty$ ,  $\tanh(x) \rightarrow 1$ , and  $\ln(1) = 0$ , such that Eq. (32) is:

$$\varphi\sigma_1 - \varphi\sigma_2 + \ln(A'_1/A'_2) \approx 0 \quad (33)$$

and the stress distribution is in accordance with flow at the constant strain rate test (van der Put 1986). For higher stresses, creep fades into viscous flow of both Maxwell elements at extended times, while for short times the creep influence is small and the mechano-sorptive effect may dominate. In that case  $p$  is small and  $q$  large and Eq. (32) is:

$$\begin{aligned} \ln\left(\tanh\left(\frac{p}{2} + \frac{q}{2}\right)\right) &= \ln\left(\frac{p/2 + \tanh(q/2)}{1 + (p/2)\tanh(q/2)}\right) \\ &\approx \ln\left(\frac{p/2}{(\cosh(q/2))^2} + \tanh(q/2)\right) \\ &= \ln(\tanh(q/2)) + \ln\left(1 + \frac{p}{\sinh(q)}\right) \end{aligned}$$

and Eq. (32) is:

$$\frac{\varphi\sigma_1}{2} - \frac{\varphi\sigma}{4} + \frac{1}{4} \ln(A'_1/A'_2) = -\frac{1}{2} \ln\left(\tanh\left(\frac{q}{2}\right)\right) - \frac{1}{2} \ln\left(1 + \frac{p}{\sinh(q)}\right) \quad (34)$$

or:

$$\varphi\sigma_1 - \varphi\sigma_2 + \ln(A'_1/A'_2) = -2 \ln\left(\tanh\left(\frac{q}{2}\right)\right) - 2 \ln\left(1 + \frac{p}{\sinh(q)}\right) \quad (35)$$

If one of the stresses p.e.  $\sigma_1$  starts to flow:  $\varphi\sigma_1 = \ln(2\dot{\epsilon}/A'_1)$ , then this equation becomes:

$$\ln(2\dot{\epsilon}/A'_2) = -2 \ln\left(\tanh\left(\frac{q}{2}\right)\right) - 2 \ln\left(1 + \frac{p}{\sinh(q)}\right) + \varphi\sigma_2 \quad (36)$$

and because the mechano-sorptive effect is a matter of bond breaking and bond reformation in a possible shifted position, this equation gives the strain rate for slip due to the mechano-sorptive effect when one of the elements flows. Because Eq. (36) can be written:

$$\varphi\sigma'_{u2} = -2 \ln\left(\tanh\left(\frac{q}{2}\right)\right) - 2 \ln\left(1 + \frac{p}{\sinh(q)}\right) + \varphi\sigma_2 \quad (37)$$

the slip due to the mechano-sorptive effect can be seen as a lowered flow value  $\sigma_{u2}$  of element 2.

Equation (35) can be split into a small creep part and a mechano-sorptive part. So:

$$\varphi\sigma_{1c} - \varphi\sigma_{2c} = -2 \ln\left(1 + \frac{p}{\sinh(q)}\right) \quad (38)$$

$$\varphi\sigma_{1m} - \varphi\sigma_{2m} = -2 \ln\left(\tanh\left(\frac{q}{2}\right)\right) - \ln\left(\frac{A'_1}{A'_2}\right), \quad (39)$$

because:  $\ln(\tanh(x)) = \ln\left(\frac{e^x - e^{-x}}{e^x + e^{-x}}\right) = \ln\left(\frac{1 - e^{-2x}}{1 + e^{-2x}}\right) \approx \ln(1 - 2e^{-2x}) \approx -2e^{-2x}$ , is Eq. (39):

$$\begin{aligned} \varphi\sigma_{1m} - \varphi\sigma_{2m} + \ln(A'_1 A'_2) &\approx 4e^{-q} \\ &= 4 \exp\left(-\varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot (\omega_e - \omega_0) \frac{e^{-at}}{a} - C_3\right) \\ &= \varphi\sigma_{1m} - \varphi\sigma_{1u} - \varphi\sigma_{2m} + \varphi\sigma_{2u} \\ &= C_4 \exp(-\varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot (\omega_0 - \omega)/a) \end{aligned} \quad (40)$$

where:  $C_4 = \varphi\sigma_{1m0} - \varphi\sigma_{2m0} + \ln(A'_1/A'_2)$ . The equation shows that the stresses are limited by the ultimate values. If this kept in mind then, because the strengths of the elements will not be far apart and  $\ln(A'_1/A'_2)$  will be small, Eq. (40) is approximately:

$$\varphi\sigma_{1m} - \varphi\sigma_{2m} \approx (\varphi\sigma_{1m0} - \varphi\sigma_{2m0}) \exp(-\varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot (\omega_0 - \omega)/a) \quad (41)$$

Equation (38) is:

$$\begin{aligned} \varphi\sigma_{1c} - \varphi\sigma_{2c} \\ = -2 \cdot \ln\left(1 + \frac{\varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot \omega_e t + C_2}{\sinh\left(-\ln\left(\frac{\varphi}{4}(\sigma_{1m0} - \sigma_{2m0})\right) + \varphi K e^{\sigma\varphi/2} \sqrt{A'_1 A'_2} \cdot (\omega_0 - \omega)/a\right)}\right) \end{aligned}$$

where  $C_2$  is determined by the zero values of the stresses:

$$C_2 = \left(\exp\left(-\frac{\varphi}{2}(\sigma_{1c0} - \sigma_{2c0})\right) - 1\right) \sinh\left(-\ln\left(\frac{\varphi}{4}(\sigma_{1m0} - \sigma_{2m0})\right)\right)$$

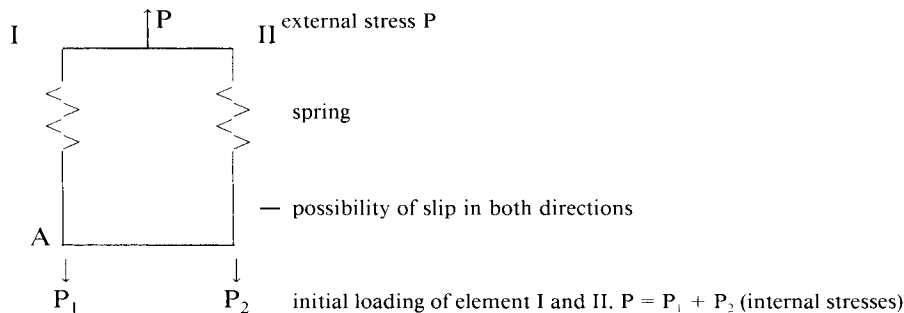
or neglecting smaller terms the equation will approximately be:

$$\begin{aligned} \varphi\sigma_{2c} - \varphi\sigma_{1c} &\approx \ln\left(1 + (\varphi\sigma_{1m0} - \varphi\sigma_{2m0}) \varphi K \sqrt{A'_1 A'_2} \omega_e t \right. \\ &\quad \left. \cdot \exp\left(\frac{\sigma\varphi}{2} - \varphi K e^{\sigma\varphi/2} \cdot \sqrt{A'_1 A'_2} (\omega_0 - \omega)/a\right)\right) \end{aligned}$$

## SIMPLIFICATION OF THE MODEL

For the purpose of explaining the behavior for creep at high moisture content cycles and higher stresses, it is sufficient to neglect the logarithmic creep and to use the property of the nonlinear Maxwell elements of an approximate elastic-full plastic behavior. This model can be compared with the model of Mukudai and Yata (1986) that consists of two parallel strings, each consisting of a Maxwell element and a Voigt element (i.e. a dashpot and a parallel spring) in series. This is totally equivalent to a model with four parallel Maxwell elements, and these four parallel Maxwell elements can be replaced by two parallel Maxwell elements with nonlinear dashpots since those dashpots contain one more parameter than the linear dashpots. It can be seen that each of the two strings of elements of Mukudai and Yata (1986) can be replaced by a spring attached to a nonlinear dashpot as was assumed for the derivation of the sorption equations. The loading of the two parallel strings in a creep test in the model (Mukudai and Yata 1986) was done by a running block that moved the total load between the strings by means of a hygroscopic element. This block may, however, be removed because this sorption effect is given by Eq. (20) or (40) and the behavior of the hygroscopic material is exactly the same as can be seen in Eq. (19), where the part:  $(k\omega_s/a)(1 - \exp(-at))$  is identical to the time function of that element. The swelling and shrinkage are proportional to the sorption of the amount of water and have this form:  $\omega = \omega_s(1 - \exp(-at))$ . In the model of Mukudai and Yata (1986) it is also assumed that the viscoelastic constants change according to this function; however Eq. (19) and Eq. (24) immediately show creep at the equilibrium moisture content of the end states, and also this changing constants function may be removed. The model of Mukudai and Yata (1986) shows that there are two diffusion processes, one slow process of sorption of water in the whole specimen with a small value of  $a = 23D/d^2 = 0.06$  of Eq. (30), and one quick process with a larger value of  $a = 0.5$ , affecting the load bearing bonds. This means that the sorptive force redistribution probably does not interact with the forces due to differential swelling or shrinking of the layers, and the swelling and shrinking forces will develop after the sorptive force redistribution.

In the following scheme, the influence of moisture cycling is given where the two elastic-plastic elements consist of: II, the layers with a dominating slip at desorption and I, layers with a pronounced slip at adsorption which show, for this scheme, (in point A) more shrinking and swelling than the layers of II.



For an initially wet specimen, the first drying cycle will give:

I	II	
$P_1 \downarrow$	$\downarrow P_2$	
$P_m \downarrow$	$\uparrow P_m$	sorpative bond breaking and reformation in a shifted position of II.
$(P_s \downarrow)$	$\uparrow P_s)$	force due to shrinking of element I.
$P_1 \downarrow$	$\downarrow P'_2$	

Total forces:  $P_m$  may reach the order of  $P_2$  in II. However, in I:  $P_1 + P_m \approx P > P_{u1}$ , where  $P_{u1}$  is the force for flow of I. So:  $P'_1 = P_{u1}$  and  $P'_2 = P - P_{u1}$  and there will be a large flow of I and a large slip of II, to be calculated from a hardening term or by the small parallel spring that has been thus far neglected. The force  $P_s$  cannot occur because of the flow of element I.

For small values of  $P$ , p.e. for  $P = 0$ ,  $P_m$  will not develop because the bonds are not stressed and will, after breaking by a moisture change, reform in the same position. If there is some interaction of this bond breaking and reformation with the force of differential shrinking, then  $P_m$  may eventually occur but will be small, having the opposite sign against the force of shrinking. Because the bond breaking process is eight times faster than the development of the shrinking stresses, the process will be finished before the shrinking stresses occur, and it can be expected that an unloaded specimen will get only the internal shrinking stresses on drying and wetting (swelling stresses).

For rewetting the specimen, after the first drying cycle, the forces will be:

I	II	
$P_{u1} \downarrow$	$\downarrow P - P_{u1}$	initial values due to first drying cycle.
$P_m \uparrow$	$\downarrow P_m$	due to sorpative bond and slip restoring II and slip of I.
$(P_s \uparrow)$	$\downarrow P_s)$	force due to swelling of element I.
$P'_1 \downarrow$	$\downarrow P'_2$	

Total forces: in general  $P'_1 = P_m - P_{u1} < P_{u1}$  except for unloading and  $P'_2 = P - P_{u1} + P_m < P_{u2}$  and the recovery of the deformation will be approximately:  $P_m/K_1$ . Also in the next drying and rewetting cycles, the increase and decrease of the deformation will be approximately this amount, and the increase of the maximal deformation and the decrease of the amplitude will depend on the slow creep process, giving an additional stress redistribution. Stresses due to differential shrinking and swelling will have an influence at a later stage.

For high loading  $P'_2$  may reach  $P_{u2}$ . At this point there is an increase in flow and slip in each cycle and the maximum deformation will not tend to a limiting value but increases until fracture. This is also known from measurements p.e. in Hearmon and Paton (1984) where, for  $P$  of about one eighth to one quarter of the ultimate load, this boundary of flow of element II is reached for bending. An analogous scheme for an initially dry specimen on first wetting is given below.

I	II	
$P_1 \downarrow$	$\downarrow P_2$	initial values.
$P_m \uparrow$	$\downarrow P_m$	sorpative bond restoring of II and slip of I.
$(P_s \uparrow)$	$\downarrow P_s)$	force due to swelling of element I.
$P_1 \downarrow$	$\downarrow P'_2$	

Total forces:  $P'_2 = P_{u2}$  causing flow of element II.  $P'_1 = P - P_{u2}$ . Element I slips

and will get the swelling deformation later, because the swelling force will not develop due to the flow of element II.

If the differential swelling movement is dominant for the large deformation, then an unloaded specimen will also give a flow of one element at large moisture changes. Because of the restraint of the other element, the large flow movement is against the swelling or shrinking movement, and is hardly noticeable as external movement.

For redrying the specimen, after the first wetting cycle, the forces will be:

$P$	I	II	
$- P_{u2}$	$\downarrow$	$P_{u2}$	initial values.
$P_m$	$\downarrow$	$\uparrow P_m$	sorpitive bond breaking and reformation causing slip in II.
$(P_s)$	$\downarrow$	$\uparrow P_s$	force due to shrinking of element I.
$P'_1$	$\downarrow$	$P'_2$	

Total forces:  $P'_1 < P_{u1}$  in general, and the increase of deformation will be of the order of  $P_m/K_1$ . Also in the next drying and rewetting cycles the increase and decrease of the deformation will be approximately this amount, and the increase of the maximal deformation at each cycle will depend on the slow creep process giving an additional stress redistribution. For greater loadings  $P'_1$  may reach  $P_{u1}$  and the stress situation of first drying occurs. In that case, however, there will always be an increasing slip at each cycle leading to fracture when the ultimate strain condition (van der Put 1986) is reached.

The schemes given here for tension can be the same for compression, because other layers may be involved for compression. For compression, the interaction with the lignin can be more pronounced and the swelling and shrinkage of element II may then dominate above element I. This will be investigated as part of a program of work sponsored by the Commission of the European Economic Communities. For bending, the situation is complex because every layer has another plastic and elastic deformation, and because of the different effects for compression and tension, there is quite a change of the internal lever arm.

#### CONCLUSION

It can be concluded that it is for the first time possible to describe the mechano-sorptive effect by the kinetic theory, and a preliminary indication is given of dominant model parameters when external loads produce a tensile or compressive stress in the fibers.

The model predicts that for large dimensions "d" of the test specimens, when  $a = 23D/d^2$  is sufficiently small, there will be only a small force exchanged between the layers, and the sorption effect is of minor importance.

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