Thixotropic behavior of cement pastes

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ABSTRACT

In this manuscript, a new rheological equation is presented to simulate thixotropic behavior of cement paste. This new material model is based on the previous work done by Hattori and Izumi[1,2]. The model is based on the so-called microstructural approach[3]. The model evaluation is done by comparing experimental data with the model prediction. The subject of the theory presented here is long and complex and hence all details cannot be presented in a single article. However, for the interested reader, a complete description of the theory can be found in author's previous work[4] and downloaded from:
www.ibri.is/rheocenter/download.html

INTRODUCTION

The interest in thixotropic phenomena is nearly as old as modern rheology[5]. An increasing number of real materials have been found to show these effects. Also, they have been applied in various industrial applications. The term thixotropy was originally coined to describe an isothermal reversible, gel-sol (i.e. solid-liquid) transition due to mechanical agitation[5]. According to Barnes et al.[6], the accepted definition of thixotropy is "*...a gradual decrease of the viscosity under shear stress followed by a gradual recovery of structure when the stress is removed...*" (with viscosity it is meant the apparent viscosity η). Additional definitions of thixotropy are given in Barnes[3].

The amount of theoretical literature on the above-mentioned time-dependent material is limited[6]. However, there is a comprehensive review article about the subject done by Mewis[5] and Barnes[3]. A shorter review was recently given by Mujumdar et al.[7] and in a newly published textbook by Tanner and Walters[8]. In these literatures, the various approaches used to measure thixotropy are represented. For example, one approach mentioned is by measuring the torque T under a linear increase and then decrease in rotational frequency f_o of the rotating part of the viscometer (here f_o is in revolutions per second or [rps]). If the test sample is thixotropic, the two torque curves produced do not coincide, causing rather a hysteresis loop. While hysteresis loops are useful as a preliminary indicator of behavior, they do not provide a good basis for quantitative treatments[3,9]. However, an attempt can be made to quantify thixotropic behavior with such torque curve by its integration[3,9,10]. Another approach possible in studying thixotropic behavior is by monitoring the decay of measured torque from an initial value T_o to an equilibrium value T_e with time t, at a constant rotational frequency[9] f_o. In some cases, a simple exponential relationship can be found, but other and more complicated relationships can also exist. For example, Lapasin et al.[11] make use of the above approach on cement pastes, using three different types of functions, however more complicated than of the simple exponential form. Nevertheless, a material model creating by this approach is limited because the apparent viscosity function η can only be valid when only one constant rotational frequency f_o is applied to each rheological experiment. Considering an apparent viscosity function η extracted from such experiment and then using it in another experiment of much more complicated shear history, will turn out to be almost impossible. Hence, such viscosity function will not represent a *true* rheological picture of the test material. As will be demonstrated in this paper, a *true* viscosity function must at least depend on (fading) memory information of both shear rate $\dot{\gamma}$ (related to dispersion rate of the cement particles) and of coagulation rate H.

In this manuscript, the analysis of thixotropic behavior consists of measuring torque $T = T(t)$ as a function of time t, under complicated rotational frequency conditions $f_\mathrm{o} = f_\mathrm{o}(t)$ shown in Fig. 2. During such condition, the processes of structural breakdown and structural rebuild (or recovery) are simultaneously present in each experiment. If both processes are occurring at equal rate, a state of microstructural equilibrium is reached. The challenge is to create a material model that is based on the microstructural approach and can simulate the measured rheological behavior of the cement paste under arbitrary and complex shear rate conditions. With a suitable apparent viscosity function $\eta = \eta(\dot{\gamma}, t, \ldots)$ used in the numerical simulation, the computed torque T_c should be able to overlap the measured torque T.

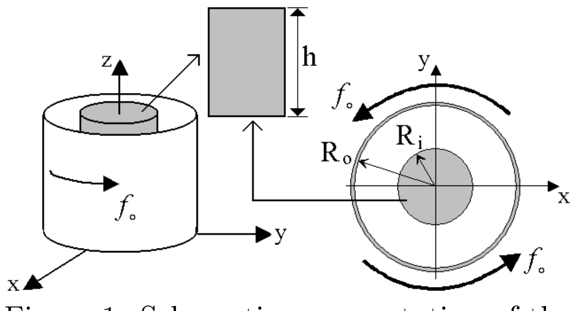

Figure 1. Schematic representation of the viscometer used in the experiment.

The viscometer used in the experiment is the ConTec Viscometer 4[12]. It is a coaxial cylinders viscometer that has a stationary inner cylinder (of radius $R_\mathrm{i} = 85\,\mathrm{mm}$) that measures torque T, and a rotating outer cylinder (of radius $R_\mathrm{o} = 101\,\mathrm{mm}$). The height of the inner cylinder is $h = 116\,\mathrm{mm}$. Shearing from the bottom part of the viscometer is filtered out by a special means[12]. Fig. 1 shows a schematic presentation of the viscometer.

The numerical software used is named Viscometric-ViscoPlastic-Flow. This software is freely available[4]. It is a finite difference model based on the ADI technique (Alternating Direction Implicit). It is designed for time-dependent (transient) and time-independent (steady state) viscoplastic materials. In fundamental terms, the pre-mentioned software solves the Newton's second law $m\, d\mathbf{v}/dt = \mathbf{F} + m\,\mathbf{g}$ inside the ConTec Viscometer 4, where m is the fluid element mass, $\mathbf{v} = \mathbf{v}(\mathbf{x}, t)$ is its velocity, $\mathbf{g}$ is gravity and $\mathbf{F}$ is the sum of surface forces applied to the fluid element from its surroundings. The term $\mathbf{x} = (x, y, z)$ is the spatial coordinates. A different apparent viscosity η gives a different force contribution $\mathbf{F} = \mathbf{F}(\eta)$, which again gives a different velocity profile $\mathbf{v} = \mathbf{v}(\mathbf{x}, t)$. This again results in a different computed torque $T_\mathrm{c} = 2\,\pi R_\mathrm{i}^2\, h\, \eta\, \dot{\gamma}$, because the shear rate is dependent on the velocity $\mathbf{v}$ (meaning $\dot{\gamma} = \dot{\gamma}(\mathbf{v})$). More precisely, the shear rate is calculated[13,14,15] according to Eq. 1.

$$\dot{\gamma} = \sqrt{2\,\dot{\boldsymbol{\varepsilon}} : \dot{\boldsymbol{\varepsilon}}} \tag{1}$$

The term $\dot{\boldsymbol{\varepsilon}}$ is the strain rate tensor and is given[13,14,15] by Eq. 2.

$$\dot{\boldsymbol{\varepsilon}} = \frac{1}{2}(\nabla\mathbf{v} + (\nabla\mathbf{v})^\mathrm{T}) \tag{2}$$

Both the shear rate and the strain rate tensor have the unit of s^{-1}. ∇ is the gradient operator and $(\nabla\mathbf{v})^\mathrm{T}$ is the transpose of the gradient velocity tensor $\nabla\mathbf{v}$. With Eqs. 1 and 2, the shear rate $\dot{\gamma}$ is not only dependent on the geometry $(R_\mathrm{i}, R_\mathrm{o}, h)$ and on the rotational frequency (f_o) of the viscometer, but also on the rheological parameters of the test material. This is because of how the shear rate $\dot{\gamma}$ is dependent on velocity $\mathbf{v}$, which is again dependent on the force $\mathbf{F} = \mathbf{F}(\eta)$, c.f. Newton's second law. This approach is very important when calculating the correct shear rate inside a fluid that has a yield value (i.e. of a viscoplastic material). This type of shear rate calculation is well known in theoretical rheology and dates back at least to 1947[14]. However, because of how this type of shear rate calculation severely complicates the analysis of the test material, the approach is not popular (and sometimes unknown) although it is very important.

The results produced by the above-mentioned software has been demonstrated to be accurate. First of all, the numerical results produced by the software have been tested against known solutions existing in the literature. Also, issues like consistency, convergence, numerical convergence and stability have been dealt with, to verify a good numerical quality[4].

EXPERIMENTAL

The water-cement ratio used for the cement paste is $w/c = 0.3$. The amount of superplasticizer is 0.5% solids by weight of cement (sbwc) of Suparex M40. This product is naphthalene based (SNF) and is produced by Hodgson Chemicals Ltd. The initial phase volume is $\Phi = 0.52$ and it is always increasing due to the chemical reactions of the cement paste.

The Hobart AE120 mixer is used when mixing the cement paste. It has three speed settings 1, 2 and 3. The fact that the test sample consisted of only pure cement paste, resulted in a reduced reproducibility (here, *reproducibility = reproduction of rheological result of different batches, of the same mix-design*). After testing different mixing procedures to seek a better reproducibility, the following one was selected:

1. *Between 0 and 3 minutes*: Mixing of cement and water at speed 1. Most of the cement particles are more or less moistened within the first 60 seconds.

2. *Between 3 and 6 minutes*: Hand mixing and resting.

3. *Between 6 and 10 minutes*: Mixing at speed 2.

4. *Between 10 and 11 minutes*: Check with hand mixing, if the cement paste is homogeneous.

At 12, 42, 72 and 102 minutes after the initial water addition, a rheological measurement with the ConTec Viscometer 4 is performed. Immediately after each measurement, a remixing by hand is done to ensure homogeneous mixture. A complete rest applies for the test material prior to any data logging in the coming measurement. The resting consisted of about 29 minutes and was considered to be sufficient for the test sample to gain a large coagulation state at the start of the next measurement. No remixing with the Hobart mixer was applied between measurements. Since the objectives is to investigate thixotropic behavior of the cement paste, it would be pointless to use the Hobart mixer to disperse the coagulated cement particles and brake up the structure that the viscometer is supposed to measure.

As mentioned just above, a rheological measurement is made at 12, 42, 72 and 102 minutes. However, in the current article, only one of these four results is shown, analyzed and discussed. This is the measurement conducted at 72 minutes after water addition. For the interested reader, all four results are available in the author's work[4].

The rotational frequency f_o of the outer cylinder (see Fig. 1) applied in the experiment and also used in the numerical simulation, is shown in Fig. 2. Each rheological experiment is made with the ConTec Viscometer 4 and begins at the (experimental) time $t = 0$ and ends at $t = 50\,\text{s}$. This time variable is not to be confused with the time duration from mixing of water and cement (inside the Hobart mixer). The former time period spans only 50 seconds as shown in Fig. 2, while the latter spans over the whole test procedure of 102 minutes.

In this work, three repeated batches are mixed and tested to examine reproducibility. In Fig. 2, the corresponding rheological results are shown with a dotted line.

All these three results apply at 72 minutes after water addition. To filter out the effect of random experimental error from thixotropic material behavior, the average of these three results is used to represent the rheological behavior of the test material. This average is shown in the same figure with a solid line. The average line is also shown in Figs. 4 and 6 and then with a dashed line.

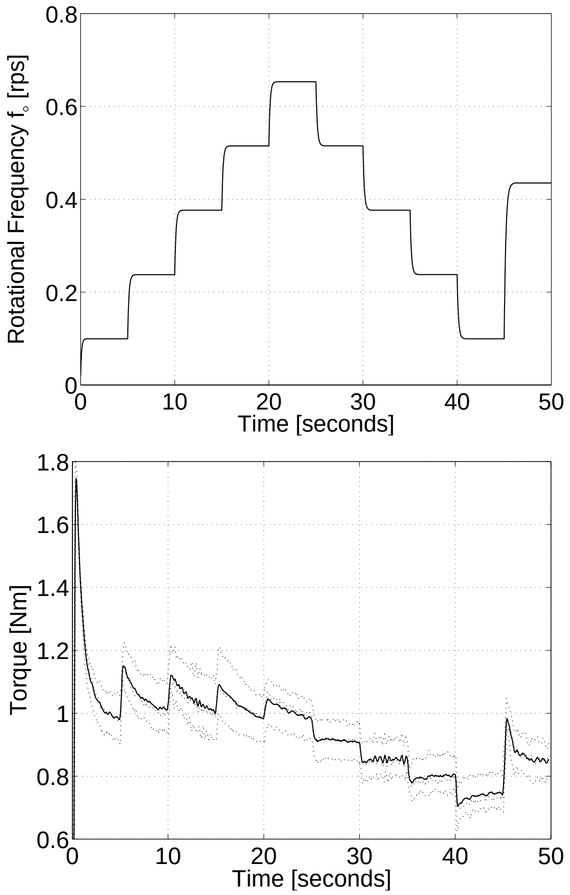

Figure 2. Rotational frequency and measured torque as a function of time.

ORIGINAL HATTORI-IZUMI THEORY

In this section, only the relevant part of the original Hattori-Izumi theory[1,2] is presented. For further information about this material model, the reader must consult with the original paper.

The apparent viscosity of Hattori and Izumi[1,2] is given by Eq. 3.

$$\eta \approx B_3\, J_\mathrm{t}^{2/3} = B_3\, n_3^{2/3}\, U_3^{2/3} \tag{3}$$

The term J_t represents the number of junctions (or connections) between the primary cement particles, per unit volume (i.e. this term has the physical unit of $[\mathrm{m}^{-3}]$). The term U_3 is an indirect microstructural parameter and is related to the direct microstructural parameter J_t with the following relationship $J_\mathrm{t} = n_3\, U_3$. With coagulation of the cement particles ($H > 0$), the value of J_t increases, but with dispersion ($\dot{\gamma} > 0$) this value decreases. The term B_3 is a so-called friction coefficient with the physical unit of $[\mathrm{N \cdot s}]$. The term n_3 will be explained shortly. The coagulation state U_3 at time t is calculated by Eq. 4, shown below[1,2].

$$U_3 = \frac{U_\mathrm{o}(\dot{\gamma}\, H\, t^2 + 1) + H\, t}{(H\, t + 1)(\dot{\gamma}\, t + 1)} \tag{4}$$

The above equation describes how the number of junctions (or contacts) between (primary) cement particles is changing, because of coagulation, dispersion and recoagulation. This is shown schematically with Fig. 3. As shown there, coagulation occurs as a result of non-zero coagulation rate $H > 0$. Likewise, dispersion occurs as a result of non-zero shear rate $\dot{\gamma} > 0$ (the latter is related to dispersion rate).

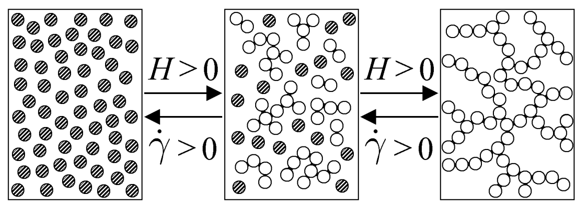

Figure 3. The effect of coagulation rate H and shear rate $\dot{\gamma}$.

Brief descriptions of the variables in Eq. 4 are as follow:

- n_3 = Number of primary particles per unit volume $[\mathrm{m}^{-3}]$. This is the number of cement particles that can coagulate.
- U_o = Coagulation state at $t = 0$. That is $U_\mathrm{o} = (J_\mathrm{t}|_{t=0})/n_3$, where the term $J_\mathrm{t}|_{t=0} = J_\mathrm{o} = n_3\, U_\mathrm{o}$ describes the number of junctions between the cement

particles, at the beginning of an experiment $t = 0$.

- H = Coagulation rate constant [s^{-1}].

As before, the term t is time and $\dot{\gamma}$ is the shear rate.

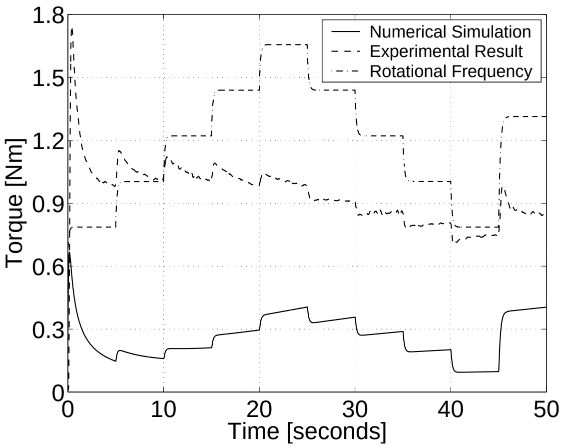

Figure 4. Numerical result when using the original Hattori-Izumi theory.

Using Eqs. 3 and 4 in the numerical simulation, a computed result T_c like shown in Fig. 4, is produced (the solid line). Also shown in this figure, is the experimental result T (the dashed line) and the rotational frequency f_o used (dashed dotted line). These two last-mentioned lines are also shown in Fig. 2. Note that the rotational frequency line in Fig. 4 is a relative line, not showing the absolute values. Its absolute values are shown in Fig. 2.

The computed torque value T_c shown in Fig. 4 is never observed experimentally in this work. The parameters used in this case are as follows $B_3\, n_3^{2/3} = 45\,\mathrm{N \cdot s/m^2}$, $U_o = 1$ and $H = 0.0005\,\mathrm{s^{-1}}$. A vide variety of other values were also tested, but without any success. Below is a description of some necessary modifications applied to Eqs. 3 and 4. Rather than being based on pure theoretical approach, much of these modifications are based on (semi) empirical considerations and intuition. The modifications are made with the objectives to calculate a torque T_c that is identical or very similar to the measured torque T.

MODIFIED HATTORI-IZUMI THEORY

By replacing the two terms $\dot{\gamma}\, t$ and $H\, t$ in Eq. 4, with the memory modules Γ and Θ, a better result started to merge. These last-mentioned two terms are defined by Eqs. 5 and 6.

$$\Gamma = \int_0^t \alpha(t - t')\ \dot{\gamma}(\mathbf{x}, t')\ dt' \tag{5}$$

$$\Theta = \int_0^t \beta(t - t')\ H(\dot{\gamma}, t')\ dt' \tag{6}$$

The two terms α and β are fading memory functions, t' is earlier time and $\mathbf{x}$ is spatial coordinates. With the above, Eq. 4 is transformed to Eq. 7.

$$U_3 = \frac{U_o(\Gamma\, \Theta + 1) + \Theta}{(\Theta + 1)(\Gamma + 1)} \tag{7}$$

With the above equation, the apparent viscosity Eq. 3 now remembers its past. That is, it remembers its past shear rate history and its past coagulation rate history. Previously, with Eq. 4, this was not possible. The memory functions α and β are designed in such manner that the apparent viscosity function η memorizes its recent past more, relative to its distant past. It is clear to anyone with background in cement-based materials that the shear history is an important factor: Working with two identical batches of different shear history will give a different rheological response. Hence, the introduction of Eq. 5 is not as peculiar as one might suppose at first consideration. Of course, the same consideration applies for the history of coagulation rate H, which suggests Eq. 6.

As shown with Eq. 3, the possibility for a yield value (of any kind) is discarded. However, in the quest of reproducing the measured torque by numerical means, it became necessary to include such term into the apparent viscosity function. In addition to this, it became necessary to include two constant terms τ_o and μ into the apparent viscosity equation as well. With these modifications, the final material model became as shown with Eq. 8.

$$\eta = \left(\mu + \frac{\tau_o}{\dot{\gamma}}\right) + \left(\tilde{\mu} + \frac{\tilde{\tau}_o}{\dot{\gamma}}\right) \quad (8)$$

In terms of shear stress, the above model is presented with the following equation.

$$\tau = \eta\,\dot{\gamma} = (\mu\,\dot{\gamma} + \tau_o) + (\tilde{\mu}\,\dot{\gamma} + \tilde{\tau}_o) \quad (9)$$

As shown with Eqs. 10 and 11, both the thixotropic plastic viscosity $\tilde{\mu}$ and the thixotropic yield value $\tilde{\tau}_o$ are dependent on $U_3^{2/3}$. This correlation is based on the relationship shown with Eq. 3.

$$\tilde{\mu} = \xi_1\, U_3^{2/3} \quad (10)$$

$$\tilde{\tau}_o = \xi_2\, U_3^{2/3} \quad (11)$$

Although determined by empirical means, the two terms ξ_1 and ξ_2 are material parameters, depending among other factors, on the surface roughness of the cement particles and phase volume Φ.

It is interesting to note that when all the cement particles are fully dispersed, meaning $U_3 = 0$, Eq. 8 returns to its pure Bingham form:

$$\eta = \mu + \frac{\tau_o}{\dot{\gamma}} \quad (12)$$

The two terms τ_o and μ are the well-known yield value and plastic viscosity, respectively.

In the modified Hattori-Izumi theory[4], it is assumed that basically two kinds of coagulation exist. The first type is the *reversible coagulation*, where two coagulated cement particles can be separated (i.e. dispersed) again for the given rate of work available to the cement paste (the rate of work, or power, is provided by the engine of the viscometer). The number of connections between cement particles that are in reversible coagulated state is given by the number J_t and is calculated with Eq. 7. In Fig. 5, the white cement particles demonstrate a reversible coagulation. As shown with Eqs. 10 and 11, the thixotropic plastic viscosity and yield value are dependent on the number of reversible connections $J_t = n_3\, U_3$ between cement particles.

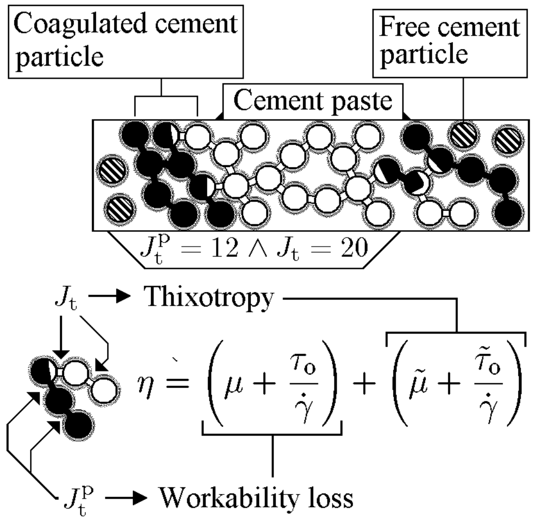

Figure 5. Relationship between Eq. 8 and the two terms J_t and J_t^p.

The second type of coagulation is the *permanent coagulation*, where the two cement particles cannot be separated for the given power available. Its number is represented with[4] J_t^p (*the reason for a permanent coagulation might be (for example) due to a damaged plasticizing polymer between the two corresponding cement particles*). Hence, the total number of junctions in the cement paste is $J_t^{tot} = J_t^p + J_t$. In Fig. 5, the black cement particles demonstrate a permanent coagulation.

Just as the thixotropic yield value $\tilde{\tau}_o$ and plastic viscosity $\tilde{\mu}$ are dependent on the number of reversible junctions J_t, the yield value τ_o and plastic viscosity μ could be considered to depend on the permanent junction number J_t^p in similar manner as shown with Eqs. 10 and 11. Therefore, one could consider that permanent coagulation J_t^p contributes to the workability loss, while reversible coagulation J_t contributes to thixotropic behavior. This correlation is shown in Fig. 5. Hence, the physical relationship between thixotropy and workability loss might be closer than one could imagine at first consideration.

Fig. 6 shows the numerical result when using the modified Hattori-Izumi theory. As shown, this theory can reproduce the measured torque much better relative to what is shown in Fig. 4. The parameters used in this simulation are: $\mu = 0.5\,\mathrm{Pa\cdot s}$, $\tau_o = 110\,\mathrm{Pa}$, $\xi_1 = 67.5\,\mathrm{Pa\cdot s}$, $\xi_2 = 22.5\,\mathrm{Pa}$ and $U_o = 1$.

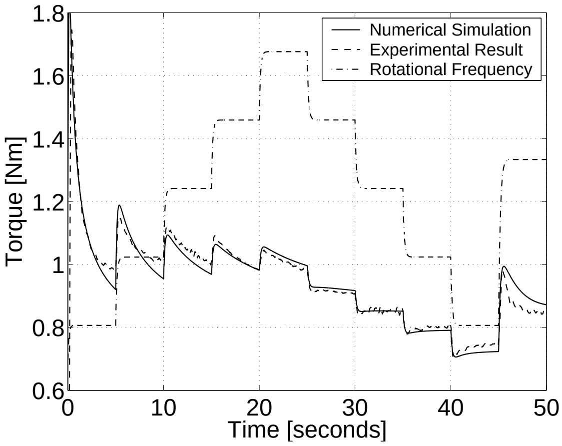

Figure 6. Numerical result when using the modified Hattori-Izumi theory.

In the original Hattori-Izumi theory[1,2], it is assumed that the coagulation rate H is a constant, only dependent on Brownian motion. Such assumption cannot hold for non-zero shear rate condition. Under such condition, the stirring ($\dot{\gamma} > 0$) causes the cement particles to be thrown together at larger rate than the normal diffusion rate, resulting in increased coagulation[16]. From this, it is clear that the coagulation rate coefficient is dependent on stirring, meaning $H = H(\dot{\gamma}, t)$. After a large number of trials in simulating the measured torque, the coagulation rate function had to have the functional form described with Eq. 13. This equation is applied for the numerical result shown in Fig. 6.

$$H(\dot{\gamma}, t) = \frac{K(t)}{\dot{\gamma}^2 + l} \tag{13}$$

The term l in the above equation, is an empirical constant and the function $K(t)$ is such that it takes a different value, depending on if the rotational frequency f_o is increasing or decreasing with time.

CONCLUSIONS

The promising results shown in Fig. 6, demonstrate that the modified Hattori-Izumi theory comes a long way in explaining the rheological behavior of cement pastes. That is, thixotropy seems to be (mostly) governed by a combination of (reversible) coagulation, dispersion and then re-coagulation of the cement particles. This is supported by the fact that the computed torque can more or less overlap with the measured torque, when using the material model described with Eq. 8.

The dispersion process (i.e. the structural breakdown) and the re-coagulation process (i.e. the structural rebuild) are always occurring simultaneously. When occurring at a different rate, a (thixotropic) transient behavior is observed. I.e. the rate of breakdown and rebuild in torque, depends on which process dominates for a given time.

As might be guessed, the extent of sophisticated mathematics involved in this work is large. Hence, a complete and detailed description of the theory used here, cannot be presented in a single paper. Rather, the objective here is to provide an overview and a short introduction to the main theory. The interested reader is rather referred to the author's work[4], where the current topic is covered by several chapters (Chapters 2, 6, 7, 8 and 9). In this particular work, the thixotropic behavior of cement paste using lignosulfonates (in addition to the SNF) is also investigated. There, in some cases, a complete match between the measured and the computed torque is attained, while in other cases, less acceptable results are gained. This indicates that the material model presented here is not yet fully complete, although it gives satisfactory results in many cases.

ACKNOWLEDGEMENTS

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