PHYSICAL AND CHEMICAL KINETICS OF STRUCTURAL BUILD-UP OF CEMENT SUSPENSIONS

La Cinétique Physico-Chimiques de la Structuration des Suspensions de Ciment

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DEDICATION

To the researchers and engineers who appreciate the value of science and knowledge.

To my beloved parents, Mohamed and Soher, who have forward me over themselves and given me all what they could. “My Lord! Bestow on them your Mercy as they did bring me up when I was young”.

To my brother and sister who always gave me their encouragement and extensive support at hard times of my life.

To my lovely wife, Rinad, who always supported me and understood my special circumstances as a researcher. To my daughters, Malk and Jana, who made a big difference in my life.
ABSTRACT

The structural build-up of fresh cement-based materials has a great impact on their structural performance after casting. Accordingly, the mixture design should be tailored to adapt the kinetics of build-up given the application on hand. The rate of structural build-up of cement-based suspensions at rest is a complex phenomenon affected by both physical and chemical structuration processes. The structuration kinetics are strongly dependent on the mixture’s composition, testing parameters, as well as the shear history. Accurate measurements of build-up rely on the efficiency of the applied pre-shear regime to achieve an initial well-dispersed state as well as the applied stress during the liquid-solid transition. Studying the physical and chemical mechanisms of build-up of cement suspensions at rest can enhance the fundamental understanding of this phenomenon. This can, therefore, allow a better control of the rheological and time-dependent properties of cement-based materials.

The research focused on the use of dynamic rheology in investigating the kinetics of structural build-up of fresh cement pastes. The research program was conducted in three different phases. The first phase was devoted to evaluating the dispersing efficiency of various disruptive shear techniques. The investigated shearing profiles included rotational, oscillatory, and combination of both. The initial and final states of suspension’s structure, before and after disruption, were determined by applying a small-amplitude oscillatory shear (SAOS). The difference between the viscoelastic values before and after disruption was used to express the degree of dispersion. An efficient technique to disperse concentrated cement suspensions was developed.

The second phase aimed to establish a rheometric approach to dissociate and monitor the individual physical and chemical mechanisms of build-up of cement paste. In this regard, the non-destructive dynamic rheometry was used to investigate the evolutions of both storage modulus and phase angle of inert calcium carbonate and cement suspensions. Two independent build-up indices were proposed. The structural build-up of various cement suspensions made with different cement contents, silica fume replacement percentages, and high-range water reducer dosages was evaluated using the proposed indices. These indices were then compared to the well-known thixotropic index (A\text{thix}.). Furthermore, the proposed indices were correlated to the decay in lateral pressure determined for various cement pastes cast in a pressure column.
The proposed pre-shearing protocol and build-up indices (phases 1 and 2) were then used to investigate the effect of mixture’s parameters on the kinetics of structural build-up in phase 3. The investigated mixture’s parameters included cement content and fineness, alkali sulfate content, and temperature of cement suspension. Zeta potential, calorimetric, spectrometric measurements were performed to explore the corresponding microstructural changes in cement suspensions, such as inter-particle cohesion, rate of Brownian flocculation, and nucleation rate. A model linking the build-up indices and the microstructural characteristics was developed to predict the build-up behaviour of cement-based suspensions.

The obtained results showed that oscillatory shear may have a greater effect on dispersing concentrated cement suspension than the rotational shear. Furthermore, the increase in induced shear strain was found to enhance the breakdown of suspension’s structure until a critical point, after which thickening effects dominate. An effective dispersing method is then proposed. This consists of applying a rotational shear around the transitional value between the linear and non-linear variations of the apparent viscosity with shear rate, followed by an oscillatory shear at the crossover shear strain and high angular frequency of 100 rad/s. Investigating the evolutions of viscoelastic properties of inert calcite-based and cement suspensions and allowed establishing two independent build-up indices. The first one (the percolation time) can represent the rest time needed to form the elastic network. On the other hand, the second one (rigidification rate) can describe the increase in stress-bearing capacity of formed network due to cement hydration. In addition, results showed that combining the percolation time and the rigidification rate can provide deeper insight into the structuration process of cement suspensions. Furthermore, these indices were found to be well-correlated to the decay in the lateral pressure of cement suspensions. The variations of proposed build-up indices with mixture’s parameters showed that the percolation time is most likely controlled by the frequency of Brownian collisions, distance between dispersed particles, and intensity of cohesion between cement particles. On the other hand, a higher rigidification rate can be secured by increasing the number of contact points per unit volume of paste, nucleation rate of cement hydrates, and intensity of inter-particle cohesion.

**Keywords:** Cement suspension, Dispersion, Dynamic rheology, Lateral pressure, Percolation time, Rigidification rate, Structural build-up, Viscoelasticity.
RÉSUMÉ

La structuration des matériaux cimentaires a un grand impact sur leur performance mécanique après le coulage. Par conséquent, la formulation des mélanges devrait être conçue afin d’adapter la cinétique de structuration conformément à l’application considérée. La structuration des suspensions à base des matériaux cimentaires est un phénomène complexe affecté par les deux processus physiques et chimiques. La cinétique de structuration est fortement liée à la formulation des mélanges, des paramètres d’essai et de l’historique du cisaillement. Une meilleure évaluation de ce phénomène est fonction du pré-cisaillement appliqué, afin d’obtenir un état complètement dispersé ainsi que la contrainte appliquée lors de la transition de l’état solide-liquide de la suspension. L’étude des mécanismes physiques et chimiques de la structuration des suspensions à base de ciment peut améliorer la compréhension fondamentale de ce phénomène. Ceci permettra un meilleur contrôle des propriétés rhéologiques en fonction du temps des matériaux cimentaires.

Cette recherche porte sur l'utilisation de la rhéologie dynamique pour étudier la cinétique de structuration des pâtes de ciment à l’état frais. Le programme de recherche a été mené en trois phases différentes et complémentaires. La première phase a été consacrée à l'évaluation de l'efficacité de diverses techniques de cisaillement. Les profils de cisaillement étudiés inclus la rotation et l’oscillation et la combinaison des deux modes de cisaillement. Les états initiaux et finaux de la structure de suspension avant et après la dispersion ont été déterminées en appliquant un cisaillement oscillatoire de faible amplitude (SAOS). La différence entre les valeurs viscoélastiques avant et après la dispersion a été utilisé pour exprimer le degré de dispersion. Une technique efficace pour disperser les suspensions concentrées de ciment a été développée.

La deuxième phase visait à établir une approche rhéologique afin de dissocier les mécanismes physiques et chimiques individuels de la structuration de pâte de ciment. En effet, la rhéométrie dynamique non destructif a été utilisé pour étudier à la fois l’évolution du module élastique et de l’angle de phase des suspensions inertes à base de carbonates de calcium et des suspensions de ciment. Deux indices de structurations indépendantes ont été proposés. La structuration de différentes suspensions à base de ciment réalisées avec différentes teneurs en ciment,
pourcentages de remplacement de fumée de silice, et dosages de superplastifiant a été évaluée en utilisant les indices proposés. Ces indices ont ensuite été comparés à l'indice de thixotropie bien connu (A_{thix}). En outre, les indices proposés ont été corrélés à la pression latérale déterminée pour différentes pâtes de ciment coulées dans une colonne sous pression de hauteur 1 m.

Le protocole de pré-cisaillement et les indices de structuration proposés (Phases 1 et 2) ont ensuite été utilisés pour étudier l'effet des paramètres de formulation sur la cinétique de structuration dans la Phase 3. Les paramètres étudiés incluent ; la teneur et la finesse du ciment, la teneur en sulfate alcalin, et la température de la suspension de ciment. Le potentiel zêta, les mesures calorimétriques et spectrométriques ont été également réalisées afin d’étudier les changements microstructuraux correspondants dans les suspensions de ciment, tels que la cohésion entre les particules, le taux de floculation Brownien, et le taux de nucléation. Un modèle reliant les indices de structuration et les caractéristiques microstructurales a été développé afin de prédire le comportement de structuration des suspensions des matériaux cimentaires.

Les résultats obtenus montrent que le cisaillement oscillatoire est plus efficace sur la dispersion de suspension de ciment concentré que le cisaillement rotationnel. Outre l'augmentation de la contrainte, le cisaillement induit permet d’améliorer la dispersion de la structure de suspension jusqu'à un point critique. Au-delà de cette valeur critique les effets épaississants dominent. Une méthode efficace de dispersion est ensuite proposée. Cette méthode consiste à appliquer un cisaillement rotationnel autour de la valeur de transition entre les variations linéaires et non linéaires de la viscosité apparente avec le taux de cisaillement, suivie d'un cisaillement oscillatoire à la contrainte de cisaillement croisée et la fréquence angulaire élevée de 100 rad/s.

Analyser l’évolution des propriétés viscoélastiques des suspensions inertes de carbonates de calcium et de ciment ont permis de développer deux indices pour quantifier la structuration des suspensions de ciment. Le premier indice (le temps de percolation) représente le temps de repos nécessaire pour former le réseau élastique. Le deuxième indice (taux de rigidification) décrit la rigidification de la structure, i.e. sa capacité à supporter des contraintes. D’autre part, les résultats montrent que la combinaison du temps de percolation et du taux de rigidification permet de mieux comprendre le processus de structuration des suspensions de ciment. De ce
fait, ces indices se sont avérés être bien corrélés avec la pression latérale de coffrage des suspensions à base de ciment. Les variations des indices de structuration proposés avec les paramètres de mélange ont montré que le temps de percolation est très probablement contrôlé par la fréquence des collisions Browniennes, la distance entre les particules dispersées, et l'intensité de la cohésion entre les particules de ciment. D'autre part, un taux plus élevé de rigidification peut être assuré en augmentant le nombre de points de contact par unité de volume de la pâte, le taux de nucléation d’hydrates de ciment et l'intensité de la cohésion inter-particulaire.

**Mots clés :** Suspension en ciment, dispersion, Rhéologie dynamique, Pression latérale, Temps de percolation, Taux de rigidification, Structuration, Viscoélasticité.
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## NOTATIONS

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<thead>
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<tr>
<td>a</td>
<td>Particle radius</td>
</tr>
<tr>
<td>~</td>
<td>Harmonic average of spherical particles radii</td>
</tr>
<tr>
<td>A</td>
<td>Hamaker constant</td>
</tr>
<tr>
<td>A'</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>A(h)</td>
<td>Free energy of the system</td>
</tr>
<tr>
<td>A*</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>Ab</td>
<td>Breakdown area</td>
</tr>
<tr>
<td>A_{thix.}</td>
<td>Thixotropic index</td>
</tr>
<tr>
<td>B'</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>B*</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>C</td>
<td>Number density of Brownian particles</td>
</tr>
<tr>
<td>D</td>
<td>Stokes-Einstein diffusivity</td>
</tr>
<tr>
<td>d_{50s}</td>
<td>Median surface-based particle size</td>
</tr>
<tr>
<td>d_{10V}, d_{50V}, d_{90V}</td>
<td>Volume-based particle sizes</td>
</tr>
<tr>
<td>d_{max}</td>
<td>Diameter of the largest particles in the system</td>
</tr>
<tr>
<td>d_{min}</td>
<td>Diameter of the smallest particles in the system</td>
</tr>
<tr>
<td>e</td>
<td>Elementary charge</td>
</tr>
<tr>
<td>f_C</td>
<td>Frequency of collisions</td>
</tr>
<tr>
<td>F_{di}</td>
<td>Force due to the divalent counter-ions</td>
</tr>
<tr>
<td>F_{mo}</td>
<td>Force due to the mono-counter-ions</td>
</tr>
<tr>
<td>F_{VDW}</td>
<td>Van der Waals attractive force</td>
</tr>
<tr>
<td>g</td>
<td>Acceleration of gravity</td>
</tr>
<tr>
<td>G</td>
<td>Growth rate (in Chapter 5)</td>
</tr>
<tr>
<td>G</td>
<td>Shear modulus</td>
</tr>
<tr>
<td>G'</td>
<td>Storage Modulus</td>
</tr>
<tr>
<td>G^*</td>
<td>Complex shear modulus</td>
</tr>
<tr>
<td>G''</td>
<td>Loss Modulus</td>
</tr>
<tr>
<td>G_{rigid.}</td>
<td>Rigidification rate</td>
</tr>
<tr>
<td>h</td>
<td>Separation distance between particles</td>
</tr>
<tr>
<td>H</td>
<td>Vane diameter</td>
</tr>
<tr>
<td>I_B</td>
<td>Nucleation rate per unit area of cement surface</td>
</tr>
<tr>
<td>I_C</td>
<td>Index of cohesion</td>
</tr>
<tr>
<td>K_B</td>
<td>Rate of covering the surface of cement particles with hydration products in a unit volume of paste</td>
</tr>
<tr>
<td>k_B</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>K_{di}</td>
<td>Probability of divalent counter-ions in the confined solution</td>
</tr>
<tr>
<td>K_G</td>
<td>Rate of filling the pore space between particles in a unit volume of paste</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>---------</td>
<td>------------</td>
</tr>
<tr>
<td>$K_{mo}$</td>
<td>Probability of mono-counter-ions in the confined solution</td>
</tr>
<tr>
<td>$L$</td>
<td>Vane height</td>
</tr>
<tr>
<td>$L_c$</td>
<td>Distance from the particle surface used as the plane of origin of the electrostatic repulsion</td>
</tr>
<tr>
<td>$l_B$</td>
<td>Bjerrum length</td>
</tr>
<tr>
<td>$m$</td>
<td>Consistency factor</td>
</tr>
<tr>
<td>$m_1$ to $m_4$</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>$n$</td>
<td>Consistency index</td>
</tr>
<tr>
<td>$n_1$ to $n_3$</td>
<td>Fitting constant</td>
</tr>
<tr>
<td>$n_{eq}$</td>
<td>Ionic concentration of the equivalent electrolyte</td>
</tr>
<tr>
<td>$O_V^B$</td>
<td>Area of cement particles per unit volume of paste</td>
</tr>
<tr>
<td>$Pe$</td>
<td>Péclet number</td>
</tr>
<tr>
<td>$Re$</td>
<td>Reynolds number</td>
</tr>
<tr>
<td>$S$</td>
<td>Scaling constant converts measured heat flow into a fractional rate of transformation</td>
</tr>
<tr>
<td>$S_1$</td>
<td>Rescaled wall-wall separation distance</td>
</tr>
<tr>
<td>$S_2$</td>
<td>Rescaled wall-wall surface charge density</td>
</tr>
<tr>
<td>$S_d$</td>
<td>Initial separation distance between particles</td>
</tr>
<tr>
<td>$S_f$</td>
<td>Solid fraction</td>
</tr>
<tr>
<td>$T$</td>
<td>Absolute temperature</td>
</tr>
<tr>
<td>$T_{max}$</td>
<td>Maximum torque</td>
</tr>
<tr>
<td>$t_{perc.}$</td>
<td>Percolation time</td>
</tr>
<tr>
<td>$\tan\delta$</td>
<td>Damping factor</td>
</tr>
<tr>
<td>$V_{Brownian}$</td>
<td>Volume of the Brownian portion</td>
</tr>
<tr>
<td>$W$</td>
<td>Stability ratio</td>
</tr>
<tr>
<td>$w/c$</td>
<td>Water-to-cement ratio</td>
</tr>
<tr>
<td>$W_\infty$</td>
<td>Stability ratio in the absence of any stabilizing forces</td>
</tr>
<tr>
<td>$Z$</td>
<td>Ion valence</td>
</tr>
<tr>
<td>$Z_{eq}$</td>
<td>Valence of the equivalent electrolyte</td>
</tr>
<tr>
<td>$\omega$</td>
<td>Angular frequency</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Shear strain</td>
</tr>
<tr>
<td>$\gamma(t)$</td>
<td>Shear strain function</td>
</tr>
<tr>
<td>$\gamma_A$</td>
<td>Amplitude of shear strain</td>
</tr>
<tr>
<td>$\dot{\gamma}(t)$</td>
<td>Shear rate</td>
</tr>
<tr>
<td>$\dot{\gamma}(t)$</td>
<td>Shear rate function</td>
</tr>
<tr>
<td>$\Delta\rho$</td>
<td>Density difference between the particle and suspending medium</td>
</tr>
<tr>
<td>$\Delta \eta_{app}$</td>
<td>Drop in apparent viscosity</td>
</tr>
<tr>
<td>$\delta$</td>
<td>Phase angle</td>
</tr>
<tr>
<td>$\varepsilon_0$</td>
<td>Relative dielectric permittivity of the vacuum</td>
</tr>
<tr>
<td>$\varepsilon_r$</td>
<td>Dielectric permittivity of the solvent</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>$\eta^*$</td>
<td>Complex viscosity</td>
</tr>
<tr>
<td>$\eta$, $\eta_0$</td>
<td>Viscosity of the suspending medium</td>
</tr>
<tr>
<td>$\mu_p$</td>
<td>Plastic viscosity</td>
</tr>
<tr>
<td>$\kappa^{-1}$</td>
<td>Debye length (thickness of the double layer)</td>
</tr>
<tr>
<td>$\xi$</td>
<td>Zeta potential</td>
</tr>
<tr>
<td>$\rho_c$</td>
<td>Density of cement</td>
</tr>
<tr>
<td>$\rho_w$</td>
<td>Density of water</td>
</tr>
<tr>
<td>$\tau$</td>
<td>Shear stress</td>
</tr>
<tr>
<td>$\tau(t)$</td>
<td>Shear stress function</td>
</tr>
<tr>
<td>$\tau_e$</td>
<td>Equilibrium shear stress</td>
</tr>
<tr>
<td>$\tau_i$</td>
<td>Initial shear stress</td>
</tr>
<tr>
<td>$\tau_0$</td>
<td>Dynamic yield stress</td>
</tr>
<tr>
<td>$\tau_{\text{rest}}$</td>
<td>Static yield stress</td>
</tr>
<tr>
<td>$\tau_{0\text{rest@20min}}$</td>
<td>Apparent yield stress measured after 20 minutes of rest</td>
</tr>
<tr>
<td>$\phi$</td>
<td>Solid fraction</td>
</tr>
<tr>
<td>$\phi_m$</td>
<td>Maximum packing fraction</td>
</tr>
<tr>
<td>$\Phi_{\text{max}}$</td>
<td>Potential energy at the energy barrier</td>
</tr>
</tbody>
</table>
CHAPTER 1: INTRODUCTION

1.1 Problem statement

Over the years, cement-based materials have been widely used worldwide in various construction projects, including buildings, bridges, and tunnels. The design of cement mixtures should be tailored to achieve proper rheological properties and to ensure adequate flow performance and successful casting (Banfill 2006). Thixotropy of cement-based suspensions has a direct impact on their placement and consolidation performance as well as on the microstructural development and overall performance of the hardened materials (Abd El Megid 2012; Banfill 2006; Khayat et al. 2012a; Kwasny et al. 2015; Omran 2009; Wang et al. 2011). Thixotropy is a time-dependent phenomenon describing the decrease in viscosity with time when a flow is applied to a sample that has been previously at rest, and the subsequent recovery of viscosity when the flow is discontinued (Barnes 1997; Mewis and Wagner 2009).

Although thixotropy includes two reversible aspects (build-up at rest and breakdown under shear), the build-up is reported to have a greater impact on the performance of fresh cement-based materials after casting. Typical applications where structural build-up is a key design parameter include:

- Tall wall elements: during casting, it is better to use a concrete with a high kinetics of structural rebuilding to reduce the maximum lateral pressure exerted on the formwork and allow a faster pressure decay after casting (Amziane and Ferraris 2006; Assaad 2004; Khayat and Omran 2011; McCarthy et al. 2012; Tchamba et al. 2008). This can result in lower values of the formwork’s design loads and significantly reduce the construction cost of concrete formwork. It is worthy to mention that in the United States, for example, it was reported that the cost of formwork can be as much as 60% (and sometimes even more) of the total cost of the completed concrete structure in place (ACI Committee 347R-14 2014).

- Multi-layer casting: it is crucial to design and use concrete with adapted kinetics of structural rebuilding to avoid possible reductions in bond strength between the cast
layers (Khayat et al. 2012a). In fact, high build-up results in a high internal shear strength of the first cast layer. This can prevent the stresses generated by the second layer from re-initiating flow in the first layer (Roussel and Cussigh 2008).

- 3D-printing of cement-based materials: in this layer–by–layer construction technique, it is necessary to optimize the degree of structural rebuilding. In fact, high kinetics of build-up can weak the bond between cast layers within the printed structure (Abd El Megid 2012; Roussel and Cussigh 2008). Meanwhile, an adequate structuration rate is needed to allow gaining a sufficient strength level capable of sustaining the weight of subsequently extruded layers (Perrot et al. 2016).

Cement-based suspensions, such as concretes and mortars, are granular materials by nature. They are in fact consist of fine and/or coarse aggregate suspended in a cement suspension. The specific reasons of structural build-up find their origins at the colloidal level (i.e. cement paste). In the case of colloidal suspensions, a three-dimensional structure can be formed at rest due to inter-particle forces, such as the van der Waals attractive forces (Ferron et al. 2013; Flatt 2004). However, in the case of cementitious suspensions, this phenomenon is more complex and is associated to combined physical and chemical effects. Indeed, as soon as cement and water are mixed, the hydration process starts, hence leading to changes in the growth rate of apparent rheological properties (Bentz et al. 1999; Roussel 2012). The degree of structural build-up of cement suspensions is further affected by several mixture parameters, including mixture composition and characteristics of its ingredients as well as temperature and shear history (Assaad and Khayat 2004; Assaad and Khayat 2006; Ferron et al. 2013; Khayat and Assaad 2006; Omran 2009).

Different techniques have been developed to quantify the structural build-up of cement-based suspensions (Amziane et al. 2008; Billberg 2006; Khayat et al. 2012b; Mahaut et al. 2008). Most of these techniques are based on assessing the structuration at rest after the breaking down the internal network structure using a rotational shear flow. Indeed, the accuracy of the measured build-up characteristics relies on the pre-shear regime as well as the shear stress applied during the liquid-solid transition (Coussot 2005; Dullaert and Mewis 2005; Ovarlez and Chateau 2008; Rueb and Zukoski 1997). Moreover, the use of rotational shear flow to measure the apparent
rheological properties at various resting periods can undergo micro-structural rearrangement within the colloidal network. This will result in a destructive regime which necessitates carrying out measurements on renewal mixtures. Furthermore, although various indices have been proposed to describe the overall effect of build-up, they did not provide an insight into the physical and chemical kinetics of structuration. Therefore, they have limited contribution to understanding the key factors affecting the build-up behavior of cement suspensions at rest.

To date, limited information exists regarding the use of oscillatory shear flow in quantifying and investigating the build-up of cement suspensions. Indeed, the use of dynamic rheology allows the application of micro shear strains to monitor the viscoelastic properties and structure’s recovery in a non-destructive manner. The overall goal of this research is to employ the dynamic oscillatory shear rheology to describe and monitor the structuration kinetics of cement suspensions at rest. Accordingly, this allows developing more reliable indices to describe the physical and chemical mechanisms of structuration. Such indices can enhance the fundamental knowledge and provide valuable information on the complex kinetics of build-up of cement-based materials. Moreover, they can be useful in understanding the effect of various mixture parameters on build-up behavior of cement-based materials after casting. Such an understanding can contribute in facilitating design and optimization of cement-based materials with adapted build-up given the application on hand.

1.2 Research objectives

Understanding how to design concrete with targeted properties cannot be attained unless a fundamental knowledge of the complex rheological behavior of cement paste is achieved. The main objective of this work is to use the dynamic rheometry to provide a deeper insight into the physical and chemical kinetics of build-up of fresh cement pastes and to identify the key factors affecting this phenomenon. The objectives of this study are:

1. Evaluate the dispersing performance of various shearing procedures that can be applied to obtain a well-dispersed state for cement suspensions.

2. Develop new build-up characteristics that can be used to quantify the physical and chemical kinetics of structural build-up of cement suspensions.
3. Evaluate the effect of various mixture parameters of neat cement suspensions, such as water-to-cement ratio (w/c), cement fineness, alkali sulfate content, and mixture’s temperature on the physical and chemical kinetics of structuration at rest.

4. Develop a prediction model that can correlate the build-up characteristics to the microstructural changes within cement suspension, such as inter-particle cohesion, Brownian interactions, and nucleation intensity.

1.3 Outline of the thesis

The thesis is divided into six chapters that might be summarized as follows:

**Chapter 1** provides an overview of the research problem and significance as well as the objectives of the research work and a brief summary of the contents of the thesis.

**Chapter 2** gives a brief introduction on fundamentals of rheology and thixotropy. In addition, it discusses the origin of thixotropy and the colloidal interactions affecting the flocculation behaviour of cement-based suspensions. This chapter also highlights the existing methods and protocols used to assess thixotropy of cement suspensions. Furthermore, it gives a background on the dynamic rheology and its advantages.

**Chapter 3** offers a performance evaluation on the different dispersing shearing procedures that can be applied by the rheometer on fresh cement pastes. The investigated shearing profiles include rotational and oscillatory shear as well as combinations of both. The results of this chapter are used to propose a shearing procedure that can be applied to allow investigating build-up from a well-dispersed state.

**Chapter 4** presents the use of non-destructive dynamic rheology in investigating build-up of inert calcite-based suspensions and cement-based suspensions. Moreover, it develops two independent build-up indices that can be used the physical and chemical kinetics of structural build-up of cement suspensions. This chapter also presents the correlation between developed indices and decay of lateral pressure of different cement past mixtures.
Chapter 5 discusses and investigates the effect of mixture parameters on the percolation time and rigidification rate. The investigated parameters include the water-to-cement ratio (w/c), cement fineness, alkali sulfate content, and temperature of suspension. In addition, the corresponding microstructural changes in inter-particle potentials, Brownian effects, and nucleation intensities is evaluated and discussed. It also correlates the developed build-up indices to the microstructural changes of cement suspensions.

Chapter 6 provides a summary and an overview of main findings obtained in the study. Recommendations for future work are also presented.

It worth mentioning that, Chapters 3, 4, and 5 were corresponding to four submitted and published technical papers in scientific journals as follows:


1.4 References


CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This chapter provides background information on rheology of different types of materials, dynamic oscillatory shear rheology, and mechanisms of attraction and repulsion between colloidal particles. In addition, a survey of the previous work on the origin of build-up of cement suspensions, the experimental methods to quantify thixotropy, and the factors affecting cementitious materials thixotropy is discussed. Finally, a brief introduction on the indices used to quantify build-up of cement-based suspensions is discussed.

2.2 Rheology of materials

Rheology can be defined as the science of the deformation and flow of matter (Barnes et al. 1989). Rheology can be used to optimize the proportions of concrete mixtures in order to obtain certain flow properties. Furthermore, rheology allows the evaluation of the effects of mixture constituents on the obtained flow performance (Banfill 2006). In general, rheology is concerned with all types of materials including elastic, viscous, and viscoelastic materials. The following sections summarize the response of different types of materials when subjected to a shear stress.

2.2.1 Elastic materials

An ideal elastic (solid) material deforms instantaneously when subjected to a stress, where the energy invested in deforming the solid is fully stored. After removing the shearing stress, the original shape is restored and induced deformation vanishes. For these materials, the elastic strain is linearly related to the stress applied hence, Hooke’s law can be applied (Equation 2-1) (Barnes 2000; Macosko 1994):

\[ \tau = G \cdot \gamma \]

Equation 2-1
where, $\tau$ is the shear stress, $G$ is the shear modulus, and $\gamma$ is the shear strain.

At a constant shear stress, the elastic deformation is constant and only depends on the value of the applied load. Once the load is removed, the solid returns back to its original shape. This is the reason why the elastic material is said to have a perfect memory (Macosko 1994).

### 2.2.2 Viscous materials

For perfectly viscous materials, Isaac Newton (1687) proposed the following relationship: “The resistance which arises from the lack of slipperiness originating in a fluid is proportional to the velocity by which the parts of the fluids are being separated from each other” (Macosko 1994). In this case, the viscous liquid deforms continuously under constant shear stress. In addition, induced deformation will not be recovered after the removal of applied stress. The flow of a perfectly viscous (Newtonian) fluid between two parallel plates is shown in Figure 2.1. In the case of a constant viscosity with time, a linear relationship between shear stress and shear rate can be obtained according to Equation 2-2:

$$\tau = \eta \cdot \frac{dv}{dy} = \eta \cdot \dot{\gamma}$$

where, $\tau$ is the shear stress, $\eta$ is the viscosity, and $\frac{dv}{dy}$ is the velocity gradient or shear rate ($\frac{d\gamma}{dt}$).

![Figure 2.1 - Shear flow of a viscous Newtonian fluid](image)
When a constant stress is applied on a perfectly viscous material, the angle of deformation changes at a constant rate. Once the stress is removed, the viscous material stays in its final shape. Therefore, the viscous material does not have any memory (Macosko 1994).

In most cases, the ratio between shear stress and shear rate (i.e. the viscosity) is not constant and depends on the instantaneous shear rate (Figure 2.2).

![Flow Curves](image)

Figure 2.2 - The flow curves for a Newtonian, shear-thinning (Pseudoplastic), shear-thickening (Dilatant) and yield stress material (Bingham)

Liquids that exhibit an increase in viscosity when the shear rate increases are known as dilatants (shear-thickening). On the other hand, fluids that exhibit a decrease of their viscosity when their shear rate increases are characterized as pseudo-plastic fluids (shear-thinning). A power-law model can be applied to describe the shear-thinning and shear-thickening behaviors (Equation 2-3):

\[ \tau = m \cdot \dot{\gamma}^n \]  

Equation 2-3

where, m is the consistency factor and n is the consistency index.

In this model, the value of “n” is used to distinguish between the shear-thinning and shear-thickening behaviors. For n < 1, the material is a shear-thinning, for n > 1, it is a shear-thickening and Newtonian if n = 1.
For some materials, the applied stress must exceed a certain value to initiate a flow (i.e. plastic behavior). This value is well-known as the yield stress. In the plot of shear stress versus shear rate, the yield stress corresponds to the point of zero shear rate. When the relationship between shear stress and shear rate remains linear once the yield stress is exceeded, the material can be described by the Bingham model shown in Equation 2-4 (Bingham 1917).

\[ \tau = \tau_o + \mu_p \cdot \dot{\gamma} \]  

Equation 2-4

where, \( \tau_o \) is the yield stress and \( \mu_p \) is the plastic viscosity.

2.2.3 Viscoelastic materials

Viscoelastic materials are materials that exhibit both elastic and viscous behaviours when undergoing deformations or stresses. At a constant stress, the viscoelastic material behaves as an elastic material and undergoes an instantaneous strain. Then, with time, strain increases due to the viscous properties. Once the load is removed, only the elastic deformation will be recovered. In other words, these materials can store some of the induced energy and use it for the recovery, and dissipate the rest by means of friction (Macosko 1994). Several tests can be used to investigate the viscoelastic properties. This includes creep, stress relaxation, and oscillatory tests. More details about the oscillatory tests and dynamic rheology will be presented in Section 2.4.

2.2.4 Thixotropic materials

Thixotropy can be defined as a decrease of the viscosity with time under a constant shear stress or shear rate, followed by a gradual recovery when the stress or shear rate is removed (Barnes 1997). This definition clearly refers to a reversible and time-dependent phenomenon (Figure 2.3).
Figure 2.3 - The thixotropic behavior during a step experiment; a) Thixotropic material, b) anti-thixotropic material

Thixotropic behavior occurs because it takes a finite time for the microstructure to change from one state to another. The decrease in apparent viscosity with time under constant shear is believed to be due to micro-structural changes in the suspension. This decrease in viscosity will continue with the shearing time until an equilibrium state (the lowest energetically possible state) is achieved. Thus, the thixotropic time, in which the micro-structural changes take place, is an important parameter when studying thixotropy (Mewis and Wagner 2012). The transition of the material from the at-rest to shearing conditions, and vice versa, is illustrated in Figure 2.4.

Figure 2.4 - Breakdown and build-up of a 3-D thixotropic structure (Barnes 1997)
Conversely to the thixotropic behaviour, a rheopectic or anti-thixotropic behaviour may be observed (Figure 2.3). For these materials, the sudden increase in shear rate causes an increase in viscosity over time. Physically, anti-thixotropy requires a structure that builds up under shear and breaks down when the shear rate is lowered or removed (Cheng and Evans 1965; Mewis and Wagner 2012).

In cement pastes, the shearing of cement suspension results in the breaking down its network structure into smaller agglomerates and releases the entrapped water within the agglomerates. The continuous shearing results eventually in reaching an equilibrium state in which the agglomerates cannot be broken into smaller fragments. At rest, the particles can form agglomerate into a network by means of weak physical bonds (Walløevik 2003). The rheological behavior of the suspension is related to the formed network structure and the rate at which it can form. It has been admitted by (Roussel 2006) that a thixotropic concrete is a concrete that displays a short flocculation characteristic time (typically several minutes) and a de-flocculation characteristic time of several tens of seconds in the 1 to 10 s$^{-1}$ shear rate range.

The size distribution of the flocs formed within the fresh state under different shearing conditions has been monitored in real-time using a Focused Beam Reflectance Measurement (FBRM) (Ferron et al. 2013). The variations of the mean chord length, representing the floc size, as well as the counts per seconds, reflecting the number of agglomerates, with different shearing conditions of 0.30 w/c mixture are shown in Figure 2.5 and Figure 2.6, respectively. At the case of a stirring intensity of 40 rpm, the mean chord length gradually increases over time, which shows that the kinetics of aggregation can dominate at low shearing conditions due to the orthokinetic aggregation. Simultaneously, the number of counts decreased reflecting the phenomena of floc formation. On the other hand, the application of a higher shearing intensity of 400 rpm resulted in a reduction in the flocs size and an increase in their number, indicating a disaggregation process. Furthermore, it was found that the aggregation and breakage kinetics of the paste matrix are highly influenced by shear history and the time scale for recovery is longer than the time needed to breakdown the structure.
Several techniques were proposed to evaluate the degree of thixotropy of cement-based materials, such as the hysteresis area, breakdown area, and start-up test. A summary for the most applicable quantifying techniques is given in Section 2.7.
2.3 Viscoelasticity versus thixotropy

Both thixotropy and viscoelasticity refer to reversible time effects (Mewis and Wagner 2009; Mewis and Wagner 2012; Sochi 2010). The distinguish between them can be highlighted from the stress response due to a sudden decrease in shear rate from $\dot{\gamma}_i$ to $\dot{\gamma}_e$ (Figure 2.7). A normal viscoelastic fluid would react by a monotonic decrease of the stress to a new plateau value (i.e. stress relaxation) as shown in Figure 2.7-b. During the stress relaxation the microstructure recovers to its new steady state level. In contrast, under similar conditions the shear stress in an inelastic thixotropic material would drop instantaneously to a lower value, and evolves gradually in the opposite direction to its new steady state (Figure 2.7-c). The most general response would be a combination of the two types, i.e. a sudden drop and a gradual stress relaxation and finally a slow, gradual increase in viscosity (Figure 2.7-d). Because of the time-dependent viscosity recovery in Figure 2.7-c and Figure 2.7-d, these two cases are considered thixotropic (Mewis and Wagner 2009).

Figure 2.7 - Various types of response to a sudden reduction in shear rate (a): b) viscoelastic; c) inelastic thixotropic; d) most general (Mewis and Wagner 2009)
2.4 Dynamic oscillatory shear rheology

The principles of the oscillatory tests can be illustrated using a two-plates-model in as shown in Figure 2.8 (Mezger 2011).

![Two-plates-model and oscillatory shear](image_url)

Figure 2.8 - The two-plates-model and oscillatory shear, adapted from (Mezger 2011)

In this model, the tested material is located between two plates where the lower plate is stationary while the upper one is oscillating by means of a drive wheel and a pushing rod. One complete rotation of the driving wheel from 0° to 360° corresponds to a one single shearing cycle. The performed number of shearing cycles per unit time represent the frequency. At positions of 90° and 270°, the deformation of the material between the two plates is maximum (i.e. maximum shear strain) and the speed is zero (i.e. zero shear rate). Conversely at 0° and 180°, the moving plate is in the zero position reflecting a zero shear strain and maximum shear rate. In the case of a perfect solid material, Hooke’s law applies as follows:

\[ \tau(t) = G^* \cdot \gamma(t) \]  

Equation 2-5

where, \( \tau(t) \) and \( \gamma(t) \) are the sine functions of shear stress and strain, respectively, and \( G^* \) is the complex shear modulus. Since \( G^* \) is constant, the shear stress response will be always “in phase” with the induced shear strain (i.e. the phase angle \( \delta = 0 \)). The induced strain function is:
\[ \gamma(t) = \gamma_A \cdot \sin \omega t \]  
\text{Equation 2-6}

where, \( \gamma_A \) is the amplitude of the induced strain and \( \omega \) is the angular frequency. In the case of an ideal elastic material, the \( G^* = G' \) where \( G' \) is the storage modulus representing the deformation energy stored by the sample. Replacing \( G^* \) with \( G' \) in Equation 2-5 and substituting with the function of \( \gamma(t) \) gives:

\[ \tau(t) = G' \cdot \gamma_A \sin \omega t \]  
\text{Equation 2-7}

![Diagram of perfect solid, perfect viscous, and viscoelastic material](image)

Figure 2.9 - The time-dependent stress, strain, and shear rate functions for the cases of perfect elastic, perfect viscous, and viscoelastic material, adapted from (Mezger 2011)

In the case of an ideally viscous material, Newton’s law applies:
\[ \tau(t) = \eta^* \cdot \gamma \]  

Equation 2-8

where, \( \eta^* \) is the complex viscosity and \( \gamma(t) \) is the shear rate function. As far as the value of \( \eta^* \) is constant, the shear stress is in phase with the shear rate and “out of phase” with the shear strain by a delay (\( \delta \)) of 90\(^\circ\) (Figure 2.9). In the case of a perfect viscous material \( \eta^* = G''/\omega \), where \( G'' \) is the loss modulus reflecting the deformation energy spent by the material to change its structure during shearing. Rearranging Equation 2-8 and keeping in mind that \( \gamma(t) = d\gamma(t)/dt \), the measured stress can take the following expression:

\[ \tau(t) = G'' \cdot \gamma \cos \omega t \]  

Equation 2-9

When performing oscillatory tests on a viscoelastic material, an in-between situation will persist, where the phase angle (\( \delta \)) will exhibit a value between 0\(^\circ\) and 90\(^\circ\) and the stress response will be a function of both \( G' \) and \( G'' \) as follows:

\[ \tau(t) = G' \cdot \gamma \sin \omega t + G'' \cdot \gamma \cos \omega t \]  

Equation 2-10

\[ \tan \delta = G''/G' \]  

Equation 2-11

where, \( \tan \delta \) is the damping factor describing the ratio of the viscous and the elastic portions of the viscoelastic deformation. A classification of the materials based on the oscillatory parameters is shown in Table 2.1 (Mezger 2011).

<table>
<thead>
<tr>
<th>Ideally viscous flow behavior</th>
<th>Behavior of a viscoelastic liquid</th>
<th>Viscoelastic behavior showing 50/50 ratio of the viscous and elastic portions</th>
<th>Behavior of a viscoelastic gel or solid</th>
<th>Ideally elastic deformation behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta = 90^\circ )</td>
<td>( 90^\circ &gt;\delta &gt; 45^\circ )</td>
<td>( \delta = 45^\circ )</td>
<td>( 45^\circ &gt;\delta &gt; 0^\circ )</td>
<td>( \delta = 0^\circ )</td>
</tr>
<tr>
<td>( \tan \delta \to \infty )</td>
<td>( \tan \delta &gt; 1 )</td>
<td>( \tan \delta = 1 )</td>
<td>( \tan \delta &lt; 1 )</td>
<td>( \tan \delta \to 0 )</td>
</tr>
<tr>
<td>( G' \to 0 )</td>
<td>( G'' &gt; G' )</td>
<td>( G'' = G' )</td>
<td>( G' &gt; G'' )</td>
<td>( G'' \to 0 )</td>
</tr>
</tbody>
</table>

2.4.1 Strain sweep

The amplitude sweep test is an oscillatory test that is carried out by increasing the induced strain values while keeping the frequency at a constant value (Figure 2.10). The main
purpose of this test is to determine the critical shear strain defining the linear viscoelastic domain (LVED). Indeed, two domains could be identified from the obtained variation of $G'$ and $G''$ with applied shear strain (Figure 2.11) (Hyun et al. 2011).

![Figure 2.10 - Schematic illustration of the strain sweep test at a fixed frequency](image)

In the first domain, which corresponds to low strain values, the storage and loss moduli are constant and independent on the value of applied strain (i.e. linear viscoelastic domain, LVED). On the other hand, for a strain values higher than a critical strain value, the nonlinear domain appears where $G'$ and $G''$ become functions of the applied strain indicating a large amplitude oscillatory shear (LAOS). Preforming the oscillatory tests at strain values within the LVED (i.e. small amplitude oscillatory shear, SAOS) can ensure non-disturbing the microstructure, hence non-destructive measurements (Mezger 2011;
Roussel et al. 2012). The critical strain value defining the LVED corresponds to the strain value at which the $G'$ or $G''$ values begin to deviate noticeably from the preceding constant values.

2.4.2 Frequency sweep

These tests are performed by varying the frequency while keeping the strain amplitude constant (Figure 2.12). The $G'$ and $G''$ at low frequencies describe the long-term behaviour of the samples. Conversely, the short-term behaviour is expressed at high frequencies (i.e. rapid motion) (Mezger 2011).

![Schematic illustration of the frequency sweep test at a constant strain amplitude](image)

Figure 2.12 - Schematic illustration of the frequency sweep test at a constant strain amplitude

The frequency sweep is very important, particularly for investigating the behaviour of polymer melts. In the case of dispersions such as paints, this test can be used to evaluate their long-term storage stability (i.e. sedimentation stability). An illustration for the variations of the shear moduli with the angular frequency for two different types of dispersions is shown in Figure 2.13. A dispersion exhibiting a $G' > G''$ corresponds to a gel-like structure and physical stability at rest. On the other hand, dispersions showing a $G'' > G'$ at low frequencies corresponds to a liquid-like structure where floating and phase separation is expected (Mezger 2011).
2.4.3 Time sweep

During the time sweep measurements, an oscillatory shear is applied at a constant strain amplitude and frequency (Figure 2.14). This allows observing the time-dependent changes in the viscoelastic properties (i.e. $G'$ and $G''$). Preforming the time sweep measurements using SAOS where the applied strain value is within the LVED ensures following the microstructural changes in a non-destructive manner (Mewis and Wagner 2009). In the case of inert suspensions or gels, the presence of a particulate network would be reflected by a plateau in the storage modulus after a given resting period.
2.5 Colloidal suspensions

Suspensions are mixtures of solid particles (suspended phase) in a liquid medium (suspending material). In the case of concrete suspensions, the suspended solid particles consist of non-colloidal particles, such as coarse and fine aggregate, as well as colloidal particles, such as cement and in some cases mineral additives such as silica fume. Colloidal particles refer to the elements which exhibit weak gravitational to Brownian effects and whose motions are affected by thermal forces (Mewis and Wagner 2012). The size of the colloidal particles ranges from a few nanometers to a few micrometers (Qin and Zaman 2003; Russel and Schowalter 1989). The smaller size limit ensures that the mass of the colloid is significantly larger than the mass of the molecules comprising the suspending fluid. On the other hand, the upper size limit ensures that thermal forces are still significant compared with the gravitational one (Mewis and Wagner 2012). It was demonstrated that cement particles larger than 40 μm in diameter seem to behave, at least to some degree, as colloid particles (Wallevik 2009).

The nature of the inter-particle forces between the colloidal particles determines the microstructure of the suspended phase, hence the flow behavior of the suspension. The colloidal suspensions can be classified as follows (Genovese 2012):

- **Hard-sphere suspensions**: no inter-particle forces other than infinite repulsion at contact. These rigid, inert, spherical particles are called hard-spheres as shown in Figure 2.15 (a-b).

- **Stabilized suspensions**: net repulsive forces keep particles separated as shown in Figure 2.15 (c-d).

- **Aggregated suspensions**: net attractive forces produce particle aggregation as shown in Figure 2.15 (e). Above the gelation concentration, aggregates interconnect into a network, forming a gel shown in Figure 2.15 (f).
Figure 2.15 - Schematic representation of different colloidal particles a) isolated hard-spheres, b) caged and packed mono-disperse spheres at random close packing (RCP), and face centered cubic array (FCC), c) isolated repelling particles (dashed line represents the range of the repulsive potential), d) caged repelling particles, e) isolated fractal clusters of aggregated particles (dashed line represents the smallest enclosing sphere), and f) network of fractal clusters. (Genovese 2012)

Generally, the forces affecting the behavior of solid particles in concrete suspensions are related to: gravity, inertia, viscous drag, dispersion (van der Waals), electrostatic and Brownian forces. The relative importance of these forces for each class of particles was examined using dimensionless numbers, in which the normalization term is the gravity force (Figure 2.16) (Flatt 2004b).
As can be observed, the most important forces in the colloidal range (silica fume) are dispersion, electrostatic and Brownian, followed by viscous drag. On the other hand, gravity, viscous, and inertia forces are the most important forces in case of non-colloidal range (coarse aggregate) (Flatt 2004b). More details on the forces governing the colloidal particles at rest will be presented in the next Sections.
2.5.1 Brownian force

Brownian motion is the random motion of particles suspended in a fluid due to their collisions with the atoms or ions in the suspending liquid. The Brownian force acting on a colloid \( F_B \) can be defined in terms of the thermal energy as (Einstein and Fürth 1956; Mewis and Wagner 2012):

\[
F_B = \frac{k_B T}{a}
\]

where, \( k_B \) is the Boltzmann constant, \( T \) is the absolute temperature, and “\( a \)” is the radius of the particle. The Brownian forces work as a thermal randomizing force, allowing the particles undergo constant translational and rotational movements. Brownian motion is only noticeable for particles smaller than roughly 1 \( \mu \)m (Macosko 1994). In this case, effect of the Brownian force becomes similar or higher than the effect of gravity. However, for larger particles, the energy exerted by temperature is too low, compared to gravity force so the thermal activation is not expected to influence the behavior of the suspension.

2.5.2 Van der Waals attractive forces

Attractive forces arise from the ever-present quantum mechanical effects caused by fluctuations in the electron clouds surrounding atoms (Mewis and Wagner 2012). The atoms of one colloid induce polarization in the atoms of another. Van der Waals force is the general term for all the weak inter-molecular attractive forces existing between neutral molecules. These forces are significant only when particles are very close to each other (by the action of Brownian motion). In regard to thixotropy of colloidal cement suspensions, the inter-molecular bonds are easily broken by shear; thus, it is likely that these weak secondary bonds will control the reversible coagulation and deflocculation. There are three main types of these secondary forces: dipole-dipole interactions, hydrogen bonds, and London dispersion force (Macosko 1994).

In 1937, Hamaker proposed a molecular model to calculate the attractive van der Waals force between particles. This model is based on the summation of the van der Waals energies between all pairs of molecules in separate particles (Overbeek 1977). In the range
of small separation distance \((h)\) between two spherical particles with radii \(a_1\) and \(a_2\), the force of attraction \(F_{\text{VDW}}\) can be given by (Flatt 2004a):

\[
F_{\text{VDW}} \approx \frac{1}{12} A \left(\frac{\tilde{a}}{h^2}\right)
\]  

Equation 2-13

where, \(\tilde{a}\) is the harmonic average of spherical particles radii and can be estimated from:

\[
\tilde{a} = \frac{a_1 + a_2}{2}
\]  

Equation 2-14

For cement particles that are not spherical, it was suggested to replace \(\tilde{a}\) with the mean radius of curvature at the contact points (Figure 2.17) (Flatt 2004a; Roussel et al. 2010).

Figure 2.17 – Average diameter, radius of curvature and surface to surface separation at the contact points (Roussel et al. 2010)

The coefficient “A” is the Hamaker constant, which depends on the properties of the particles and the dispersion fluid. A retardation approximation that allows to estimate the magnitude of the Hamaker constant from the non-retarded Hamaker constant at zero separation distance was proposed in (Flatt 2004a). The correlation between normalized Hamaker constant and the separation distance is shown in Figure 2.18. Accurate values of non-retarded Hamaker constant for cement are not known. However, its value is around 0.055, 0.20, 0.70, and 1.6 \(\times\) 10\(^{-21}\) J for ettringite, C-S-H with non-structural water, C-S-H crystallites, and C\(_3\)S, respectively (Flatt 2004a). The atomic force microscopy was used to
determine the Hamaker constant of cement where it was that its value is close to that of $C_3S$ (Lomboy et al. 2011).

![Figure 2.18](image1)

**Figure 2.18** – Correlation between normalized Hamaker constant and the separation distance between cement particles (Flatt 2004a)

The attractive force is directly proportional to the size of the particle and inversely proportional to the square of the distance separating the particles. For a given particle size, the attractive potential decays with the separation distance as shown in Figure 2.19.

![Figure 2.19](image2)

**Figure 2.19** – Attractive energy as a function of distance between particles (Ravina and Moramarco 1993)
In the particular case of the attraction between two homogenous plates, the van der Waals force can be expressed as:

\[ F_{\text{VDW}} \approx \frac{A}{6\pi h^3} \]

Equation 2-15

where, \( h \) is the separation distance between the two plates.

### 2.5.3 Electrostatic repulsion

Suspending particles in a liquid leads to charging their surface, by either surface acids or bases, by adsorption of free ions, surfactants, or polyelectrolytes. As a result, the ions in water that have a sign opposite to the particle charge will be drawn toward the particle (Macosko 1994; Mewis and Wagner 2012). Thus, near the surface of the particle, a layer of these charges will develop, which is known as the Stern layer. The Stern layer is strongly attached to the surface of the particle and the potential at its outer limit is often taken as zeta potential (\( \zeta \)). Outside of the Stern layer is a diffuse layer of counter ions. In the diffuse layer, the concentration of counter ions is high near the surface of the Stern layer and decreases linearly with distance from the charged surface until equilibrium is reached with the counter ions concentration in the bulk solution (Figure 2.20) (Ravina and Moramarco 1993).
Figure 2.20 – Schematic representation of the double layer (Ravina and Moramarco 1993)

The attached counter ions in the Stern layer and the charged atmosphere in the diffuse layer together are called the double layer. The Debye-Hückel length \( (1/\kappa) \) represents the thickness of the double layer, which depends upon the type and concentration of ions in the solution and the dielectric properties of the suspending medium. As far as various ionic species are present in cement suspensions, the valence describing the aqueous phase becomes non-ideal. Therefore, a non-integer symmetric electrolyte was proposed to replace the case of normally symmetric electrolyte (i.e. 1:1, 2:2, or 3:3), where the Debye length \( \kappa^{-1} \) can be estimated as follows (Flatt and Bowen 2003):

\[
\kappa^{-1} = \sqrt{\frac{\varepsilon_0 \varepsilon_r k_B T}{2e^2 Z_{eq}^2 n_{eq}}}
\]

Equation 2-16

where, \( \varepsilon_0 \) is the permittivity of the vacuum, \( \varepsilon_r \) is the relative dielectric constant of the dispersion medium, \( e \) is the elementary charge, \( n_{eq} \) is the ionic concentration of the equivalent electrolyte, and \( Z_{eq} \) is the valence of the equivalent electrolyte. As can be observed in Equation 2-16, the Debye length depends on the square of the ion valence and only the first power of the ions concentration. Therefore, divalent ions, such as \( \text{Ca}^{2+} \), are much more effective in screening the electrostatic potential around particles. Multivalent counter-ions are also much more readily adsorbed in the Stern layer and can even lead to charge reversal (Jönsson et al. 2004; Labbez et al. 2006; Labbez et al. 2011; Mewis and Wagner 2012).

The zeta potential and the Debye-Hückel length are the two parameters of the double layer that control the repulsive potential around the charged particles. For the case of low potentials, such as those measured for neat cement suspensions, an expression for estimating the electrostatic repulsion between two particles \( (F_{ES}) \) was given in (Flatt and Bowen 2003; Flatt and Bowen 2006; Russel and Schowalter. 1989) as follows:
\[ F_{ES} \approx 2\pi\varepsilon\varepsilon_0 \left( \frac{1}{1 + e^{-h/(2L_e)}} \right) \]

Equation 2-17

where, \( L_e \) is the distance from the particle surface used as the plane of origin of the electrostatic repulsion. This expression indicates that a maximum value for the repulsive energy is obtained when the particles are in close contact, and it decreases to zero outside of the double layer as shown in Figure 2.21.

![Figure 2.21 - Repulsive energy as a function of distance between particles (Ravina and Moramarco 1993)](image)

It has been reported that the concept of zeta-potential may be applied to hydrating materials such as cement suspensions (Nägele 1985). Furthermore, it was concluded that during the induction period and at the later phases of the hydration a well-defined zeta-potential can be identified. However, it worthy to mention that the value of \( \zeta \) at the shear plane is different from the actual surface potential which is often not known. In pure cement paste, the value of zeta potential typically ranges from -10 to 20 mV (Nägele 1985; Nägele 1986; Yang et al. 1997). For this small values of zeta potential, the maximum electrical repulsion will not be strong enough to overcome the van der Waals attractive forces between the particles, and, as a result, cement particles can flocculate.
2.5.4 Steric repulsion

Surface-active agents are organic molecules that have the ability to be adsorbed at the interfaces, thereby altering the physical properties at those interfaces (Cosgrove 2005). The addition of polymer layer inhibits flocculation in colloidal suspensions due to interaction of long-chain molecules adsorbed on the particles. The bigger the thickness of the polymer layer, the longer the range of developed repulsive hindrance. The incorporation of a high-range water-reducer (HRWR) in cement suspensions has shown to significantly change their flow behaviour (i.e. the yield value and viscosity) (Flatt 1999; Khayat 1999).

2.5.5 DLVO theory and state of flocculation

The DLVO theory, developed by Derjaguin–Landau–Verwey–Overbeek (Derjaguin and Landau 1941; Verwey and Overbeek 1948), linearly combines the attractive van der Waals, electrostatic repulsion, and steric hindrance repulsion potential curves. The resulting potential curve (net interaction energy) can be used to explain the tendency of colloids to either remain dispersed or to flocculate.

The state of flocculation of cement suspensions was investigated in (Yang et al. 1997). Three types of total potential curves can occur in cement suspensions with the variation of the ionic strength (Figure 2.22). At low ionic strengths, the repulsive potential exceeds the attractive one at all the inter-particle separations, therefore, a repulsive energy barrier is produced with a height of ($\psi_{\text{max}}$). Consequently, the particles repel each other and the suspension becomes stable. On the other hand, at moderate ionic strengths a secondary minimum ($\psi_{\text{sec}}$) can be developed. At this attractive well, the flocculation strength was proposed to depend on ($\psi_{\text{sec}} / k_BT$). The further increase in the ionic concentration above a critical ionic concentration value results in diminishing $\psi_{\text{max}}$ and the existence of only an attractive primary minimum ($\psi_{\text{min}}$) (i.e. coagulated suspension). The theoretical value of the critical ionic concentration was found to be around 0.012 M for cement pastes exhibiting zeta potential less than 20 mV.
2.5.6 Cohesion

In the case of cement suspensions with added superplasticizer, the use of mean field approach has shown very encouraging results with respect to yield stress predictions. However, the adequacy of the mean field double layer model has been vigorously challenged in the case of highly coupled systems (i.e. high surface charge + high ionic concentration + multivalent counter-ions), such as the case of neat cement suspensions (Flatt and Bowen 2003; Guldbrand et al. 1984; Labbez et al. 2006; Lesko et al. 2001). For these systems, a major limitation of the mean filed approach is neglecting the ions correlations between interacting particles. At very small separation distances of few nanometers, correlations between unsymmetrical distribution of the counter-ions between interacted surfaces (i.e. ion-ion correlations) can result in additional electrostatic attractive forces (Pellenq et al. 1997; 1997). In highly correlated cement suspensions, these attractive ion correlations were found to arise between accumulated divalent calcium ions at the negatively charged C-S-H surfaces (Jönsson et al. 2004; Plassard et al. 2005).

A dielectric continuum model taking into account the ionic interactions within a dispersion of C-S-H particles was proposed in (Jönsson et al. 2005; Jönsson et al. 2004). A schematic
representation of the two charged plates of C-S-H and the dissolved ions in the pore solution is shown in Figure 2.23.

![Diagram of charged plates and ions](image)

Figure 2.23 - Planar model system of two C-S-H particles with neutralizing mono- and divalent counter-ions as well as co-ions (Jönsson et al. 2005).

In their model, the total osmotic pressure consisted of the summation of the entropic repulsion, electrostatic attraction correlation, and the repulsive hard core pressure (which was found to be negligible). The repulsive entropic pressure originates from the “gas” pressure of the counter-ions. Its magnitude is proportional to the concentration of counter-ions at the mid-plane. As the surface charge density rises, the number of accumulated counter-ions increases and the entropic pressure decreases dramatically (Figure 2.24). Obviously, this is in contrast to the mean field result, where the pressure increases asymptotically. For C–S–H particles in solutions, the surface density ($\sigma$) ranges between 2.5–5 nm$^2$ with the change in pH from 11.6–12.6 (Jönsson et al. 2004). The correlation pressure represents the attractive force caused by correlations between the counter-ions on either side of the mid-plane. The resulting attraction is related to the fact that an excess of counter-ions on one side is correlated with a lack of counter-ions on the opposite side. It has been found that the magnitude of the correlation effect decreases with increasing $\sigma$, although its relative importance increases (Figure 2.24). The reduction of the attractive correlation pressure was attributed to the fact that high surface charge densities lead to compact layers of counter-ions at each surface. At high surface charge densities such as
those found for cement suspensions at high pH, the entropic pressure collapses, and the total pressure turns attractive (Figure 2.24).

Figure 2.24 – Entropic, correlation, and total osmotic pressure of the divalent counterions, as a function of the surface charge density (σ) for different separation distances (h) (Jönsson et al. 2004)
Based on the osmotic pressure model, it was found that the cohesion of cement pastes is affected by the pH of the solution, the presence of di- or multivalent cations, and the relative concentration of mono- and divalent cations (Jönsson et al. 2005).

### 2.6 Origin of thixotropic build-up of cement suspensions

In the case of cement-based suspensions, thixotropy is generally associated to a physico-chemical phenomenon (Billberg 2006; Roussel 2006). At rest, and during the dormant period, a growth of the apparent rheological properties is noted while the application of a sufficient shearing can erase it. “Structural build-up” and “loss of workability” are two terms that are used to describe the structuration of cement suspensions at rest (Feys 2009; Roussel 2012). As long as the applied shear is strong enough to get the structure back to its initial state, the developed structuration at rest is expressed by the term “structural build-up”. However, the “loss of workability” is often used when the applied shearing cannot break the formed permanent chemical bonds between cement particles.

The origin of structural build-up of cement suspensions at rest is still under debate. A recent study suggested a short, medium, and long terms structuration at rest (Figure 2.25) (Roussel et al. 2012). It was suggested that at the end of the mixing phase, all cement particles are dispersed (Figure 2.25-a). A couple of seconds after the end of mixing, cement particles start flocculating and form a soft colloidal network that is able to resist external stresses (Figure 2.25-b). Simultaneously, a nucleation of C-S-H bridges occurs at the pseudo contact points between cement particles within the network, which can result in turning the colloidal interactions to a more rigid one (Figure 2.25-c). Then, the increase of the size or numbers of C-S-H bridges between cement particles leads to further increase in the macroscopic elastic modulus of the network (Figure 2.25-d). Based on this scenario, it was concluded that the colloidal flocculation only affects build-up on a few seconds time scale and the build-up is mainly affected by the nucleation of C-S-H.
Although, several hydration products nucleate during the dormant period, the rigidification process can be mainly attributed to the nucleation of C-S-H (Roussel et al. 2012). This is based on the fact that C₃S pastes have shown similar evolution behaviors to that of cement pastes (Nachbaur et al. 2001). In addition, most of the other formed hydrates are much bigger than a few nm, hence their nucleation is not expected to occur in the pseudo contact points between flocculated cement particles (Aïtcin 2007; Aïtcin and Flatt 2015; Flatt 2004a).

2.7 Experimental quantification of thixotropy

A number of test protocols were constructed to evaluate the thixotropy of cement-based suspensions, based on their breakdown or build-up. Some of these protocols will be discussed in the following sections in more details.

2.7.1 Hysteresis area

Thixotropic materials have typical hysteresis loops that can be plotted from shear stress vs. shear rate experiments. Ish-Shalom and Greenberg used the hysteresis measurements to characterize the flow properties of cement paste (Green and Weltmann 1946). In such tests, the shear rate is increased from zero to a maximum value and then decreased back to zero. When the shear stress is plotted as a function of shear rate, the up (loading) and down (unloading) curves can be obtained, as illustrated in Figure 2.26. It has to be noted that this
hysteresis loop appears only if the duration of the applied shear rate steps is not sufficient for steady state to be reached (Roussel 2006). The area enclosed between the ascending and descending flow curves (i.e. hysteresis area) can be used as a thixotropic index (Barnes 1997). In addition, the relative hysteresis area, defined as the ratio of the hysteresis area to the area beneath the ascending shear curve, can also be used to reflect the degree of thixotropy (Dolz et al. 1995).

![Hysteresis Loop Diagram](image)

Figure 2.26 – Example of thixotropic loop obtained with a cement paste submitted successively to increasing and decreasing shear rate ramps (Roussel 2006)

Although the hysteresis loop testing procedure has been used for measuring the thixotropic behaviour of cement pastes, the shape of the hysteresis loop was criticized by several researchers. For example, Worral et al. 1964, have shown experimentally that two suspensions of quite different thixotropic properties could give similar hysteresis loops (Banfill and Saunders 1981). Indeed, for a given cement suspension, the estimated hysteresis area depends on the test conditions, such as the shear history, maximum shear rate. Furthermore, this index couples the shear rate and time effects (Barnes 1997; Mewis and Wagner 2009).

### 2.7.2 Structural breakdown curves

Another method that can be used to evaluate thixotropy of cement-based systems is the steady state approach. This approach consists in measuring the behavior of shear stress
versus time while fixing a constant shear rate (N). The initial shear stress necessary to breakdown the structure ($\tau_i$) corresponds to the initial structural condition. On the other hand, the shear stress decay with time towards to an equilibrium value ($\tau_e$) corresponds to an equilibrium condition that is independent of the shear history (Shaughnessy and Clark 1988). The area comprised between the initial and equilibrium flow curves can be used to quantify thixotropy of cement suspensions (Assaad 2004; Lapasin et al. 1983a). This area was referred to as the breakdown area ($A_b$), where it provides a measure of the breakdown energy done per unit time and volume of concrete.

Example of the variations in shear stress with shearing time for SCC made with ternary cement containing silica fume (SF) and fly ash (FA) and a set-retarding admixture (RET) is shown in Figure 2.27. The estimation of the structural breakdown area ($A_b$) is shown in Figure 2.28 (Assaad et al. 2003).

In addition to the simplicity of this approach, it also provides an advantage compared to the hysteresis loop tests as it enables measuring the entire shear stress range as a function of time for a given shear rate. However, the value of $A_b$ is affected by the measuring procedure such as the time of rest before the test, the differences between the rotational velocities applied and the accuracy of the torque sensor.

![Figure 2.27 – Typical example of structural breakdown curves for SCC (Assaad et al. 2003)](image-url)
The drop in apparent viscosity (Δ η\textsubscript{app}) at a constant shear rate was also used as an index to evaluate the degree of thixotropy (Assaad et al. 2003). At a given rotational speed, the concrete is sheared until equilibrium state is reached. The difference between the initial shearing stress representing initial destruction and the equilibrium shearing stress measured over the applied shear rate (i.e. Δ η\textsubscript{app}) can be calculated as follows:

\[
\text{Index of thixotropy} = \frac{\tau_i - \tau_e}{\tau_i} \cdot \eta_{\text{app},e} = \Delta \eta_{\text{app}} \quad \text{Equation 2-18}
\]

Where τ\textsubscript{i}: initial shear stress, τ\textsubscript{e}: equilibrium shear stress, and \( \gamma \): applied shear rate.

### 2.7.3 Specific rebuilding energy

A protocol based on the hysteresis loops was developed to quantify the degree of structural rebuilding in cement pastes (Ferron et al. 2007). In this protocol, an equilibrium loop was carried out by increasing the shear rate from 0 s\textsuperscript{-1} to 600 s\textsuperscript{-1} and holding the maximum shear rate (600 s\textsuperscript{-1}) for 8 minutes, before going back to 0 s\textsuperscript{-1}. Then, the specimen was allowed to rest in the rheometer for 10 minutes, before performing the hysteresis loop measurement. The hysteresis loop was conducted during 60 second-interval from 0 s\textsuperscript{-1} to 300 s\textsuperscript{-1} to 0 s\textsuperscript{-1}. This procedure was repeated eight more times (rest for 10 minutes, hysteresis loop, rest for
10 minutes, hysteresis loop, etc.). An example of the measured hysteresis and equilibrium loops is shown in Figure 2.29. The area within 100 s\(^{-1}\) and 200 s\(^{-1}\) of the up-curve of each hysteretic loop and the initial equilibrium line was calculated and used as the specific rebuilding energy (SRE). A plot of the SRE versus its corresponding rest time was used to determine the rate of rebuilding by looking at the slope of the line in this plane.

![Hysteresis loop comparison](image)

**Figure 2.29** – An example showing the specific rebuilding energy (SRE) for resting time of 90 minutes (Ferron 2008)

Indeed, the SRE provides a measure of the rebuilding that occurred relative to the reference state initially determined by the equilibrium loop protocol. In this technique, the effects of irreversible structural buildup and reversible structural buildup are coupled. In order to decouple the irreversible and reversible buildup, an equilibrium condition should be established after each hysteresis loop. This allows a comparison of the difference between the initial equilibrium condition and the following equilibrium conditions. However, this requires a new specimen for each resting time as well as extensive amounts of time.
2.7.4 Growth rate of static yield stress at rest

The static yield stress can be used as a measure of the strength and number of inter-particle bonds that are ruptured due to the applied shear rate or stress (Assaad et al. 2003; Dzuy and Boger 1985). The start-up test adopted for the determination of static yield stress at rest ($\tau_{\text{rest}}$) consisted of applying a low and constant rotational speed to a vane immersed in the undisturbed material following a certain period of rest while recording the resulting torque as a function of time.

Figure 2.30 shows an example for the variation of torque at 0.03 rps for a SCC that was allowed to rest for 5 minutes. The profile shows a linear elastic region followed by a yielding moment where the torque exerted on the vane shaft reaches a maximum value ($T_{\text{max}}$). This yield value corresponds to the beginning of the microscopic destruction of the bonds between the particles, where the material start flowing. Beyond this value, the torque decays towards a steady state region.

![Figure 2.30 – Typical torque-time profile for concrete (Assaad et al. 2003)](image)

The calculation of the peak shear stress value ($\tau_{\text{rest}}$) from the measured maximum torque ($T_{\text{max}}$) requires knowledge of the geometry of the yield surface and the shear stress distribution on the surface. Therefore, the material is assumed to be sheared along a localized cylindrical surface circumscribed by the vane and the shear stress is uniformly distributed over the cylindrical sheared surface (Dzuy and Boger 1985). Hence, a good approximation of the shear stress can be calculated from Equation 2-19 and Equation 2-20.
\[ \tau_{\text{rest}} = \frac{T_{\text{max}}}{K_s} \]  \hspace{1cm} \text{Equation 2-19}

\[ K_s = \text{constant} = \frac{\pi H^3}{2} \left[ \frac{L}{H} + \frac{1}{3} \right] \]  \hspace{1cm} \text{Equation 2-20}

where, \( L \) and \( H \) are, respectively, the height and diameter of the vane.

The structural build-up is the time-dependent growth of the static yield stress. Plotting the static yield stress as a function of the previous rest time can provide data on the thixotropic recovery after shearing. Billberg, in his doctoral project, investigated the increase in static yield stress at rest for cement mixtures (Billberg 2006). For example, the observed effect of changing \( w/c \) between 0.34 and 0.42 on the measured static yield stress is shown in Figure 2.31. The static yield stresses were determined during 40 minutes at successive rest periods of 10 minutes by subjecting the mixture to an increasing stress from 0 to 300 Pa at a rate of 3.33 Pa/s until the structure breaks. The criterion for breaking down the structure was when the shear rate reaches 0.5 s\(^{-1} \), i.e., when the deformation due to the broken structure increases. It was observed that the static yield stress increases linearly with the resting time, with constant inclination \( A_{\text{thix}} \), which was considered as a thixotropic index.

In addition, Billberg adapted a testing protocol to distinguish the reversible flocculation due to thixotropy from the irreversible evolution due to normal slump loss (Figure 2.32). In this regard, the Bingham model was used to determine the dynamic yield stress using the down curves of the first and last loops before and after the 40 minutes resting period. The variations of the dynamic yield stress of each mixture are shown in Figure 2.31. The area between the static and dynamic curves was suggested to represent the reversible structure, which is the total structural build-up minus the irreversible structure over time.
Figure 2.31 – Results of dynamic yield stress development and structural build-up of cement mixtures made with w/c ranging from 0.34 to 0.42 (Billberg 2006)

Figure 2.32 – The test protocol to assess the reversible and nonreversible components of thixotropy (Billberg 2006)
The evolution of static yield stress at rest was used by different authors to evaluate the structural build-up and was correlated to the lateral pressure of SCC and the reductions in bond strength due to multi-layer casting (Khayat et al. 2012a; Khayat et al. 2012b; Omran 2009; Ovarlez and Roussel 2006). It is worthy to mention that the accuracy of the measured static yield stress depends on the rotation speed of the measuring cylinder. Although slow rotation is desirable to capture the peak stress, very slow rotation can reconstruct the suspension during the measurement time (Billberg 2006; Roussel 2012). In addition, it should be kept in mind that this technique is destructive. As the recovered structure is destroyed after the start-up, the whole procedure of shearing and resting should be repeated for each data point within the experiment.

2.7.5 Dynamic oscillatory shear

In this shearing mode, the recovery of structure can be followed at rest in a non-destructive manner by applying a small amplitude oscillatory shear (SAOS). The induced shear strain amplitude should be small to ensure not disturbing or reorganizing the particles. Indeed, two critical strain were reported for cement pastes in (Roussel et al. 2012). The first one was identified as the largest critical strain where its value in the order of a few % and corresponds to the yielding and the flow onset (Figure 2.33 - left). It was shown that this shear strain is associated to the breakage of the colloidal interactions between cement particles. On the other hand, the second one is of the order of several hundredths of % and corresponds to the shear strain defining the LVED in the oscillatory strain sweep test (Figure 2.33- right). Applying a shear strain higher than this smallest critical strain results in the breakage of early hydrates, which form at the pseudo contact points between cement particles.
Figure 2.33 – Sketch for the two critical strains. (Left): largest critical strain in a yield stress measurement; (right): smallest critical strain in a strain sweep measurement (Roussel et al. 2012)

The possibility of using the SAOS to measure the viscoelastic properties of self-consolidating pastes was investigated in (Ferron 2008). As a first step, the strain sweep measurements were carried out to determine the smallest critical strain. The measurements were carried out from a shear strain of $3.87 \times 10^{-3}$ % (which was the lowest capacity of the rheometer) to a strain value of 1%. It was found that the $G'$ plateau of the LVED was not well-defined and the value of the critical strain was smaller than the limits of the rheometer. Therefore, the rebuilding energy technique was used to evaluate the build-up in this study.

In another study, Roussel et al. attempted to use the dynamic rheology to isolate the structuration due to the colloidal network from the one due to the chemical hydration of 0.40 w/c suspension (Roussel et al. 2012). For this, a shear strain of 0.50%, which is larger than the smallest critical strain value (0.03%), was applied to break the C-S-H bridges between cement particles. In addition, it was found that the frequency of the applied oscillations should be sufficiently high to reduce the influence of the C-S-H nucleation when the system reaches a zero strain rate configuration. The variation of the complex modulus with frequency at a constant strain of 0.5%, revealed that applying a frequency higher than 5 Hz can ensure a minimization of the time spent at rest, hence not allowing the new C-S-H bonds to form. The measured evolution of the storage modulus with time at a strain of 0.5% and frequency of 10 Hz after pre-shearing at 150 s$^{-1}$ for 200 s is shown in Figure 2.34. As can be observed, the elastic modulus increased during the first 10 s and
then reached a plateau. The colloidal percolation characteristic time is therefore suggested to be of the order of a few seconds.

![Figure 2.34 – Storage modulus as a function of time for w/c = 0.40 cement paste. Frequency 10 Hz, amplitude 0.5% (Roussel et al. 2012)](image)

### 2.8 Factors affecting thixotropy of cement-based materials

Various studies have shown that the thixotropy of cement-based systems is strongly dependent on their mixture composition, cement characteristics, type and dosage of chemical admixtures, and the presence of supplementary cementitious materials, as well as the processing parameters, such as mixing and vibration (Assaad 2004; Banfill 2006; Kawashima et al. 2013; Omran 2009; Quanji et al. 2014). For example, it was reported that cement pastes proportioned with a w/c of 0.36 is more thixotropic than those made with a w/c of 0.42 (Papo 1988). Furthermore, a significant effect of w/c on the variations of the thixotropy of self-consolidating concrete (SCC) mixtures proportioned with a similar initial slump flow was observed (Khayat and Assaad 2006). It was shown that 0.46 w/c mixtures exhibited lower thixotropy compared with those proportioned with w/c of 0.40 and 0.36.

The combined effect of cement content and specific surface area was also investigated by means of an inter-particle distance parameter (Figure 2.35) (Lapasin et al. 1983b). It was shown that higher cement content or surface area (i.e. lower particle distance) can result in a higher work needed to breakdown the structural network.
The effect of $C_3A$ amount in cement on the hysteresis area of 0.50 $w/c$ cement pastes was investigated by Ish-Shalom and Greenberg as reported in (Billberg 2006). It was found that the changes in $C_3A$ content did not result in significant variations in the thixotropic hysteresis area until 45 minutes after mixing (Figure 2.36). However, higher dependence on the amount of $C_3A$ was observed at 2 and 3 hours for $C_3A$ content higher than almost 5%. This was attributed to the formation of ettringite needles within the structure.
The effect of alkalis content on the hysteresis loop was investigated in (Grzeszczyk and Kucharska 1988). It has been shown that high alkalis content can change the shape of hysteresis loops of clinker suspensions from thixotropic into anti-thixotropic. However, no alterations in the hysteresis loop were observed in the case of cement suspensions. Therefore, it was concluded that the effect of alkalis content may depend on the reactivity of clinker in cement pastes.

Ferron in her doctoral project investigated the effect of C₃A and alkali contents on the specific rebuilding energy (SRE) of self-consolidating pastes (Ferron 2008). The w/c ratio was held constant at 0.35, and the superplasticizer dosage was adjusted to keep a given initial slump flow. Seven different cements were selected for this study (Table 2.2). It was shown that faster rates of structural rebuilding were seen in paste mixtures made with cement 4, 6, and 7. However, slower rates of rebuilding were seen in the paste mixtures made with cement 2, 1, 3, and 5 (Figure 2.37).

<table>
<thead>
<tr>
<th>Table 2.2 – The different cement used by (Ferron 2008)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cement</strong></td>
</tr>
<tr>
<td><strong>Oxide Analysis</strong></td>
</tr>
<tr>
<td>CaO (%)</td>
</tr>
<tr>
<td>SiO₂ (%)</td>
</tr>
<tr>
<td>Al₂O₃ (%)</td>
</tr>
<tr>
<td>Fe₂O₃ (%)</td>
</tr>
<tr>
<td>SO₃ (%)</td>
</tr>
<tr>
<td>MgO (%)</td>
</tr>
<tr>
<td>Equivalent Alkali (%)</td>
</tr>
<tr>
<td>Free lime (f-CaO) (%)</td>
</tr>
<tr>
<td>LOI (%)</td>
</tr>
<tr>
<td>Blaine specific surface (m²/kg)</td>
</tr>
<tr>
<td><strong>Compound</strong></td>
</tr>
<tr>
<td>C₃S (%)</td>
</tr>
<tr>
<td>C₃A (%)</td>
</tr>
<tr>
<td>C₄AF (%)</td>
</tr>
<tr>
<td>Initial Set</td>
</tr>
</tbody>
</table>
Furthermore, a correlation between the C₃A content and the rate of rebuilding was observed. With the exception of cement 1, the rate of structural rebuilding increased as the C₃A content decreased (Figure 2.38). However, no clear correlation was observed between the total equivalent alkali and structural rate of rebuilding (Figure 2.39). In summary, it was concluded that (C₃A/alkali) seems to be inversely correlated to the rate of structural rebuilding of cement pastes. This was attributed to the different cement-superplasticizer interactions.

Figure 2.37 – The effect of cement type on the specific rebuilding energy (SRE) (Ferron 2008)

Figure 2.38 – Rate of rebuilding versus C₃A content for pastes made with a superplasticizer (Ferron 2008)
Conversely, it was indicated that cement paste made with high alkali content (1.38%) resulted in a higher thixotropic hysteresis area than other types of cement (Quanji 2010). This was explained by the dissolution of alkali ions in the aqueous phase and their combination with the released Ca$^{+2}$ and OH$^{-}$ ions. Consequently, higher ionic strength (i.e. smaller thickness of the double layer) and higher tendency to form flocs.

The effect of binder composition and content on the thixotropic breakdown curves of SCC and concrete equivalent-mortar (CEM) mixtures were investigated (Assaad and Khayat 2004). The mixtures were made using Type 10 and Type 30 cements along with three other blended cements. The blended cements included: a binary cement (BIN) containing 8% silica fume (SF) and 92% T10 cement; a ternary cement (TER) made with 6% SF, 22% Class F fly ash (FA), and 72% T10 cement; and finally a quaternary cement (QUA) containing 6% SF, 28% FA, 16% slag cement (SC), and 50% T10 cement. The structural breakdown tests were carried at different times after the contact of cement and water. It was found that greater breakdown area values were obtained for SCC mixtures prepared with the one having the lowest binder content. This was related to the relative presence of coarse aggregate in concrete that increases internal friction and leads to higher shear stresses needed to breakdown the structure (Figure 2.40). The opposite tendency was
observed for mortars, where mixtures made with the highest binder contents exhibited greater breakdown areas.

![Breakdown area for SCC and CEM mixtures made with ternary cement](image1)

Figure 2.40 – Breakdown area for SCC and CEM mixtures made with ternary cement (Assaad and Khayat 2004)

Furthermore, for a given binder content, mixtures made with ternary cement resulted in a higher degree of thixotropy compared with those prepared with binary cement (Figure 2.41). However, mixtures made with quaternary cement were shown to be less thixotropic compared to mixtures made with other cement types.

![Breakdown area for SCC and CEM mixtures made with 550 kg/m³ of binder](image2)

Figure 2.41 – Breakdown area for SCC and CEM mixtures made with 550 kg/m³ of binder (Assaad and Khayat 2004)
An intensive research program was carried out to evaluate the effect of the incorporation of chemical admixtures on the thixotropic breakdown area ($A_b$) of SCC (Assaad and Khayat 2006; Khayat and Assaad 2006). It was shown that the thixotropic behaviour of SCC is highly dependent on the type and dosage of the viscosity-enhancing agents and high-range water-reducers (HRWR) used.

The structural build-up of cementitious systems has been shown to be temperature dependent (Nehdi and Al Martini 2007; Petit et al. 2006; Vanhove et al. 2013). Indeed, a nonlinear increase in yield stress and storage modulus values was observed when the temperature of cement paste varied between of 20 and 45°C (Nehdi and Al Martini 2007). Furthermore, the coupled effect of time and temperature on the variations of yield stress for mortar mixtures extracted from SCC was shown to be greatly affected by the type and dosage of HRWR (Petit et al. 2006).

The effect of incorporating viscosity-modifying agent (VMA) and/or superplasticizer (SP) on the kinetics of aggregation of cement pastes was studied using FBRM (Figure 2.42) (Ferron et al. 2013).

![Figure 2.42 - Influence of VMA and SP on number of flocs (Ferron et al. 2013)](image)

It was shown that the addition of VMA (mixture P1-VMA_H) did not result in significant changes in the number of chords observed (i.e. number of agglomerates) compared with
the neat mixture (P1). Based on these results, it was concluded that the VMA may not have any influence on the flocculation process and floc properties and the increase in cohesiveness is generated from the polymers binding to the water phase.

On the other hand, the presence of SP was shown to be the dominating factor affecting the aggregation and breakage kinetics. A significant increase in the number of flocs occurred when SP was used in mixture (P1-SP) compared with the neat mixtures (P1). When both VMA and SP are used together, the aggregation kinetics were more similar to that of a paste with just SP, regardless of the dosage of added VMA.

### 2.9 Structural build-up indices

Structural build-up of cement-based suspensions has a great impact on some concrete applications, such as the lateral pressure of SCC on the formwork, the bond strength between concrete layers in multi-layer casting, and the slip-form paving construction. For example, in the case of casting tall wall elements, higher kinetics of build-up corresponds to a faster rate of building the structure. This results in a higher ability to withstand the load from concrete cast above it without increasing the lateral pressure against the formwork and leads to lower construction costs and faster casting rates. Many studies attempted to predict and model the rate of build-up of cement-based suspensions to optimize their thixotropic behavior according to the application on hand (Abd El Megid 2012; Assaad 2004; Billberg 2005; Ferron 2008; Khayat et al. 2012a; Omran and Khayat 2014; Ovarlez and Roussel 2006).

In the majority of previous works, the structural build-up was expresses using the generally used $A_{\text{thix}}$. Experimental results showed that the value of $A_{\text{thix}}$ can vary between 0.1 and 1.7 Pa/s (Assaad et al. 2003). A classification of the type of SCC based on the value of $A_{\text{thix}}$ was done by (Roussel 2006) (Table 2.3).
The build-up index ($A_{\text{thix}}$) was used in (Abd El Megid 2012) to characterize the SCC mixtures and correlate its value to the workability indices. The variations of static yield stress measured using MK-III rheometer of eight SCC mixtures with rest time (RT) are shown in Figure 2.43.

It was observed that some mixtures have different static yield stress after 15 min of resting time $\tau_s(15)_{\text{MK-III}}$ but with the same structural build-up rate $R_{\text{SBU}}_{\text{MK-III}}$. For example, $R_{\text{SBU}}_{\text{MK-III}}$ of both SCC3 and SCC4 are the same and equal to 2.3 Pa/min but they have different $\tau_s(15)_{\text{MK-III}}$ of 350 and 380 Pa, respectively. Moreover, the $R_{\text{SBU}}_{\text{MK-III}}$ of both SCC6 and SCC7 were the same and equal to 3.3 Pa/min but with different $\tau_s(15)_{\text{MK-III}}$ of 520 and 1100 Pa, respectively. Therefore, three thixotropic indices were considered. The first one is $A_{\text{thix1}}_{\text{MK-III}}$, which is directly obtained as the value of $\tau_s(15)_{\text{MK-III}}$. The second index is the $R_{\text{SBU}}_{\text{MK-III}}$. The third index of thixotropy was $A_{\text{thix2}}_{\text{MK-III}}$, which is calculated by multiplying $\tau_s(15)_{\text{MK-III}}$ with $R_{\text{SBU}}_{\text{MK-III}}$. The estimated thixotropic indices are shown in

---

**Table 2.3 – Classification of SCC according to $A_{\text{thix}}$. (Roussel 2006)**

<table>
<thead>
<tr>
<th>Flocculation rate $A_{\text{thix}}$ (Pa/s)</th>
<th>SCC type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Less than 0.1</td>
<td>Non-thixotropic SCC</td>
</tr>
<tr>
<td>Between 0.1 and 0.5</td>
<td>Thixotropic SCC</td>
</tr>
<tr>
<td>Higher than 0.5</td>
<td>Highly thixotropic SCC</td>
</tr>
</tbody>
</table>

---
Table 2.4. As it is shown, the obtained results suggest that cement-based suspensions may have different thixotropic ranking based on the used build-up indices.

Table 2.4 – Various build-up indices used in (Abd El Megid 2012)

<table>
<thead>
<tr>
<th>Mixtures</th>
<th>SCC1</th>
<th>SCC2</th>
<th>SCC3</th>
<th>SCC4</th>
<th>SCC5</th>
<th>SCC6</th>
<th>SCC7</th>
<th>SCC8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{thix1_{MKIII}}$</td>
<td>270</td>
<td>330</td>
<td>350</td>
<td>380</td>
<td>440</td>
<td>520</td>
<td>1100</td>
<td>2000</td>
</tr>
<tr>
<td>$RSBU_{MKIII}$ Pa/min</td>
<td>2.80</td>
<td>2.35</td>
<td>2.30</td>
<td>2.30</td>
<td>3.00</td>
<td>3.30</td>
<td>3.30</td>
<td>17.30</td>
</tr>
<tr>
<td>$A_{thix2_{MKIII}}$ Pa*Pa/min</td>
<td>760</td>
<td>780</td>
<td>820</td>
<td>870</td>
<td>1300</td>
<td>1700</td>
<td>3600</td>
<td>35000</td>
</tr>
</tbody>
</table>

Recently, various build-up indices were compared in order to recommend the indices giving good correlations with the formwork pressure characteristics of concrete (Omran and Khayat 2014). It was found that a better correlation between the relative lateral pressure and the build-up values is obtained when considering the product of static yield stress at 15 minutes of rest and its evolution with rest time than considering the single index of initial static yield stress or its growth with rest time.

### 2.10 Concluding remarks

Based on the above literature survey, it is obvious that the build-up of cement suspensions is a complex phenomenon affect by both physical and chemical processes. Furthermore, the degree of build-up is influenced by the mixture composition, including cement content, type, and the presence of mineral and chemical admixtures as well as the suspension temperature and shearing conditions. The literature survey showed that several techniques can be used to quantify the thixotropy of cement suspensions based on their breakdown or build-up. It has also been seen several indices were proposed to describe the structural build-up of cement suspensions. The use of dynamic oscillatory shear in investigating the kinetics of structural build-up of cement suspensions in non-destructive manner is a promising approach. This can allow better identification of the key parameters affecting the complex kinetics of structural build-up of cement suspensions at rest.
2.11 References


Chapter 2: Literature Review


CHAPTER 3: DISPERSING OF FLOCCULATED CEMENT SUSPENSIONS

Foreword

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3.1 Abstract

Build-up of cement-based suspensions is a complex phenomenon affected by the mixture concentration and testing parameters as well as the shear history. Accurate measurements of build-up rely on the efficiency of the applied pre-shear regime to achieve an initial defined and dispersed structure to eliminate the shear history. This can therefore enable understanding mechanisms of build-up and quantifying the structuration of cement suspension from a reproducible dispersed state. Dispersing efficiency of various disruptive shear techniques, including rotational, oscillatory, and combination of both was evaluated. The initial and final states of suspension’s structure were determined by applying small-amplitude oscillatory shear (SAOS). Test results showed that oscillatory shear has a greater effect on dispersing concentrated cement suspension than the rotational shear. Furthermore, the increase in the oscillatory shear strain enhanced the breakdown of suspension’s structure until a critical point, after which thickening effects dominate. An effective dispersing method is then proposed. This consists of applying a rotational shear around the transitional value between the linear and non-linear variations of the apparent viscosity with shear rate, followed by an oscillatory shear at the crossover shear strain and a high angular frequency of 100 rad/s.

Keywords: Build-up, Concentrated cement suspension, Dispersion, Disruptive oscillatory shear, Small amplitude oscillatory shear.
3.2 Introduction

Cement-based suspensions are thixotropic materials (Bouras et al. 2008; Flatt 2004a; Wallevik 2009). Thixotropy, or the structural build-up at rest, refers to the change from liquid to solid-like states when cement suspension is left at rest (i.e. increase in static yield stress at rest) (Roussel 2012). Flow performance, placement, and consolidation of cement-based materials are affected by their thixotropic properties (Banfill 2006; Khayat et al. 2012a; Wang et al. 2011). For example, the structural build-up of concrete has a great impact on its behavior in various applications, including multi-layer casting, cast in place concrete, and slip-form paving construction (Khayat and Omran 2011; Roussel and Cussigh 2008; Wang et al. 2011). Furthermore, build-up kinetics affects the maximum lateral pressure exerted on formwork and its decay with time until cancellation (Amziane and Ferraris 2006; Khayat and Omran 2011; McCarthy et al. 2012; Tchamba et al. 2008). Lower build-up kinetics results in higher lateral pressure, hence increasing formwork costs and limiting the maximum allowable placement height (McCarthy et al. 2012). On the other hand, using a highly thixotropic concrete in multi-layer casting will result in reducing the bond strength between the cast layers, hence resulting in poor mechanical performance for the structure. Indeed, in this case, and due to the highly internal structure of the first cast layer, the stresses generated by the second layer may be not sufficient to re-initiate the flow in the first layer, thus preventing good bonding between the two layers (Roussel and Cussigh 2008).

Various studies have been conducted to investigate build-up of cement-based materials (de Oliveira Romano et al. 2013; Flatt 2004b; Jiang et al. 1995; Roussel 2005; Roussel et al. 2012). This phenomenon originates from the colloidal jamming due to particles flocculation and the chemical bridging resulting from cement hydration. Different techniques can be used to quantify build-up of cement-based materials (Amziane et al. 2008; Billberg 2006; Khayat et al. 2012b; Mahaut et al. 2008). Most of these techniques are based on assessing the structuration at rest after breaking down the internal network structure. The accuracy of measured build-up characteristics relies on the pre-shear regime and the shear stress applied during the liquid-solid transition (i.e. flow stoppage) (Coussot 2005; Dullaert and Mewis 2005; Ovarlez and Chateau 2008; Rueb and Zukoski 1997). Recently, in-situ backscattering measurements confirmed the significant influence of shear history on both aggregation and breakage kinetics of fresh cement.
pastes (Ferron et al. 2013). The applied pre-shear regime may be chosen to reproduce the application on hand. For example, rotational shear is probably the most suitable to reproduce the pumping, while in the case of vibration the oscillatory shear is the most appropriate. In fact, applying relatively high-shear rates can break the network interactions and decrease flocs size (Ferron et al. 2013; Yim et al. 2013). In most of the published literature, a rotational shear rate ranging between 100 s$^{-1}$ and 200 s$^{-1}$ for 1 to 3 minutes is applied to achieve an initial dispersed structure (Billberg 2006; Ovarlez and Chateau 2008; Roussel et al. 2012), regardless of the concentration, inter-particle forces, and hydration kinetic of the cement suspension. However, the efficiency of disruptive rotational shear varies depending on the suspension characteristics and the competition between shear-induced breakdown and hydration-induced build-up (Barnes 1997). Alternatively, other studies reported the possibility of using large amplitude oscillatory shear in inducing structural breakdown of flocculated suspensions (Kanai and Amari 1993; Mezger 2011; Raghavan and Khan 1995). The disruptive intensity of oscillatory shear was found to depend on the value and duration of induced shear strain. Furthermore, numerical simulations were adopted to model and predict the dispersion behavior of single spherical agglomerates subjected to different steady and unsteady shearing fields (Fanelli et al. 2006a; Fanelli et al. 2006b).

The main objective of this study is to evaluate the dispersing performance of various shearing procedures that can be used for concentrated cement suspensions, including rotational, oscillatory, rotational followed by oscillatory, and oscillatory followed by rotational shears. This can then help to propose an efficient disruptive technique to achieve a well-defined dispersed initial state and allow accurate build-up measurements of concentrated cement suspensions, regardless of the shear history (Roussel 2012). Furthermore, a well-dispersed state is also necessary to enable identifying the physical and chemical components of structuration and understand the sole effect of mixture parameters on the build-up of cement suspensions.
3.3 Experimental program

3.3.1 Materials and mixture proportions

The cement paste mixtures investigated in this study were systematically proportioned using a General Use (GU) cement complying with ASTM C150M standards and at two different water-to-cement ratios (w/c) of 0.35 and 0.50. The chemical and physical properties of cement are summarized in Table 3.1. Cement paste mixtures were mixed in batches of 0.5 L using a high-shear mixer in accordance with the procedure described in ASTM C1738M. High shear mixing regime was used to provide paste mixtures with rheological properties similar to those in concrete (Helmuth et al. 1995). The temperature of mixing water was controlled and cooled to 10 ± 1°C to compensate for heat generation during mixing. Following the end of mixing, all mixtures had a constant temperature of 23 ± 2°C. The mixing sequence consisted of introducing cement gradually over 1 minute, while the mixer was turned on. After a rest period of 150 seconds, the mixing was presumed for a total mixing time of 4 minutes and 30 seconds. Immediately after mixing, the samples were conserved in sealed containers to prevent water evaporation. The rheological measurements were carried out after 20 minutes from the first contact between water and cement to allow performing measurements after the occurrence of early hydration reactions.

Table 3.1- Mineralogical and physical characteristics of used GU cement

<table>
<thead>
<tr>
<th>C&lt;sub&gt;3&lt;/sub&gt;S (%)</th>
<th>C&lt;sub&gt;2&lt;/sub&gt;S (%)</th>
<th>C&lt;sub&gt;3&lt;/sub&gt;A (%)</th>
<th>C&lt;sub&gt;4&lt;/sub&gt;AF (%)</th>
<th>Blaine surface area (m&lt;sup&gt;2&lt;/sup&gt;/kg)</th>
<th>BET surface area (m&lt;sup&gt;2&lt;/sup&gt;/kg)</th>
<th>Median size, d&lt;sub&gt;50&lt;/sub&gt; (µm)</th>
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<tr>
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<td>17</td>
<td>7.2</td>
<td>7.9</td>
<td>390</td>
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<td>13.2</td>
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3.3.2 Test procedures

3.3.2.1 Rheological measurements

All performed rheological measurements were carried out using a coaxial cylinder rheometer with a serrated surface (Anton Paar MCR 302). The diameters of used cup and bob are 28.911 and 26.660 mm, respectively, providing a shear gap size of 1.126 mm (Figure 3.1). This
corresponds to almost 15 times the max particle size of cement particles. The effective height of tested sample is 42 mm. The test protocol consisted of shearing the paste at a shear rate of 20 s\(^{-1}\) in 30 seconds to ensure a homogeneous suspension within the gap (Mezger 2011). The sample was then allowed to rest for 30 seconds to allow temperature stabilization at 23°C before performing any rheological measurements. The sample was then pre-sheared at 500 s\(^{-1}\) for 60 seconds to ensure reaching equilibrium condition before obtaining the flow curve. The descending flow curve was determined by decreasing the shear rate in 7 steps from 500 s\(^{-1}\) to 1 s\(^{-1}\). Each step was maintained for 10 seconds to ensure achieving the steady state.

![Figure 3.1 - (a) MCR 302 coaxial cylinder rheometer; (b) Dimensions of used profiled bob and cup](image)

The storage (G’) and loss (G”) moduli were determined under different shear strains using strain sweep measurements. Shear strain amplitude was increased from 0.0001% to 20% at a constant angular frequency of 10 rad/s to identify the linear viscoelastic domain (LVED) and the critical shear strain. The critical shear strain is needed to perform the time sweep measurements in a non-destructive manner. A low value of the angular frequency was used to minimize the interference between applied shear during build-up measurement and the recovery kinetics. In most performed experiments available in literature, the non-destructive oscillatory shear was
applied at a frequency values ranging from 1 Hz (i.e. 6.28 rad/s) to 1.59 Hz (i.e. 10 rad/s) (Joshi et al. 2013; Lootens et al. 2004; Mezger 2011; Roussel et al. 2012). Additional strain sweep measurements were performed at a high angular frequency of 100 rad/s and shear strains ranging from 0.0001% to 250%. This angular frequency will be used in this study to perform the disruptive oscillatory shear. In fact, a high angular frequency can minimize the time spent at zero shear rate, hence reducing the influence of C-S-H nucleation during disruption intervals (Roussel et al. 2012).

### 3.3.2.2 Shear procedure to quantify dispersion efficiency

The shear procedure consisted of three intervals, including initial, disruptive, and growth intervals (Figure 3.2).

![Figure 3.2 - Schematic representation of the proposed testing procedures](image)

Initially, time sweep measurements are carried out using a small amplitude oscillatory shear (SAOS) to define and ensure a similar initial structure of investigated suspension in terms of
shear moduli and shear stress (Mezger 2011). The SAOS was performed by applying a strain amplitude within the LVED and at a constant angular frequency of 10 rad/s for 60 seconds. Immediately after the initial SAOS regime, a disruptive shear interval was applied. This consists of applying different shear profiles, including rotational shear, oscillatory shear, and rotational-oscillatory combinations. Finally, time sweep measurements under strain and frequency conditions similar to those used in the initial interval were performed for 60 seconds. The measurements carried out during the growth interval were conducted 1 second after the disruptive interval. The monitored shear moduli (G’ and G”) and shear stress (τ) were then compared with those determined at the initial interval (i.e. initial state) to evaluate the efficiency of the disruptive method.

3.4 Test results and discussions

3.4.1 Flow behaviour

Cement paste mixtures investigated in this study were prepared several times to ensure performing the rheological measurements at the same age and shearing history. For each prepared sample, the flow curve was determined to verify the reproducibility of the sample. It is worthy to mention that all the obtained flow curves showed comparable behaviour (differences in shear stresses values limited to ±5% with respect to the average flow curve). The typical measured flow curves of 0.35 and 0.50 w/c suspensions and the variations of their apparent viscosities with shear rate are shown in Figure 3.3. As can be observed, cement suspensions showed a plastic flow accompanied by a shear-thinning behavior (Barnes 2000). This was reflected by a marked decrease in the apparent viscosity below a certain shear rate. Beyond this shear rate, the rate of decrease in the apparent viscosity slows down and becomes linear. For both 0.35 and 0.50 w/c suspensions, the value of this critical (transition) shear rate is around 225 s⁻¹. The flow behaviour of flocculated cement suspensions is more likely to be controlled by the balance between van der Waals attraction and hydrodynamic forces between cement particles. An ordered state prevails if the hydrodynamic forces are enough to overcome the attractive forces and ensure a dispersed system. Accordingly, the system behaves as a shear-
thinning material characterized by a decrease in its apparent viscosity with shear rate (Rastogi et al. 1996).

Figure 3.3 - Typical measured flow curve (solid line) and apparent viscosity (dashed line) for 0.35 and 0.50 w/c suspensions

3.4.2 LVED and the critical strain

The shear moduli determined for 0.35 w/c suspension at a strain sweep ranging from 0.0001% to 20% and an angular frequency of 10 rad/s is shown in Figure 3.4-a and those measured at strain sweep from 0.0001% to 250% and an angular frequency of 100 rad/s in Figure 3.4-b. As can be observed, cement paste exhibited a linear viscoelastic domain (LVED) characterized by constant shear moduli and a linear relationship between shear stress and shear strain till a critical shear strain of 0.0025%. The value of this critical strain corresponds to the shear strain where \( G' \) curve starts deviating noticeably from the LVED plateau (Mezger 2011). At shear strains lower than the critical strain, cement suspension behaves as a solid structure. Imposing higher shear strains over the critical value results in breaking the C-S-H links between cement particles and decreasing the shear moduli (Roussel et al. 2012). It is observed that beyond the LVED, the \( G' \) measured at 100 rad/s showed a sharper decrease compared to that obtained at 10 rad/s. This can be attributed to a more brittle behavior of internal structure at this high frequency (Mezger 2011), hence resulting in a lower flow strain. It is also observed that in the case of a higher
angular frequency of 100 rad/s, the storage modulus increased with strain amplitudes beyond 3.5%. This is believed to be an indication of a strain-thickening response (Lee and Wagner 2003; Raghavan and Khan 1997).

Figure 3.4 - Variation of structural parameters with shear strain for 0.35 w/c suspension. (a) Strain sweep from 0.0001% to 20% at angular frequency of 10 rad/s; (b) Strain sweep from 0.0001% to 250% at angular frequency of 100 rad/s

The time sweep measurements were performed at strain amplitude of 0.001%, which is lower than the critical strain value (0.0025%), to ensure non-disruptive measurements. It is worthy to
mention that applying this very low shear strain (0.001%) does not induce any reorganization of the cement particles and, therefore, any shear banding effects (Ianni 2007; Roussel 2012; Roussel et al. 2012). Based on author’s knowledge, this is the lowest strain value ever used to study the viscoelastic properties of cement suspensions.

Damping factors (\(\tan\delta\)) obtained for different shear strain amplitudes at 10 rad/s and 100 rad/s are shown in Figure 3.5. Damping factor is calculated as the ratio \(\frac{G''}{G'}\), and measures the relative proportion of viscous to elastic properties at a given frequency. For an ideal solid, \(\tan\delta = 0\) (i.e. \(\delta = 0^\circ\)), and the response is purely elastic, whereas for a purely viscous response, \(\tan\delta \rightarrow \infty\) (i.e. \(\delta = 90^\circ\)). As can be observed in Figure 3.5, the increase in shear strain beyond the critical value increased the damping factor, which is an indication of a transition from gel-like state to less gel-like state. Below the critical strain (i.e. within the LVED), the damping factor did not show a significant change. As expected, the increase in damping factor has occurred more rapidly at the higher angular frequency of 100 rad/s compared to that observed with 10 rad/s. This is due to the fact that at high frequency, the contribution of C-S-H nucleation on structure may be limited (Roussel et al. 2012). Furthermore, for the case of high frequency of 100 rad/s, the damping factor reached its maximum value at 3.5% shear strain, indicating the most attainable liquid-like state at this frequency. As strain increases above this crossover strain, damping factor decreases confirming the occurrence of a strain-thickening.

![Figure 3.5 - Damping factor of 0.35 w/c suspension under different shear strains and angular frequencies](image-url)
3.4.3 Dispersion efficiency of various shear procedures

3.4.3.1 Rotational disruptive shear

The structural parameters \((G', G'', \tau)\) measured before, during, and after applying a disruptive rotational shear of 225 s\(^{-1}\) during 100 seconds for 0.35 w/c mixture are shown in Figure 3.6. The structural parameters determined at the initial interval can be used to define the initial structure of tested cement suspension. The application of a rotational shear during the disruptive interval resulted in a decay of shear stress indicating a breaking down of the internal structure and a formation of relatively more dispersed flocs. After the disruption period (going back to the SAOS regime), it was observed that the structural parameters are lower than those of the initial state. The difference between initial and growth structural parameters (i.e. before and after the disruptive interval) is a result of the disruption of network’s structure and therefore, can be used to quantify the efficiency of applied rotational shear (225 s\(^{-1}\)) in dispersing 0.35 w/c suspension.

![Figure 3.6 - Shear stress and shear moduli before, during, and after applying a shear rate of 225 s\(^{-1}\) for 100 s, w/c = 0.35](image)

In addition to a shear rate of 225 s\(^{-1}\), various shear rate values of 50, 150, 300, and 500 s\(^{-1}\) were also studied. The recovered shear stresses and storage moduli during the growth interval as well as the initial values of \(G'\) and \(\tau\) before shearing are presented in Figure 3.7-a and b, respectively.
As can be observed, increasing the disruptive shear rate from 50 to 150 and 225 s$^{-1}$ lowered the structural parameters ($G'$ and $\tau$) in the growth interval. Surprisingly, shearing at higher values, such as 300 and 500 s$^{-1}$ resulted in higher growth structural parameters compared to those obtained with a shear rate of 225 s$^{-1}$. This anomalous behaviour was also observed for 0.50 w/c mixture (Figure 3.8).

Figure 3.7 - (a) Shear stress response before and after rotational disruption; (b) Storage modulus response before and after rotational disruption, w/c = 0.35
In general, the increase in structural parameters at high shear rates may be related to induced grain inertia effects, slippage artifacts, or real changes in flocs structure. However, for the colloidal cement suspensions, no grain inertia effects are expected even at high values of rotational shear such as 500 s\(^{-1}\). This was verified by estimating the particle Reynolds number (Re\(p\)) (Feys 2009; Macosko 1994). For instance, in the case of a w/c of 0.50 and a shear rate of 500 s\(^{-1}\), the measured apparent viscosity was 0.1 Pa.s. Assuming that the density of cement paste is 2000 kg/m\(^3\), estimated Re\(p\) yields values of 2.5\times10^{-6} and 2.5\times10^{-2} for a particle/floc sizes of 1 and 100 μm, respectively. These values of Re\(p\) are less than 0.1, hence no significant grain inertia effects are expected. In order to find out if the observed behaviour is related to the wall-slip artefacts, the three interval shearing procedure was re-performed using different coaxial geometries. The testing geometries included smooth cup-smooth bob, serrated cup-serrated bob, and smooth cup-serrated bob. The same dispersing manner was obtained for the different geometries (i.e. decrease and then increase in the level of growth structural parameters for lower and higher shear rates than 225 s\(^{-1}\)). Accordingly, these results suggest that this anomalous behaviour is not due to wall-slip artefacts, and it may be due to real changes in breakage and aggregation kinetics.

Indeed, during the disruptive interval, the changes in flocs structure are affected by the competition between breaking down due to shearing as well as both shear-induced build-up and aging due to cement hydration (Barnes 1997; Mewis and Wagner 2012). Therefore, in the case

Figure 3.8 - Storage modulus response before and after rotational disruption, w/c = 0.50
of shearing at relatively low shear rates, such as 50 s$^{-1}$, a limited transformation of initially existing agglomerates into smaller flocs may be expected. This can allow the sheared structure to recover and reach its initial state after a short rest time (less than 60 seconds in the case of 0.35 w/c mixture). On the other hand, when higher shear rates corresponding to 150 and 225 s$^{-1}$ are applied, more network linkages can be disrupted, promoting the formation of smaller isolated flocs instead of the larger ones (i.e. more breakdown effect) (Barnes 1997; Mewis and Wagner 2012). Accordingly, after shearing the system can exhibit a limited recovery process and is expected to require a longer time to reach the initial state. However, although the further increase in disruptive shearing values of 300 and 500 s$^{-1}$ can lead to a smaller size of formed flocs, some other changes in the density and shape of formed flocs can occur (Mewis and Wagner 2012). For example, the application of relatively high shear rates has been shown to redistribute the particles within the isolated flocs, hence densifying them and increasing their compactness (i.e. higher fractal dimension) (Lin et al. 1989; Sonntag and Russel 1986; Varadan and Solomon 2001; Vermant and Solomon 2005). In this case, after the cessation of shearing, the restored structure can be formed due to the interactions between stronger individual elements. This can result in a higher strength of reformed network and may explain the anomalous increase in measured structural parameters during the growth interval compared with the critical shear rate (225 s$^{-1}$).

It is worthy to note that changes in both shear stress and storage modulus before and after disruption are similar. Indeed, the shear stress is a product of the complex storage modulus, which almost equals G’, and the shear strain value applied within the SAOS regime (i.e. 0.001%). Accordingly, only the variations of G’ will be presented in the next sections to describe the changes in the stress-bearing capacity of suspension’s network.

A non-dimensional parameter, normalized storage modulus, was used to quantify the effectiveness of various shear rate values in dispersing investigated cement suspensions. The normalized G’ was calculated as the ratio between G’ obtained at the middle of the growth interval (i.e. at 190 seconds) and the initial G’ immediately before disruption. The decrease in normalized G’ indicates a better-dispersed state of the structure. The variations of estimated normalized G’ with shear rate for 0.35 and 0.50 w/c are shown in Figure 3.9. As can be observed, lower normalized G’ is obtained with the increase shear rate value up to 225 s$^{-1}$. Shearing at 225
s\(^{-1}\) resulted in decreasing the levels of growth G’ be almost 80% of their initial values at the initial interval, which corresponds to decreasing the viscosity by five times. However, increasing the shear rate beyond this critical value resulted in a higher normalized G’ reaching 30% at 500 s\(^{-1}\). As discussed earlier, this is probably due to the densification of individual flocs and higher kinetics of restructuration that may take place at rest beyond the critical shear.

![Normalized storage modulus for various disruptive shear rates](image)

Figure 3.9 - Normalized storage modulus for various disruptive shear rates

It is worthy to note that the lowest normalized G’ for either 0.35 or 0.50 w/c suspensions was obtained at the same shear rate (225 s\(^{-1}\)). Furthermore, the transition shear rate presented in Figure 3.3 had the same value for both cement contents. These observations suggest that a correlation may exist between the transition shear rate and the value of most disruptive shear rate.

### 3.4.3.2 Oscillatory disruptive shear

The dispersion performance of oscillatory shear was evaluated by applying a large amplitude oscillatory shear (LAOS) at an angular frequency of 100 rad/s for 60 seconds. In LAOS, the applied disruptive shear strain is higher than the critical strain of 0.0025% (Figure 3.4). The typical measured structural parameters before, during, and after shearing at 3.5% shear strain are shown in Figure 3.10. As can be observed, measured shear moduli during the disruptive interval decreased drastically and reached their equilibrium values after only a couple of
seconds. In general, after 5 seconds of oscillations, there is no significant change in the structural parameters. An oscillatory disruptive period of 5 seconds was then adopted to carry out the oscillatory disruption measurements in this study.

Figure 3.10 - Shear stress and shear moduli before, during, and after imposing strain of 3.5% and angular frequency of 100 rad/s for 60 seconds, w/c = 0.35

Various shear strain amplitudes including 0.1%, 1%, 3.5%, 10%, 50%, and 200% were applied at an angular frequency of 100 rad/s for 5 seconds to evaluate the effect of oscillatory strain amplitude on dispersion efficiency of 0.35 w/c suspension. It is worthy to mention that for all the applied disruptive shear strains, the structural parameters during the disruptive interval reached their equilibrium values in less than 5 seconds. The storage moduli measured during the growth interval are shown in Figure 3.11. As can be observed, the level of storage moduli decreased when the disruptive shear strain increased from 0.1 to 1 and 3.5%. Moreover, the application of shear strains between 1 and 10% resulted in comparable growth storage moduli. The lowest storage modulus was attained at a shear strain of 3.5%. This value corresponds to the crossover strain shown in Figure 3.5, where the damping factor reached its maximum value. The application of higher shear strains of 50% and 200% resulted in higher growth storage moduli (i.e. higher strength of the structural network). This may be attributed to the strain-thickening behavior that can take place at these high shear strains (Kanai and Amari 1993; Lee and Wagner 2003; Raghavan and Khan 1997) (Figure 3.5). It is worthy to mention that the
achieved equilibrium shear moduli during the disruptive interval for shear strains of 50 and 200% were higher than that obtained for the case of 3.5%, confirming the presence of strain-thickening effects.

![Graph showing storage modulus responses](image)

Figure 3.11 - Storage modulus responses obtained before and after oscillatory disruption, w/c = 0.35

The increase in shearing strain enhances the external agitation applied on suspension’s network. For the case of strain amplitude below the strain-thickening region, this can loosen the existing flocs, hence decreases their compactness and leads to a lower viscosity. However, inducing higher shear strain, within the strain-thickening region, may result in reconstructing the loosen constituents and thus forming more porous flocs with higher volume fractions (i.e. lower packing density). The decrease in packing density of formed agglomerates can lead to higher structural parameters during and after the disruptive interval (Yim et al. 2013). The phenomenon of strain-thickening was also observed in flocculated ferric-oxide suspensions, where higher levels of recovered G’ were observed after applying LAOS within the strain-thickening region (Kanai and Amari 1993). Based on these results, it can be concluded that increasing the disruptive strain up to the crossover strain (3.5% in the case of 0.35 w/c suspensions) can enhance the dispersion of cement suspensions. However, the use of strain beyond the crossover value may result in a less effective dispersion.
The comparison between the structural parameters measured after applying a transitional rotational shear of 225 s\(^{-1}\) (Figure 3.6) with those obtained under crossover oscillatory shear at strain amplitude of 3.5% (Figure 3.10) revealed that oscillatory shear can result in lower storage modulus and viscosity compared with the rotational shear. Indeed, the viscosity decreased by 5 and 70 times after imposing 225 s\(^{-1}\) rotational shear and 3.5 s\(^{-1}\) oscillatory shear, respectively. In the case of oscillatory shear, the increase in shear stress due to transition from the initial interval to the disruptive interval is small compared to that observed in rotational shear, while the decrease in shear stress after LAOS (i.e. disruption) is high compared to that obtained in disruptive rotational shear. The smaller increase of shear stress in case of LAOS is related to the lower shear rate in oscillatory shear compared to that in the rotational shear (3.5 s\(^{-1}\) vs. 225 s\(^{-1}\)). The shear rate of 3.5 s\(^{-1}\) in LAOS is calculated as the strain amplitude times the angular frequency (i.e. 3.5% * 100) (Mezger 2011). Despite its low dynamic shear rate, the oscillatory shear is shown to have a greater effect in reducing the viscosity of cement suspension. The higher dispersion efficiency of an oscillatory shear at 3.5%, compared to a rotational one at 225 s\(^{-1}\), may be attributed to its ability to loosen the floc phase by inducing alternating tensile and compressive stresses on the individual sites of cement agglomerates (Feke 2007). Furthermore, the oscillatory shearing can induce additional rotational diffusion of cement particles (Leahy et al. 2013). This rotational diffusion may affect the orientation of cement particles and contributes in destroying the existing C-S-H bridges. However, in the case of disruptive rotational shear, the system consists of smaller flocs in which the transitional diffusion enhances their alignment with a limited effect on C-S-H bridges (Barnes 1997; Leahy et al. 2013; Roussel 2012).

### 3.4.3.3 Combined rotational and oscillatory disruptive shear

Additional investigations were carried out to evaluate the efficiency of combining rotational and oscillatory shears. In the first step, experiments were performed by applying two different rotational disruptive shears of 150 and 225 s\(^{-1}\) for 95 seconds. Each rotational shear was followed by 5 seconds of oscillatory shear at an angular frequency of 100 rad/s and different strain amplitudes of 0.1%, 3.5%, and 50%. One second waiting period was introduced between the disruptive rotational and oscillatory shears to minimize the perturbation effects following the high shear rate. The measured G’ in the growth interval and its initial value before disruption are shown in Figure 3.12. As can be observed in Figure 3.12-a, applying an oscillatory shear
after a rotational shear of 150 s\(^{-1}\) resulted in considerable reduction in storage modulus compared with that obtained after a rotational shear of 150 s\(^{-1}\) only. Furthermore, it is observed that the growth of G’ after disruption is similar to that obtained after shearing at individual transition shear rate of 225 s\(^{-1}\). On the other hand, applying LAOS after a rotational shearing of 225 s\(^{-1}\) did not result in a significant change (Figure 3.12-b). These results suggest that dispersion efficiency obtained after rotational shear lower than the transition one can be improved by a post-oscillatory shearing at strain amplitude around the crossover one.

![Figure 3.12](image)

**Figure 3.12** - Storage modulus responses obtained before and after applying a rotational followed by an oscillatory shear. (a) Rotational shear of 150 s\(^{-1}\) followed by various LAOS at angular frequency of 100 rad/s; (b) Rotational shear of 225 s\(^{-1}\) followed by various LAOS at angular frequency of 100 rad/s, w/c = 0.35
In the second step, experiments were carried out by applying LAOS at strain amplitudes of 0.1%, 3.5%, and 50% and an angular frequency of 100 rad/s for 5 seconds before applying the rotational shear values of 150 and 225 s\(^{-1}\) for 95 seconds. The measured initial and growth storage moduli values are presented in Figure 3.13.

![Figure 3.13 - Storage modulus responses measured before and after applying an oscillatory followed by a rotational shear. (a) Various LAOS at angular frequency of 100 rad/s followed by rotational shear of 150 s\(^{-1}\); (b) Various LAOS at angular frequency of 100 rad/s followed by rotational shear of 225 s\(^{-1}\), w/c = 0.35](image)

It is observed that for both shear values of 150 and 225 s\(^{-1}\), the storage moduli showed comparable levels, regardless of the applied disruptive strain. Furthermore, G’ measured after...
disruption are similar to those measured after applying the rotational shear only. The application of disruptive oscillations before the rotational shear was not effective in enhancing the dispersion efficiency of concentrated cement suspension.

### 3.4.4 Consequences on the efficiency of disruptive procedures

Normalized $G'$ was used again to evaluate the dispersion efficiency of investigated shear procedures. Additionally, the normalized damping factor was calculated as the ratio between $\tan\delta$ obtained 30 seconds after the end of disruption and its initial value. The variations of normalized $G'$ and $\tan\delta$ for various disruptive shear combinations investigated using 0.35 w/c suspension are shown in Figure 3.14. As described earlier, a normalized storage modulus lower than unity indicates that the growth storage modulus is lower than the initial value (i.e. before disruption), which means a reduction in network strength after disruption. On the other hand, a higher normalized damping factor indicates higher structural changes from solid-like state to liquid-like state, denoting more unassociated cement particles. Based on the results presented in Figure 3.14, the following observations can be drawn:

1. The use of disruptive oscillatory shear at strain amplitudes higher than the critical strain and lower than 10% is shown to be more efficient than the disruptive rotational shear to disperse concentrated cement suspensions. The oscillatory shear resulted indeed in lower normalized storage modulus and higher normalized damping factor compared with those measured at a rotational shear rate of 225 $s^{-1}$ (i.e. the transition shear rate).

2. In the case of oscillatory shear, the best-attained dispersion state, characterized by highest normalized damping factor (2.5) and lowest normalized storage modulus (0.015), was obtained at strain amplitude of 3.5%. This strain amplitude was identified as the crossover strain defined in Figure 3.5.

3. The application of 225 $s^{-1}$ pre-shear before the disruptive oscillatory shear at strain amplitudes other than the crossover strain (3.5%) increased the normalized damping factors compared with LAOS only. The increase in normalized damping factors after combining rotational shear and oscillatory shear at 10% and 50% strains may be related to the structural changes induced by the rotational shear (Barnes 1997; Roussel 2012). Applying a pre-rotational shear probably changes
the instantaneous value of the crossover strain which in turn can reduce the thickening effects obtained at these high shear strains. On the other hand, the normalized storage moduli were increased, but still lower than those achieved in the case of individual rotational shearing at 225 s\(^{-1}\). In other words, the combination of pre-rotational shear with disruptive oscillatory shear improved the dispersion degree obtained at strain amplitudes higher than the crossover strain.

![Graph showing normalized storage modulus and damping factor for various shearing procedures](image)

Figure 3.14 - (a) Normalized storage modulus for various shearing procedures; (b) Normalized damping factor for various shearing procedures, w/c = 0.35

4. In the case of LAOS preceded by rotational shearing at 225 s\(^{-1}\), the normalized structural parameters are close to each other, regardless of the value of applied shear strain, contrarily to those values obtained with LAOS only. Changing the shear strain amplitude between 0.1 and
50% resulted in small changes in normalized storage moduli from 0.15 to 0.2 and from 1.7 to 2 for normalized damping factors. This results in a comparable reference state, regardless of the applied shear strains ranging between 0.1 and 50%.

5. For shear strains between 1 and 10%, the application of a rotational shear of 150 s$^{-1}$ or 225 s$^{-1}$ before applying the oscillatory shear resulted in comparable normalized storage modulus and damping factor. This indicates that applying disruptive oscillatory shear at strains around the crossover strain after rotational shear rate lower than the transition shear rate can compensate for the lower dispersion efficiency obtained at this shear rate.

6. The application of LAOS before a rotational shear of 225 s$^{-1}$ resulted in improving the normalized damping factor with no significant changes in the normalized storage modulus. Applying a rotational shear of 150 s$^{-1}$ instead of 225 s$^{-1}$ resulted in normalized structural parameters near to unity. The application of rotational shear after LAOS can densify dispersed elements and induce microstructural arrangements due to the shear induced-build-up (Barnes 1997). This can result in a network strength similar to that obtained after rotational shear alone. These results suggest that applying LAOS before rotational shear does not lead to significant improvement in the dispersion efficiency compared with the case of rotational shear followed by oscillatory shear.

According to these observations, it is recommended to follow the traditional rotational disruptive technique with LAOS to ensure well-dispersed systems before measuring their structural build-up. This combination showed a higher efficiency to disperse concentrated suspension compared to the rotational shear rate only. Moreover, this combination achieved a comparable reference state for various shear strains compared with LAOS which achieved different states depending on the strain value.

### 3.5 Conclusions

The effect of various disruptive shearing techniques, including rotational, oscillatory, and rotational-oscillatory combinations on dispersion efficiency of flocculated cement suspensions is investigated. Small amplitude oscillatory shear measurement technique was used to quantify
the structure before (initial) and after (growth) applying the different disruptive shearing regimes. Based on the obtained results, the following conclusions can be pointed out:

1. In the case of flocculated cement suspensions, the use of disruptive rotational shear rate lower than 150 s$^{-1}$ for 100 seconds may not be enough to achieve a well-dispersed state.

2. An efficient dispersion of cement suspension can be obtained by applying a shear rate corresponding to the transition shear rate, where the rate of decrease in the apparent viscosity becomes slight and linear. In the case of 0.35 and 0.50 w/c mixtures, this value is around 225 s$^{-1}$. Applying higher values of disruptive shear rates resulted in higher levels of recovered storage modulus after shearing.

3. Large amplitude oscillatory shear (LAOS) at high frequency can be applied to disperse concentrated cement suspensions. This should be done at shear strain near the crossover value corresponding to the maximum damping factor (i.e. maximum liquid state).

4. The oscillatory disruptive shear is more efficient than the rotational one to disperse concentrated cement suspensions. Oscillatory disruptive shear is shown to reduce viscosity by 70 times compared 5 times obtained with rotational shear.

5. The dispersion efficiency of rotational shear performed at shear rates lower than the transitional value can be enhanced by applying a post-oscillatory shear at strain around the crossover value corresponding to the maximum damping factor.

6. The application of rotational shear followed by an oscillatory shear is found to achieve a comparable dispersion degree for shear strain and shear rate values different than the optimum ones (i.e. cross over shear strain and transitional shear rate).

7. The application of disruptive oscillatory shear before the rotational shear was not effective in enhancing the dispersion degree of concentrated cement suspensions.

8. An effective dispersion method for concentrated cement suspension is proposed. This consists of applying a rotational shear around the transitional value followed by an oscillatory shear at the crossover shear strain and high angular frequency of 100 rad/s.


3.6 References


CHAPTER 4: NEW APPROACH TO ASSESS BUILD-UP OF CEMENT-BASED SUSPENSIONS

Foreword

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4.1 Abstract

The structural build-up of cement suspensions at rest is a complex phenomenon affected by both physical and chemical structurations. Better understanding of this phenomenon relies on the efficiency of measurement approach. Dynamic rheometry was used to investigate the evolution of both storage modulus and phase angle of cement and inert calcium carbonate suspensions. Two independent build-up indices were proposed to identify the rest time needed to build a percolated elastic network and its rigidification rate with time. The structural build-up of various cement suspensions was evaluated using the proposed indices. These indices were then compared to the well-known thixotropic index ($A_{\text{thix}}$). It was found that combining the percolation time and the rigidification rate can provide deeper insight into the structuration process of cement suspensions. Furthermore, these indices were found to be well-correlated to the decay in lateral pressure of cement suspensions.

**Keywords:** Build-up, Cement paste, Dynamic shear moduli.
4.2 Introduction

Cement-based materials such as concrete, mortar, and cement paste are thixotropic materials (Ferron et al. 2013; Flatt 2004; Khayat et al. 2002; Lapasin et al. 1979; Wallevik 2009; Yim et al. 2013). Thixotropy is a reversible and time-dependent phenomenon. Indeed, thixotropy is the continuous decrease of viscosity with time when flow is applied to a sample that has been previously at rest (i.e. breakdown), and the subsequent recovery of viscosity when the flow is discontinued (i.e. build-up) (Mewis and Wagner 2009). In the case of colloidal suspensions, a three-dimensional structure can be formed at rest due to van der Waals attractive forces and breaks down during flow into separate flocs (Flatt 2004; Mewis and Wagner 2009). Recently, laser backscattering technique was used to monitor the flocculation and breakage of cement clusters within concentrated cement pastes. It has been shown that kinetics of aggregation and breakage are highly influenced by shear history, paste ingredients, and rate of shear strain (Bentz et al. 1999; Ferron et al. 2013; Yim et al. 2013). Besides aggregation of cement flocs at rest, an additional time-dependent process occurs due to cement hydration, which is irreversible and can cause slump loss (Roussel 2012). Therefore, structural build-up at rest of cement suspensions can be related to the combined effects of colloidal structuration due to inter-particles interactions and chemical rigidification resulting from cement hydration (Bentz et al. 1999; Roussel 2012).

Although thixotropy includes two aspects (build-up at rest and breakdown under shear), structural build-up is reported to have a greater impact on the performance of fresh cement-based materials after casting (Khayat and Omran 2011; Roussel and Cussigh 2008; Wang et al. 2011). For example, in the case of multi-layer casting, it is crucial to design and use concrete with weak kinetics of structural rebuilding to avoid possible reductions in bond strength between cast layers (Khayat et al. 2012a). In fact, high build-up results in high internal shear strength of the first cast layer. This can prevent the stresses generated by the second layer from re-initiating flow in the first layer (Roussel and Cussigh 2008). On the other hand, concrete with high kinetics of build-up is preferred for casting tall wall elements to reduce the lateral pressure exerted on formwork and allow faster pressure decay after casting (Assaad 2004; Billberg 2006; Khayat and Omran 2011).
Various experimental approaches have been employed to describe and quantify thixotropy of cement suspensions based on either their structural breakdown or structural build-up. The traditional method for quantifying thixotropy consists of subjecting the sample to an increasing shear rate from zero to a maximum value, before returning to zero at the same rate (Green and Weltmann 1946), which is known as the loop test. The area enclosed between the ascending and descending flow curves (i.e. hysteresis area) is used as a thixotropic index (Barnes 1997). Although this test is quick and qualitative, the estimated hysteresis area depends on test conditions, such as shear history, maximum shear rate, and step duration. Furthermore, the variation of this index is due to the combined effects of shear rate and time (Barnes 1997; Mewis and Wagner 2009). Another approach based on the structural breakdown curves was proposed (Assaad et al. 2003). This approach involves monitoring the shear stress decay under different shear rate values. For each shear rate, the initial and equilibrium shear stresses are identified. The area comprised between the initial and equilibrium shear stress values is then estimated. This is referred to the breakdown area ($A_b$) and can be used as a measure of thixotropy (Assaad et al. 2003).

Hysteresis loops and rebuilding energy method was used to evaluate the build-up of cementitious suspensions (Ferron et al. 2007). In this method, hysteresis loop test is performed after different resting periods. For a given resting period, the area enclosed between the up-curve of the hysteresis loop and the equilibrium down-curve is determined and defined as the specific rebuilding energy (SRE). The slope of variation of SRE with resting periods was taken as the rate of build-up. Billberg employed another approach to quantify build-up that consist of determining the stress needed to breakdown the structure of cement suspension and initiate flow (i.e. static yield stress) after various resting periods (Billberg 2006). Longer resting periods allow more structuration, hence resulting in higher static yield stress. The slope of static yield stress vs. resting period curve is referred to ($A_{thix}$) and has been used as an indication of structural build-up at rest (Khayat and Omran 2011; Khayat et al. 2012b; Ovarlez and Roussel 2006; Roussel 2006). Furthermore, this approach can be used to isolate the reversible thixotropic component by estimating the area enclosed between static and dynamic yield stress curves for a given resting period (Billberg 2006). However, this approach is destructive and therefore, necessitates to carry out measurements on renewal mixtures for each resting period (Mewis and Wagner 2009).
Recently, dynamic rheology has been used to investigate the aging process of thixotropic cement suspensions (Coussot et al. 2006; Ovarlez and Chateau 2008; Roussel et al. 2012). In this approach, recovery of structure is monitored by applying a small amplitude oscillatory shear (SAOS). In this regime, the induced shear strain is lower than the critical value defining the linear viscoelastic domain (LVED). This can allow therefore performing non-destructive measurements on undisturbed network (Roussel et al. 2012). The oscillatory shear stress response is determined and storage modulus (G’) is evaluated. The evolution of G’ with time can be used to describe structuration of cement suspensions at rest (Roussel et al. 2012).

Although various indices have been proposed to evaluate the build-up of cement suspensions, they do not provide an insight on the physical and chemical kinetics of structuration. Therefore, they have limited contribution in understanding the key factors affecting build-up behavior of cement suspensions at rest. Furthermore, it was reported that these indices may not allow a consistent ranking of mixtures in terms of their build-up (Abd El Megid 2012). The main objective of this study is to develop new indices that can be used to better understand and quantify build-up of cement suspensions. Two independent indices were proposed: the first one describes the rate of colloidal network structuration, while the second one is related to chemical rigidification of the network. These indices were used to describe build-up of various cement mixtures and compared to $A_{\text{thix}}$ index which is generally used to describe thixotropy. Furthermore, a combined index that take into account the two proposed indices was proposed and correlated with the variation of lateral pressure using a column of 1-meter height.

4.3 Research significance

Structural build-up of cementitious materials is a complex phenomenon originating from physical and chemical processes. This phenomenon is influenced by mixture parameters, such as water-to-cement ratio ($w/c$), cement type and fineness, as well as presence of chemical and/or mineral admixtures (Assaad and Khayat 2006; Bentz et al. 1999; Ferron et al. 2013; Khayat and Assaad 2006). The indices proposed in this study to describe the physical and chemical structurations of cement suspensions can enhance the fundamental knowledge of build-up mechanisms. Moreover, they are useful in understanding the effect of various mixture parameters on build-up behavior of cement-based materials after casting. Such an understanding
can contribute in facilitating design and optimization of cement-based materials with adapted build-up given the application on hand.

4.4 Experimental program

4.4.1 Materials and mixture proportions

A General Use cement (GU) complying with ASTM C150M specifications was used to proportion the cement paste mixtures investigated in this study. The cement was used at two different finenesses: normal (NF-GU) and high fineness (HF-GU). In addition, calcium carbonate (CaCO$_3$) was used to prepare calcite-based suspensions. Silica fume (SF) was used as a partial replacement of cement in selected mixtures. The chemical and physical characteristics of cement, calcium carbonate, and silica fume are summarized in Table 4.1. The particle size distributions of NF-GU and HF-GU cements and CaCO$_3$ are presented in Figure 4.1. A polycarboxylate high-range water-reducer (HRWR) was incorporated in some mixtures as a percentage of the optimum dosage. The optimum dosage corresponds to the dosage beyond which there is no significant decrease in yield stress. The yield stress was determined using the down flow curve obtained by decreasing the shear rate from 100 s$^{-1}$ to 0.1 s$^{-1}$ in 10 steps in 150 seconds. Then, the yield stress was estimated using Bingham model. For 0.35 w/c suspensions, the optimum dosage was found to be 0.44%, by weight of cement. The mixture proportions of investigated suspensions are summarized in Table 4.2. The 50% and 100% of the optimum dosage of HRWR corresponded to 0.22% and 0.44% by mass of cement, respectively.

Table 4.1 - Chemical and physical characteristics of used cement, silica fume, and calcium carbonate

<table>
<thead>
<tr>
<th>Material</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>SO$_3$</th>
<th>MgO</th>
<th>K$_2$O</th>
<th>Na$_2$O</th>
<th>CO$_2$</th>
<th>Median size, $d_{50}$ (µm)</th>
<th>Specific surface area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NF-GU</td>
<td>63.7</td>
<td>19.9</td>
<td>3.5</td>
<td>2.7</td>
<td>3.8</td>
<td>1.9</td>
<td>0.8</td>
<td>0.2</td>
<td>---</td>
<td>13.62</td>
<td>1.30</td>
</tr>
<tr>
<td>HF-GU</td>
<td>10.29</td>
<td>1.38</td>
<td>10.23</td>
<td>0.15</td>
<td>25.30</td>
<td>1.40</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SF</td>
<td>0.4</td>
<td>99.8</td>
<td>0.1</td>
<td>0.1</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>0.2</td>
<td>0.15</td>
<td>25.30</td>
<td>1.38</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>55.7</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.22</td>
<td>---</td>
<td>---</td>
<td>44</td>
<td>10.23</td>
<td>1.38</td>
<td>25.30</td>
</tr>
</tbody>
</table>
Figure 4.1 - Particle size distribution of NF-GU and HF-GU cements and calcium carbonate

Table 4.2 - Mixture proportions of cement and calcium carbonate pastes

<table>
<thead>
<tr>
<th>Mixture</th>
<th>(W/C, HRWR, SF)</th>
<th>Water-to-solid ratio, by weight</th>
<th>HRWR as a percentage of the optimum dosage (%)</th>
<th>Partial replacement content of SF (%)</th>
<th>Solid fraction, Sf</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>(0.45, 0%, 0%)</td>
<td>0.45</td>
<td>0</td>
<td>0</td>
<td>0.41</td>
<td>1.95</td>
</tr>
<tr>
<td></td>
<td>(0.40, 0%, 0%)</td>
<td>0.40</td>
<td>0</td>
<td>0</td>
<td>0.44</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>(0.35, 0%, 0%)</td>
<td>0.35</td>
<td>0</td>
<td>0</td>
<td>0.48</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>(0.35, 50%, 0%)</td>
<td>0.35</td>
<td>50</td>
<td>0</td>
<td>0.48</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>(0.35, 100%, 0%)</td>
<td>0.35</td>
<td>100</td>
<td>0</td>
<td>0.48</td>
<td>2.08</td>
</tr>
<tr>
<td></td>
<td>(0.40, 0%, 2%)</td>
<td>0.40</td>
<td>0</td>
<td>2</td>
<td>0.47</td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>(0.40, 0%, 4%)</td>
<td>0.40</td>
<td>0</td>
<td>4</td>
<td>0.45</td>
<td>1.99</td>
</tr>
<tr>
<td>Calcium carbonate</td>
<td>0.40</td>
<td>0.40</td>
<td>---</td>
<td>---</td>
<td>0.48</td>
<td>1.85</td>
</tr>
<tr>
<td>(CaCO₃)</td>
<td>0.45</td>
<td>0.45</td>
<td>---</td>
<td>---</td>
<td>0.45</td>
<td>1.80</td>
</tr>
<tr>
<td></td>
<td>0.50</td>
<td>0.50</td>
<td>---</td>
<td>---</td>
<td>0.43</td>
<td>1.73</td>
</tr>
</tbody>
</table>

The investigated mixtures were prepared in batches of 0.5 L using a high-shear blender in accordance with the procedure described in ASTM C1738M standard. High-shear mixing regime was used to provide paste mixtures with rheological properties similar to those in concrete (Helmuth et al. 1995). The temperature of mixing water was controlled and maintained at 8 ± 1°C to compensate for heat generation during mixing. Following the end of mixing, all mixtures had constant temperatures of 23 ± 2°C. The mixing sequence consisted of introducing cement (or binder) gradually over 1 min, while the mixer was turned on. After a resting period
of 150 seconds, the mixing was presumed for a total mixing time of 4 minutes and 30 seconds. Immediately after mixing, the samples were conserved in sealed containers to prevent water evaporation. The rheological measurements were carried out after 20 minutes from the first contact between water and cement to allow performing measurements after the occurrence of early hydration reactions.

The mixtures used for lateral pressure testing were prepared in batches of 12 L using a high-shear mixer. The change in mixture volume and mixer model can influence the properties of prepared mixtures (Han and Ferron 2015). Therefore, the mixing variables were optimized to produce mixtures with comparable rheology to those obtained in 0.5 L batches. The adapted mixing sequence consisted of introducing water and HRWR into the mixing bowl. Then, powders were introduced slowly in 4 minutes, while the mixer is rotating at 3000 rpm. After introducing solid materials, the rotational speed was increased to 6000 rpm and mixing was continued for 1 minute. After a resting period of 3 minutes, the mixing was presumed at 6000 rpm for a total mixing time of 10 minutes. Then, the sample was covered and allowed a resting period of 9 minutes to ensure an age of 20 minutes similar to that used for the rheometric measurements. The mixing was then presumed for an additional time of 1 minute at 6000 rpm. Immediately after mixing, the sample was poured in the pressure column. In parallel, rheometric measurements were conducted on mixtures used for lateral pressure to verify their reproducibility compared to those prepared in 0.5 L batches.

### 4.4.2 Test methods

All performed rheometric measurements were conducted using a coaxial cylinder rheometer with a serrated surface. The diameters of the cup and bob are 28.911 and 26.660 mm, respectively, providing a shear gap size of 1.126 mm. The measuring system and tested mixture were enclosed in a moisture trap to prevent water evaporation during measurements. After introducing paste sample to the rheometer, a shear rate of 20 s\(^{-1}\) was maintained for 30 seconds to ensure a uniform distribution of sample within the gap. The sample was then allowed one minute of rest for temperature stabilization at 23\(^\circ\)C before performing measurements.

The structural build-up at rest was quantified after subjecting the sample to a pre-shear period. The application of pre-shear aims to achieve a well-defined initial dispersed state, hence
eliminating the effects of shear history and ensuring good reproducibility (Ferron et al. 2013; Roussel 2012). Recently, the authors have shown that the dispersing performance of rotational shear can be enhanced by applying a large amplitude oscillatory shear (LAOS) at high frequency (Mostafa and Yahia 2015). Furthermore, the use of shear strain value close to the crossover shear strain was shown to achieve a well dispersed state. The crossover shear strain corresponds to the shear strain that achieves a maximum damping factor, reflecting the highest liquid state in the strain sweep test performed at a high angular frequency of 100 rad/s. The pre-shear protocol used in this study consisted in applying a rotational shear rate of 200 s\(^{-1}\) for 90 seconds, followed by LAOS at a shear strain of 6\% and an angular frequency of 100 rad/s for 10 seconds. It is worthy to mention that all the investigated mixtures showed almost zero storage modulus at the end of pre-shear period, confirming good dispersion and well-defined initial state.

One second after the pre-shear period, the build-up was determined during 20 minutes using two different approaches, including time sweep and static yield stress measurements. For time sweep measurements, a small amplitude oscillatory shear (SAOS) was applied at a constant angular frequency of 10 rad/s and shear strain value within the linear viscoelastic domain (LVED). This allowed monitoring the evolution of both the storage (\(G'\)) and loss (\(G''\)) moduli with rest time. The identification of the LVED and critical shear strain was done using strain sweep test (Mezger 2011). In this test, the investigated suspensions were subjected to an increasing shear strain from 0.0001% to 20% at a constant angular frequency of 10 rad/s. In the second approach, the evolution of static yield stress with rest time was determined at different resting periods of 5, 10, 15, and 20 minutes after the pre-shear period. For each resting period, the static yield stress was determined by monitoring the stress response at a constant shear rate of 0.01 s\(^{-1}\) for 1.5 seconds. The applied shear rate of 0.01 s\(^{-1}\) is similar to that used in literature (Billberg 2006; Mikanovic et al. 2006). The static yield stress corresponds to the peak value of measured stress growth curve.
4.5 Results and discussion

4.5.1 Critical strain

The G’ and G” moduli determined from strain sweep measurements for selected mixtures are shown in Figure 4.2. As can be observed, all mixtures exhibited a linear viscoelastic behavior till a certain critical shear strain. The determined critical shear strain ranges between 0.0025% and 0.2% depending on the mixture formulation. Within the linear viscoelastic domain, G’ and G” moduli are independent of applied shear strain. However, the increase in shear strain beyond the critical value resulted in decreasing the shear moduli, reflecting the destruction of the network due to breakage of C-S-H bridges between cement particles (Roussel et al. 2012). Based on these results, a shear strain of 0.001% (lower than 0.0025%) was selected to perform the time sweep measurements in a non-destructive manner.

![Figure 4.2](image.png)

Figure 4.2 - Variations of shear moduli with shear strain between 0.0001% and 20% and at angular frequency of 10 rad/s. (G’: full symbol, G”: empty symbol)

4.5.2 Percolation time and rigidification rate

Build-up of cement suspensions originates from physical and chemical processes. Determination of physical structuration necessitates the elimination of chemical hydration effects of cement. The use of inert systems, such as calcite-based suspensions, can allow...
producing physical effects similar to those occurring in cement suspensions during the first hour after mixing (Mikanovic et al. 2006). The build-up characteristics of three different calcium carbonate suspensions proportioned with various solid fractions ($S_f$) of 0.43, 0.45, and 0.48 were determined using time sweep measurements. The evolution of storage modulus ($G'$) and phase angle ($\delta$) with rest time is presented in Figure 4.3. The phase angle ($\delta$) was calculated as $\tan^{-1}(G''/G')$ and can vary between 0° and 90°. The value of 0° corresponds to perfect solid state (i.e. elastic) in which there is no delay between induced oscillatory strain and measured stress response. In the case of perfectly viscous structure, the value of $\delta$ is 90° (Mezger 2011).

Figure 4.3 - Time sweep measurements at shear strain of 0.001% and angular frequency of 10 rad/s for various solid fractions ($S_f$) of inert CaCO$_3$ suspensions. Evolutions of (a) storage modulus; (b) phase angle with rest time
As can be observed in Figure 4.3, the build-up of CaCO₃ suspensions is characterized by an increase in G’ accompanied by a decrease in δ during a certain period of rest, after which the evolutions of G’ and δ became non-significant. Immediately after pre-shearing, limestone particles are dispersed and the system is perfectly viscous reflected by G’ and δ values of 0 and 90°, respectively. At rest, the particles start to flocculate due to the van der Waals attraction forces (Flatt 2004), resulting in formation of a network of interacted particles and flocs (Barnes 1997). This is reflected by an increase in G’ and a decrease in δ corresponding to a transition from liquid state to less liquid state. This transition is accompanied with an increase in number of pseudo contact points between flocculated particles at rest, which results in formation of successive paths of interconnected flocs, namely percolation paths (Mewis and Wagner 2012; Roussel et al. 2012). The formation of successive paths allows transmitting stresses with lower delay and results in increasing the rigidity of formed network (Mezger 2011). As a consequence, the system exhibits a higher storage modulus and lower phase angle. After a certain resting period, the evolving structure reaches its final configuration and the enhancement in network’s rigidity and elasticity becomes negligible (i.e. stabilization of G’ and δ). This time can be defined as the percolation time (tperc) describing the resting period needed for colloidal particles to reach their favourable and equilibrium positions (Coussot 2005). The percolation phenomenon corresponds to the formation of a sample-spanning connectivity between the structural elements (Mewis and Wagner 2012).

It is worthy to mention that in the case of inert suspensions, such as calcium carbonate, the evolution of G’ after the percolation time is expected to be null. Nevertheless, the small evolutions observed after the percolation time could be related to the effects of Ostwald ripening phenomenon (Baldan 2002) due to the dissolution and precipitation of CaCO₃ particles. This can therefore promote the recrystallization of larger and more stable particles (Lakshtanov et al. 2014), resulting in a small and limited rigidification of formed percolated network.

As expected, at a given rest time, the increase in solid fraction resulted in higher rigidity of formed network (i.e. higher G’). Moreover, higher solid fraction allowed a faster formation of the elastic percolated network reflected by lower percolation time. Indeed, increasing the solid fraction from 0.43 to 0.45, and 0.48 resulted in decreasing tperc from 15 to 11, and 5.5 minutes, respectively.
In addition to time sweep measurements on CaCO$_3$ suspensions, further measurements were performed on a cement-based mixture to evaluate the influence of chemical effects on the evolutions of G’ and δ at rest. A Cement paste mixture proportioned with HF-GU cement and a solid fraction of 0.48 was tested at 20 and 110 minutes of age. These ages were chosen to experience different nucleation rates of formed hydrates, hence allowing different hydration effects (Aïtcin 2007). The age of 20 minutes is within the dormant period, while the age of 110 minutes corresponds to a higher hydration activity after the dormant period.

The evolutions of G’ and δ were determined and compared to those obtained on corresponding CaCO$_3$ suspension proportioned at the same solid fraction (Figure 4.4). It is worthy to mention that both HF-GU cement and CaCO$_3$ powder have comparable particle size distributions and median sizes (d$_{50}$) as shown in Figure 4.1 and Table 4.1. Furthermore, NaCl was added to the aqueous phase of CaCO$_3$ suspension to obtain zeta potential comparable to that of HF-GU cement suspension. The effect of varying the ionic strength of NaCl electrolyte on zeta potential, conductivity, and Debye length was investigated on diluted CaCO$_3$ suspension proportioned with (solid / liquid) of 30%. The obtained electro-kinetic values of both HF-GU cement and CaCO$_3$ suspensions measured at an age of 40 minutes are summarized in Table 4.3. As can be observed, both HF-GU cement and CaCO$_3$ suspensions showed comparable low zeta potential values. For CaCO$_3$ suspension, the increase in NaCl ionic strength resulted in increasing conductivity. However, non-significant variations were observed for both zeta potential and Debye length within the examined range of ionic strength (i.e. from 61.1 to 610.7 mmol/l). These results are in good agreement with those presented and discussed in (Mikanovic et al. 2006). Indeed, it was reported that the increase in NaCl ionic strength of CaCO$_3$ suspensions did not significantly alter their sedimentation rate or packing density characteristics. This was justified by the fact that examined ionic strengths are much higher than the critical coagulation concentration (CCC) estimated by the DLVO theory. Based on these results, the NaCl amount used with concentrated CaCO$_3$ suspension was optimized to induce ionic strength roughly similar to that of cement suspensions. For a given solid fraction, CaCO$_3$ and HF-GU cement suspensions can then undergo comparable physical structural kinetics during the early stage of hydration (Flatt and Bowen 2003; Mikanovic et al. 2006; Roussel et al. 2010).
Figure 4.4 - Time sweep measurements at shear strain of 0.001% and angular frequency of 10 rad/s for CaCO₃ and HF-GU cement suspensions having solid fraction of 0.48. Evolutions of (a) storage modulus; (b) phase angle with rest time

Table 4.3 - Zeta potential of HF-GU cement and calcium carbonate suspensions proportioned at 30% solid content

<table>
<thead>
<tr>
<th>Material</th>
<th>Added NaCl (g/l)</th>
<th>Ionic strength (mmol/l)</th>
<th>Conductivity (mS/cm)</th>
<th>Zeta potential (mV)</th>
<th>Debye length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>0.0</td>
<td>0.0</td>
<td>0.068</td>
<td>10.47</td>
<td>12.50</td>
</tr>
<tr>
<td></td>
<td>3.6</td>
<td>61.1</td>
<td>6.1</td>
<td>5.8</td>
<td>1.43</td>
</tr>
<tr>
<td></td>
<td>14.3</td>
<td>244.3</td>
<td>15.5</td>
<td>2.92</td>
<td>0.88</td>
</tr>
<tr>
<td></td>
<td>35.7</td>
<td>610.7</td>
<td>29.7</td>
<td>5.58</td>
<td>0.63</td>
</tr>
<tr>
<td>HF-GU</td>
<td>----</td>
<td>----</td>
<td>10.9</td>
<td>3.81</td>
<td>1.05</td>
</tr>
</tbody>
</table>
As can be observed in Figure 4.4, the evolution of $G'$ within the percolation period is influenced by the degree of hydration for a given colloidal system (i.e. comparable median size, inter-particle distances, zeta potential, ionic strength, and suspension’s temperature). Cement suspension tested after 110 minutes of age resulted in higher rate of evolution of $G'$ than that obtained after 20 minutes. Furthermore, cement suspensions exhibited higher $G'$ than that obtained for the inert calcium carbonate suspension. The dependency of $G'$ (i.e. rigidity) on the degree of hydration may be related to the precipitation of hydration products, such as C-S-H at the pseudo-contact points between particles (Bentz et al. 1999; Garrault-Gauffinet and Nonat 1999; Nachbaur et al. 2001). Indeed, during cement hydration, calcium and hydroxyl ions dissolve from the anhydrous cement and lead to the formation of a gelatinous, poorly crystalline skin over the particles (Banfill 2006; Sujata and Jennings 1992). The precipitated C-S-H contributes in turning the soft colloidal interactions to a more rigid ones (Roussel 2012; Roussel et al. 2012). These observations suggest that the evolution of $G'$ of cement suspensions during the percolation period is due to the combined effects of chemical and physical structurations.

It is interesting to note that the determined percolation times ($t_{perc.}$) obtained for calcium carbonate and cement suspensions at ages of 20 and 110 minutes were around 5.5 minutes, regardless of the degree of hydration. This suggests that $t_{perc.}$ may not be affected by the chemical process in the sense that the occurred precipitation due to hydration does not necessarily create new contact points through the formed network, and therefore does not affect the liquid-solid transition or the formation of percolated network.

For resting periods longer than the percolation time, $\delta$ stabilized for both CaCO$_3$ and cement suspensions, while $G'$ continued to increase in the case of cement suspensions, but stabilized for CaCO$_3$. The rate of evolution of $G'$ after the percolation time can be referred to as the rigidification rate ($G_{rigid}$). This represents the increase in stress-bearing capacity (strengthening) of formed percolated structure due to the formed hydrates (Jiang et al. 1995; Roussel 2012). In the case of inert CaCO$_3$ suspension, the rigidification rate is almost zero, however it is constant for cement paste tested at 20 minutes. The linear increase of $G'$ during the dormant period was also reported in literature (Roussel et al. 2012). It was shown that during the dormant period (i.e. constant rate of hydration heat), the volume of formed hydrates increases linearly with time, hence resulting in a linear increase of $G'$ after the percolation period. After the dormant period,
the hydration rate accelerates and a non-linear rigidification is observed for cement suspension tested after 110 minutes of age (Figure 4.4).

In summary, it can be stated that the percolation time ($t_{\text{perc.}}$) can represent the time needed to build-up a percolated elastic network and allow transition from liquid to solid. Furthermore, test results showed that $t_{\text{perc.}}$ is not affected by the degree of hydration. This suggests that $t_{\text{perc.}}$ can be used to describe the solely physical structural changes. On the other hand, the rigidification rate ($G_{\text{rigid.}}$) expresses the stiffening process of formed structure at rest during the dormant period. For a given colloidal network, this rigidification rate can define the contribution of chemical hydration of cement paste on its build-up at rest. Therefore, $t_{\text{perc.}}$ and $G_{\text{rigid.}}$ can be used together to describe the complex kinetics of build-up of cement suspensions.

### 4.5.3 Build-up of cement suspensions

Build-up of various cement mixtures was evaluated using $t_{\text{perc.}}$ and $G_{\text{rigid.}}$ as well as $A_{\text{thix.}}$ index. The $A_{\text{thix.}}$ index has been widely used to quantify build-up of cement-based materials (Khayat and Omran 2011; Khayat et al. 2012a; Khayat et al. 2012b; Mahaut et al. 2008; Omran et al. 2011; Perrot et al. 2009; Roussel 2006; Roussel and Cussigh 2008). The investigated cement mixtures were proportioned using various $w/c$, different dosages of HRWR, and two different replacement percentages of SF to cover a wide range of build-up kinetics (Table 4.4). For each mixture, the evolution of static yield after 5, 10, 15, and 20 minutes of rest after the initial pre-shearing was evaluated and the slope of this curve was referred to $A_{\text{thix.}}$ (Figure 4.5 and Table 4.4).
1. As can be observed, the decrease in \( w/c \) from 0.45 to 0.40, and 0.35 resulted in increasing both static yield stress and \( A_{thix} \) values. This can be attributed to the increase in cement fraction and the decrease in inter-particle distances, which can promote the flocculation and formation of internal network. For a fixed \( w/c \) of 0.40, the partial replacement of cement by 2% and 4% SF resulted in higher static yield stresses and \( A_{thix} \) due to the higher nucleation effect of SF and lower inter-particle distances (Aïtcin 2007). The incorporation of HRWR at dosages corresponding to 50% and 100% of the optimum dosage resulted in reducing the static yield stress values of 0.35 \( w/c \) suspension, but surprisingly without a significant effect on \( A_{thix} \) of mixtures containing 0% and 50% HRWR. This may give an indication that these two mixtures have similar build-up behaviours. Similar results were also reported in literature, where mixtures with different mix designs resulted in comparable \( A_{thix} \). (Abd El Megid 2012; Billberg 2006).

2. Furthermore, despite the fact that 0.35 \( w/c \) mixture proportioned with 50% HRWR showed higher \( A_{thix} \) than that of 0.45 \( w/c \) mixture made without HRWR, it exhibited lower static yield stress at rest after 5 and 10 minutes. These observations suggest that the use of \( A_{thix} \) individually may not properly describe the structural build-up of cement suspensions. In order to overcome this weakness, the initial static yield stress should be taken into account. Therefore, a modified \( A_{thix} \) index calculated as the product of \( A_{thix} \) and the static yield stress determined after 5 minutes of rest was proposed (Abd El Megid 2012; Khayat et al. 2012b). As can be observed in Table 4.4, the use of modified \( A_{thix} \) index resulted in different classification of mixtures based on their
degrees of build-up. For example, the 0.45 w/c mixture (0.45, 0%, 0%) is more thixotropic than 0.35 w/c mixture made with 50% HRWR (0.35, 50%, 0%), which is opposite to the classification based on $A_{\text{thix.}}$ index. It is worthy to mention that the apparent yield stress measured after 20 minutes of rest ($\tau_{0\text{rest@20min}}$) can also be used to quantify structural build-up. This index takes into account both the initial static yield stress value and its growth rate ($A_{\text{thix.}}$). The measured $\tau_{0\text{rest@20min}}$ values are summarized in Table 4.4. As can be observed, this index resulted in a new build-up ranking of the investigated cement mixtures.

Table 4.4 - Build-up indices of various cement suspensions

<table>
<thead>
<tr>
<th>(W/C, HRWR, SF)</th>
<th>$A_{\text{thix.}}$</th>
<th>Modified $A_{\text{thix.}}$</th>
<th>$\tau_{0\text{rest@20min}}$</th>
<th>$G_{\text{rigid.}}$</th>
<th>tperc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0.45, 0%, 0%)</td>
<td>0.0097</td>
<td>0.064</td>
<td>15.5</td>
<td>29.33</td>
<td>15</td>
</tr>
<tr>
<td>(0.40, 0%, 0%)</td>
<td>0.0141</td>
<td>0.117</td>
<td>20.9</td>
<td>39.83</td>
<td>10</td>
</tr>
<tr>
<td>(0.35, 0%, 0%)</td>
<td>0.0193</td>
<td>0.233</td>
<td>29.6</td>
<td>61.98</td>
<td>8</td>
</tr>
<tr>
<td>(0.35, 50%, 0%)</td>
<td>0.0168</td>
<td>0.051</td>
<td>18.2</td>
<td>10.29</td>
<td>1</td>
</tr>
<tr>
<td>(0.35, 100%, 0%)</td>
<td>0.0011</td>
<td>0.001</td>
<td>2.0</td>
<td>0.79</td>
<td>1</td>
</tr>
<tr>
<td>(0.40, 0%, 2%)</td>
<td>0.0275</td>
<td>0.336</td>
<td>37.5</td>
<td>84.13</td>
<td>6</td>
</tr>
<tr>
<td>(0.40, 0%, 4%)</td>
<td>0.0468</td>
<td>0.847</td>
<td>60.7</td>
<td>177.67</td>
<td>4</td>
</tr>
</tbody>
</table>

The evolutions of $G'$ and $\delta$ during 20 minutes of rest presented in Figure 4.6 were used to determine tperc. and $G_{\text{rigid.}}$ for the various cement mixtures (Table 4.4). As expected, the decrease in w/c resulted in higher $G'$ (i.e. higher rigidity) and faster formation of the colloidal network (i.e. lower tperc.). This is due to the higher number of contact points and the lower inter-particle distances. Furthermore, the partial replacement of cement by 2% and 4% SF resulted in lower tperc. and higher $G_{\text{rigid.}}$. The mixtures containing HRWR showed a faster formation of the elastic network (tperc. of 1 minute) despite of their low rigidification rates ($G_{\text{rigid.}}$). This may be related to the enhanced particle-particle correlation lengths resulting from the dispersing action of HRWR (Mikanovic and Jolicoeur 2008). This is in good agreement with strain sweep measurements presented in Figure 4.2 where mixture proportioned with HRWR showed relatively high critical shear strain, reflecting high ductility of the network. Indeed, 0.35 w/c mixture containing 100% HRWR was able to sustain a shear strain up to 0.2% before breaking down compared to 0.0025% obtained with mixture made without HRWR. Mixture with such high critical strain is considered as a stable dispersion (Goodwin 1990; Mikanovic et al. 2006).
Figure 4.6 - Time sweep measurements at shear strain of 0.001% and angular frequency of 10 rad/s for various cement mixtures. Evolutions of (a) storage modulus; (b) phase angle as a function of rest time

In sterically stabilized suspensions, such as those proportioned with 0.35 w/c and containing HRWR, cement particles can be considered as hard spheres characterized by an effective radius larger than their true radius by an amount corresponding to the characteristic range of the induced repulsion (Mewis and Wagner 2012). For such systems, the observed solid-like state can be attributed to a structural arrest of particles. In this case, each hard sphere is surrounded by neighbouring particles that are not necessarily in direct contact (i.e. caged), but not allowing it to diffuse away beyond its position (Sciortino 2002). On the other hand, the presence of short-
range inter-particle attractive interactions allow the particles to stick together and shrink the size of confining cage. This can result in empty regions where small Brownian particles can diffuse; hence less-glassy state can form. On the other hand, deep short-range attraction can again result in structural arrest, but in this case due to clustering formation caused by the physical bonding between particles (Mewis and Wagner 2012; Poon 2002; Sciortino 2002).

The glassy dispersed network configuration achieved using HRWR was verified using scanning electron microscopy (SEM). Cement mixtures with w/c of 0.35 and containing 0% and 100% HRWR were imaged inside sealed capsules at age of 30 minutes using a technique similar to that employed to follow up the early hydration of cement paste (Katz et al. 2007; Venkiteela and Sun 2010). As can be observed in Figure 4.7-a, in the case of cement suspension proportioned with 100% HRWR, particles showed uniform distribution at rest similar to the theoretical initial dispersed state. This caging situation can explain the short rest time needed for the particles to reach their equilibrium positions (i.e. small $t_{perc}$). In this case, dispersed particles need to undergo small displacements to reach their equilibrium positions. On the other hand, the formed structure in the case of flocculated mixture (i.e. without HRWR, Figure 4.7-b) consisted of irregular arrangement of interconnected agglomerates. Particles may necessitate longer rest time to reach their final positions, hence resulting in longer $t_{perc}$. Furthermore, the SEM images confirmed the enhanced particle-particle lengths in the presence of HRWR compared to the flocculated mixture, reflecting higher strain needed to breakdown the formed structure. These findings suggest that the addition of HRWR can result in two different effects. First, HRWR is adsorbed on cement particles to disperse them, hence increasing the rigidification distances and decreasing the nucleation rate (Artioli et al. 2015; Bentz et al. 1999; Gu et al. 1994), reflected by decreasing $G_{rigid}$. On the other hand, the presence of HRWR enhances the formation of elastic network able to deform and store energy under low stresses. It should be emphasized that faster formation of elastic-glassy network implies achieving a more rapid connectivity within the formed network with rest time, which is necessary, but not sufficient to provide stress-bearing capacity. Indeed, the stress-bearing capacity is related to the physical and chemical bonds generated within the structure. These findings suggest that faster rate of internal network formation does not necessarily means higher rigidity of formed network.
Based on these observations, it seems that the use of rigidification rate ($G_{\text{rigid}}$) alone as one-dimensional index to express the structural build-up behaviour of cement suspensions may not be sufficient. The combination of $t_{\text{perc}}$ and $G_{\text{rigid}}$ can allow proper quantification and deeper understanding of the build-up behaviour of cement suspensions at rest.

Figure 4.7 - SEM of 0.35 $w/c$ cement suspensions after 30 minutes of age. (a) 100% HRWR; (b) 0% HRWR

4.5.4 Build-up vs. lateral pressure

Structural build-up of fresh cement-based materials has a significant effect on the lateral pressure exerted on formwork. The use of mixtures with higher build-up can result in lower
The usefulness of $t_{\text{perc.}}$ and $G_{\text{rigid.}}$ in quantifying the structural build-up and consequently predicting lateral pressure was evaluated. Various cement mixtures were prepared and used to cast a column having 1 m in height and $10 \times 10$ cm$^2$ in cross-section. The pressure column is equipped with a Honeywell pressure sensor located at 15 cm from the base. The pressure sensor has a diameter of 20 mm and was perfectly flushed with the inner side of the column. The mixtures were cast from top of the column at a constant casting rate of 1 m/min. The lateral pressure measurements were started 20 minutes after the initial contact between cement and water and continued till the pressure cancellation. The variation of lateral pressure with time after casting is shown in Figure 4.8.

![Figure 4.8 - Variation of lateral pressure with time for various cement mixtures](image_url)

For all investigated mixtures, the initial lateral pressure remained almost constant during a certain period before starting to decay. Based on this general trend, two characteristic times can be identified, namely time to reach 50% of the initial pressure and time to pressure cancellation. The variations of these characteristic times with $A_{\text{shix.}}$, modified $A_{\text{shix.}}$ and $t_{0\text{rest}@20\text{min}}$ are shown in Figure 4.9.
Figure 4.9 - Variations of characteristic times of lateral pressure and (a) $A_{thix}$; (b) Modified $A_{thix}$; (c) $\tau_{0rest@20\text{min}}$
As expected, mixtures exhibiting low build-up, such as that containing 100% HRWR (0.35, 100%, 0%), resulted in longer characteristic times. Indeed, the initial pressure decreased by 50% (17.3 KPa) after 250 minutes and reached zero pressure 295 minutes after casting. On the other hand, highly thixotropic mixtures, such as the 0.4 w/c mixture containing 4% SF (0.40, 0%, 4%), resulted in shorter characteristic times (90 minutes vs. 250 minutes and 180 minutes vs. 295 minutes). However, the use of $A_{\text{thix}}$ or modified $A_{\text{thix}}$ resulted in inconsistent trend for some other mixtures (Figures 4.9-a and 4.9-b). For example, the 0.35 w/c mixture containing 50% HRWR exhibited higher $A_{\text{thix}}$ than 0.4 w/c mixture, but showed longer characteristic times. Similarly, the 0.35 w/c mixture containing 50% HRWR showed lower characteristic times compared to 0.45 w/c mixture despite its lower modified $A_{\text{thix}}$. On the other hand, the variations of characteristic times showed good correlations with $\tau_{\text{rest@20min}}$. In summary, these observations show that although $A_{\text{thix}}$ or modified $A_{\text{thix}}$ can achieve an acceptable correlation with the decay in lateral pressure at rest, they may yield inaccurate estimates for some mixtures, hence resulting in some inconsistent trends. However, the apparent static yield stress after 20 minutes of rest seems to provide better correlations with the variation in lateral pressure.

The proposed indices $G_{\text{rigid}}$ and $t_{\text{perc}}$ were used to quantify build-up of cement suspensions. As the build-up is directly proportional to $G_{\text{rigid}}$ and inversely proportional to $t_{\text{perc}}$, a combined index defined by $G_{\text{rigid}}/t_{\text{perc}}^{1/2}$ was proposed and correlated with the measured characteristic times (i.e. time at half and zero pressure) as shown in Figure 4.10. As can be observed, mixtures with higher ($G_{\text{rigid}}/t_{\text{perc}}^{1/2}$) resulted in lower characteristic times of lateral pressure. Furthermore, obtained variations showed a more consistent trend for the covered build-up range compared with $A_{\text{thix}}$ and modified $A_{\text{thix}}$ (Figure 4.9-a and Figure 4.9-b). Indeed, the previously misrepresented thixotropic mixtures including (0.35, 50%, 0%), (0.40, 0%, 0%), and (0.45, 0%, 0%) showed better fitting with measured characteristic times of lateral pressure. This can stand as an indication of the pertinence of using $G_{\text{rigid}}$ and $t_{\text{perc}}$ in describing the kinetics of build-up of cement suspensions at rest.
Figure 4.10 - Variations of characteristic times of lateral pressure with \((G_{\text{rigid}}/t_{\text{perc.}})^{1/2}\) for various cement mixtures

### 4.6 Conclusions

New indices to properly describe and quantify build-up of cement suspensions are proposed. Based on the obtained results, the following conclusions can be pointed out:

1. Time sweep measurements can be used to monitor the evolution of both storage modulus \((G')\) and phase angle \((\delta)\) and quantify the structuration of cement suspensions at rest.

2. The evolution of phase angle \((\delta)\) is not affected by the degree of hydration. It can be used to describe the rate of formation of internal percolated elastic network reflecting the physical structural changes at rest. The time needed to form the colloidal percolated network where the phase angle reaches its lowest and steady value is referred to the percolation time \((t_{\text{perc.}})\).

3. The evolution of storage modulus \((G')\) at rest can represent the increase in stress-bearing capacity of formed colloidal structure. Its linear increase at rest within the dormant period describes the chemical rigidification rate of formed network \((G_{\text{rigid}})\).

4. Unlike the commonly used indices to quantify build-up, the percolation time \((t_{\text{perc.}})\) and rigidification rate \((G_{\text{rigid}})\) can be used in combination to describe the physical and chemical structurations of cement suspensions.
5. The $t_{\text{perc.}}$ and $G_{\text{rigid.}}$ indices are proved to be efficient and sensitive to quantify the structural build-up of cement suspensions proportioned with various water-to-cement ratios, superplasticizer dosages, and silica fume replacement contents.

6. A combined index of build-up ($G_{\text{rigid.}}/t_{\text{perc.}}^{1/2}$) is proposed. This index showed a good correlation with the lateral pressure behaviour of various cement suspensions.

7. The apparent yield stress measured after 20 minutes of rest showed better correlations with lateral pressure decay compared with $A_{\text{thix.}}$ and modified $A_{\text{thix.}}$.

4.7 References


CHAPTER 5 : PHYSICO-CHEMICAL KINETICS OF STRUCTURAL BUILD-UP OF NEAT CEMENT-BASED SUSPENSIONS

Foreword

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Journal Title: Elsevier – Cement and Concrete Research

5.1 Abstract

The rate of structural build-up of cement-based suspensions at rest is a result of combined physical and chemical structuration processes. These processes are strongly dependent on the mixture parameters. The non-destructive dynamic rheometry was used to investigate the influence of cement fineness and content, alkali sulfate content, and temperature of the suspension on the percolation time and rigidification rate of neat cement suspensions. Zeta potential, calorimetric, and spectrometric measurements were performed to explore the corresponding microstructural changes in cement suspension, such as inter-particle cohesion, rate of Brownian flocculation, and nucleation rate. Test results showed that the percolation time is controlled by the frequency of Brownian collisions, the distance between dispersed particles, and intensity of cohesion between cement particles. On the other hand, a high rigidification rate can be secured by increasing the number of contact points per unit volume of paste, nucleation rate of cement hydrates, and intensity of inter-particle cohesion. A semi-empirical model correlating the build-up indices and the microstructural characteristics was developed and validated.

Keywords: Brownian collisions, Cement suspension, Cohesion, Nucleation intensity, Percolation time, Rigidification rate, Structural build-up.


5.2 Introduction

The build-up of cement suspensions is a time-dependent phenomenon reflecting the growth rate of apparent rheological properties, such as static yield stress, zero-shear rate viscosity, and storage modulus with time (Barnes 1997; Mewis and Wagner 2009). The degree of structural build-up is a key property that affects the macroscopic behavior of cement-based materials after casting (Abd El Megid 2012; Assaad 2004; Khayat et al. 2002; Omran 2009; Roussel and Cussigh 2008; Wang et al. 2011). Indeed, in the case of casting tall wall elements, it is preferred to use concrete with high kinetics of structural build-up to reduce the lateral pressure exerted on the formwork and allow faster pressure decay after casting (Assaad 2004; Billberg 2006; Khayat and Omran 2011). Furthermore, in the case of a layer by layer construction in the 3D-printing of cement-based materials, it is crucial to optimize the degree of structural build-up to ensure successful casting. In fact, high kinetics of build-up can affect the bond between cast layers within the printed structure (Roussel and Cussigh 2008). Meanwhile, an adequate structuration rate is required to allow gaining a sufficient strength level capable of sustaining the weight of subsequently extruded layers (Perrot et al. 2016).

The structural build-up of cement suspensions is a complex phenomenon associated to the combined effect of both physical structuration due to inter-particles colloidal interactions and chemical rigidification resulting from cement hydration (Roussel 2012). When a cement suspension is allowed to rest after shearing, cement particles flocculate and form a three-dimensional structure due to the induced van der Waals and electrostatic forces (Flatt 2004a; Roussel et al. 2010). The change in size of cement clusters of concentrated cement suspensions has been recently monitored using a laser backscattering technique. It has been confirmed that the kinetics of aggregation are highly influenced by shear history, paste ingredients, and rate of shear strain (Ferron et al. 2013; Yim et al. 2013). In addition to the aggregation of cement flocs at rest, an additional time-dependent process occurs due to nucleation of cement hydrates (Garrault-Gauffinet and Nonat 1999; Jiang et al. 1995; Roussel et al. 2012). Through this process, the nucleated C-S-H at the pseudo contact points between cement particles can rigidify the formed network, leading to increasing the stress-bearing capacity of formed structure.
The kinetics of build-up of cement-based suspensions is affected by several mixture parameters, including mixture composition, characteristics of its constituents, temperature of suspension, and shear history. For example, it was reported that neat cement pastes proportioned with a water-to-cement ratio (w/c) of 0.36 is more thixotropic than those made with a w/c of 0.42 (Papo 1988). Furthermore, a significant effect of w/c on the variations in lateral pressure and thixotropy of self-consolidating concrete (SCC) mixtures proportioned with a similar initial slump flow was observed (Khayat and Assaad 2006). It was shown that 0.46 w/c mixtures exhibited greater initial lateral pressure and lower thixotropy compared with those proportioned with w/c of 0.40 and 0.36. Additionally, for a given w/c, the increase in binder content from 400 to 550 kg/m³ resulted in a higher degree of restructuration of concrete equivalent-mortar (CEM) mixtures (Assaad and Khayat 2004).

The change in binder type was also reported to affect the time-dependent behavior, where CEM and SCC mixtures prepared with Type 30 CSA cement exhibited higher thixotropy than those prepared with binary or ternary cement (Assaad and Khayat 2004). Additionally, some studies have reported the change in both rheological and thixotropic properties of cement mixtures with the change in cement properties, such as specific surface area, C₃A and alkalis contents (Banfill 2006; Gołaszewski 2008; Grzeszczyk and Kucharska 1988; Lapasin et al. 1979). For example, the increase in specific surface area of cement has shown to increase the energy needed to breakdown structure of cement pastes (Lapasin et al. 1979). On the other hand, the effect of alkalis content has shown to depend on the reactivity of clinker in cement pastes. Higher alkalis content was found to change the shape of hysteresis loops of clinker suspensions from thixotropic into anti-thixotropic, but did not alter the hysteresis loop in the case of cement suspensions (Grzeszczyk and Kucharska 1988). Besides, many studies have reported the considerable influence of type and dosage of various chemical and mineral admixtures on the level and rate of structural build-up and consequently on the lateral pressure of cementitious systems (Assaad et al. 2003; Assaad and Khayat 2006; Bouras et al. 2008; Khayat and Assaad 2006; Quanji et al. 2014; Saleh Ahari et al. 2015).

The structural build-up of cementitious systems has been shown to be temperature dependent (Nehdi and Al Martini 2007; Petit et al. 2006; Vanhove et al. 2013). Indeed, a nonlinear increase in static yield stress and storage modulus values was observed when the temperature of cement
paste varied between of 20 and 45°C (Nehdi and Al Martini 2007). The coupled effect of time and temperature on the variations of yield stress for mortar mixtures extracted from SCC is shown to be greatly affected by the type and dosage of HRWR (Petit et al. 2006).

Although various studies have been conducted on the build-up of cement-based suspensions and its variation with the change in mixture’s composition and casting conditions, there is limited data regarding the effect of mixture parameters on the physical and chemical kinetics of structural build-up. The objective of this study is to evaluate the effect of w/c, cement fineness, alkali sulfate content, and temperature of the mixture on physical and chemical components of structuration at rest. The non-destructive dynamic rheometry was used to monitor the evolutions of viscoelastic properties of cement suspensions, including storage modulus (G’) and phase angle (δ). Two independent indices of build-up describing the rest time needed to form the structural colloidal network and its chemical rigidification rate were used to quantify build-up (Mostafa and Yahia 2016). The corresponding microstructural changes, including inter-particle cohesion, Brownian interactions, and nucleation intensity were evaluated and discussed. Furthermore, a model that can predict the build-up indices knowing the microstructural characteristics of fresh cement pastes was proposed.

### 5.3 Research significance

The present study provides quantitative data on the physical and chemical kinetics of structuration of neat cement suspensions at rest and their variations with the mixture parameters, such as w/c, fineness of cement, alkali sulfate content, and temperature of the suspension. The provided data can contribute in enhancing the fundamental knowledge related to the kinetics of structural build-up of cement-based suspensions. This can lead to better understanding and adequate control of the degree of structural build-up of cement-based materials at rest given the application on hand.
5.4 Experimental program

5.4.1 Materials, mixture proportions, and mixing sequence

Cement paste mixtures investigated in this study were systematically proportioned using General Use (GU) and Low Alkali (LA) cements complying with ASTM C150M. The chemical characteristics of used cements are summarized in Table 5.1. In addition, the GU cement was ground in a Hosokawa Alpine 100 AFG jet mill to produce various GU cements with different fineness values. The grinding levels were varied by controlling the grinding speeds at 4000 rpm, 8000 rpm, and 12000 rpm while keeping a constant feeding rate. The produced ground GU cements will be referred to as GU-4000, GU-8000, and GU-12000. The particle size distributions (PSDs) of GU and LA cements are summarized in Figure 5.1. On the other hand, the Blaine and BET surface areas, as well as particles distribution characteristics, are presented in Table 5.2.

Table 5.1 - Chemical characteristics of used GU and LA cements

<table>
<thead>
<tr>
<th>Composition (%)</th>
<th>GU</th>
<th>LA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>63.73</td>
<td>65.15</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19.89</td>
<td>19.81</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3.54</td>
<td>3.41</td>
</tr>
<tr>
<td>SO₃</td>
<td>3.79</td>
<td>3.21</td>
</tr>
<tr>
<td>Fe₂O₃</td>
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</tr>
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</tr>
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<td>Na₂O</td>
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</tr>
<tr>
<td>K₂O</td>
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<td>0.50</td>
</tr>
<tr>
<td>Na₂Oₑq</td>
<td>0.71</td>
<td>0.46</td>
</tr>
</tbody>
</table>
In order to identify and capture the microstructural parameters governing the kinetics of structural build-up of neat cement suspensions, four different groups of cement mixtures were prepared (Table 5.3). The first group of mixtures was proportioned to evaluate the effect of solid concentration on the kinetics of build-up. Various mixtures were made using a GU cement and different water-to-cement ratios (w/c) varying from 0.35 to 0.55. These mixtures were tested at a constant temperature of 23°C. In the second group, the effect of cement fineness was evaluated. The mixtures were made with various ground GU cements and three different w/c of 0.45, 0.50, and 0.55. The investigated mixtures had a constant temperature of 23°C. On the other hand, the third group consisted in evaluating the effect of temperature of the suspension on the kinetics of build-up of 0.40 w/c mixtures. Different temperature values of 3, 13, 23, and 33°C were evaluated. The mixtures investigated in the fourth group aimed to evaluate the effect of
different additions of alkali sulfate (Na$_2$SO$_4$), by mass of cement, on the kinetics of build-up of 0.35 w/c cement suspensions made with LA cement.

Table 5.3 - The mixture parameters of investigated cement pastes

<table>
<thead>
<tr>
<th>Parameters</th>
<th>w/c</th>
<th>Cement type</th>
<th>Temperature</th>
<th>Added Na$_2$SO$_4$, by weight of cement</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Solid content</td>
<td>0.35, 0.40, 0.45, 0.50, 0.55</td>
<td>GU-original</td>
<td>23°C</td>
<td>0%</td>
</tr>
<tr>
<td>2. Fineness of cement</td>
<td>0.45, 0.50, 0.55</td>
<td>GU-original, GU-4000, GU-8000, GU-12000</td>
<td>23°C</td>
<td>0%</td>
</tr>
<tr>
<td>3. Temperature of suspension</td>
<td>0.40</td>
<td>GU-original</td>
<td>3, 13, 23, 33°C</td>
<td>0%</td>
</tr>
<tr>
<td>4. Alkali sulfate content</td>
<td>0.35</td>
<td>LA</td>
<td>23°C</td>
<td>0%, 2.1%, 4.2%</td>
</tr>
</tbody>
</table>

All the investigated cement mixtures were mixed using a high-shear mixer according to the procedure described in ASTM C1738M. The temperature of mixing water was controlled to compensate for heat generation during mixing. Following the end of mixing, all mixtures had the targeted temperature with a precision of ± 2°C. The mixing sequence consisted in introducing the binder gradually over 1 minute while the mixer is turned on. After a rest period of 150 seconds, the mixing was presumed for a total mixing time of 4 minutes and 30 seconds. Immediately after mixing, the sample was conserved in a sealed container to prevent water evaporation. The rheometric measurements were determined after 20 minutes from the first contact between water and cement. This was selected to allow performing measurements after the occurrence of early hydration reactions.

### 5.4.2 Test methods

All the performed rheometric measurements were conducted using a coaxial cylinder rheometer (MCR 302) with serrated surfaces. The diameters of cup and bob cylinders are 28.911 and 26.660 mm, respectively, providing a shear gap size of 1.126 mm. The effective height of tested sample is 40 mm. The test procedure consisted in pre-shearing the sample at 20 s$^{-1}$ for 30 seconds to ensure a homogeneous distribution of the sample in the rheometer’s shear gap (Mezger 2011).
The sample was allowed a rest period of 1 minute to ensure temperature equilibrium before carrying out the build-up measurements.

The structural build-up was determined after subjecting the sample to a disruptive shear interval to ensure an initial dispersed state. The disruptive shear consisted in applying a rotational shear followed by a large amplitude oscillatory shear (LAOS) at a high frequency of 100 rad/s. This combination was shown to provide a good dispersing performance (Mostafa and Yahia 2015). The disruptive interval used in this study consisted of applying a rotational shear rate of 200 s\(^{-1}\) for 90 seconds, followed by LAOS at a shear strain of 6\% and an angular frequency of 100 rad/s for 10 seconds.

Immediately after the disruptive regime, build-up measurements were performed during 45 minutes. The test procedure consisted of applying a small-amplitude oscillatory shear (SAOS) at a constant angular frequency of 10 rad/s and a shear strain value within the linear viscoelastic domain (LVED). This allowed monitoring the evolution of both storage (\(G'\)) and loss (\(G''\)) moduli with rest time in a non-destructive regime. The LVED was identified using strain sweep test in which the sample is subjected to an increasing shear strain from 0.0001\% to 20\% at a constant angular frequency of 10 rad/s.

The measurements of zeta potentials (\(\xi\)), conductivities, and pH of cement suspensions were performed using a Probe Analyser from Colloidal Dynamics. Diluted suspensions were prepared at a solid concentration of 30\% and used to carry out the measurements. The prepared suspensions were continuously stirred for 20 minutes after mixing. Then, the electro-kinetic measurements were performed for an additional 20 minutes (i.e. an age of 40 minutes).

The concentration of dissolved ions, such as Ca\(^{2+}\), K\(^{+}\), Na\(^{+}\), and SO\(_4\)^{2-}, in the pore solution of cement suspensions were measured using an ICP spectrophotometer. The pore solutions were extracted from the suspensions at an age of 30 minutes (i.e. during the build-up measurements) by centrifugation for 5 minutes. Immediately after extraction, the obtained pore solutions were diluted to 1:2500 with 2\% nitric acid. Each sample was analyzed two times to verify the reproducibly of the measured ionic concentrations. Additionally, the pH and conductivity values of the extracted pore solutions were determined.
The heat flow due to hydration of cement was monitored using an isothermal TAM Air calorimetry. The testing protocol consisted in lowering a glass ampoule containing an estimated amount of cement powder into the measuring position inside the calorimeter. After reaching the steady state, given the w/c of the mixture, the corresponding amount of mixing water was injected into the ampoule. The mixing was performed using an internal stirring mechanism for 40 seconds. The heat of hydration was recorded per gram of paste during 24 hours after mixing.

5.5 Results and discussions

5.5.1 Structural build-up measurements

5.5.1.1 LVED and critical strain

The variation of storage ($G'$) and loss ($G''$) moduli determined from strain sweep measurements for selected mixtures are shown in Figure 5.2.

![Figure 5.2 - Variations of shear moduli with shear strain at an angular frequency of 10 rad/s (mixtures are identified by their w/c, temperature, cement type)]
As can be observed, below a critical strain of 0.0025%, all mixtures exhibited a linear viscoelastic domain (LVED) characterized by a constant storage (G’) and loss (G’”) moduli. At shear strain values lower than the critical strain, the suspension can recover elastically and acts as a solid structure (i.e. undisturbed) (Mezger 2011). However, the increase in shear strain beyond the critical value resulted in decreasing the shear moduli, reflecting the destruction of the network due to the breakage of C-S-H bridges between cement particles (Roussel et al. 2012). Based on these results, a shear strain of 0.001% (lower than 0.0025%) was selected to perform the time sweep measurements in a non-destructive manner.

5.5.1.2 Physico-chemical structuration

The structural build-up of various cement mixtures (Table 5.3) was determined by monitoring the evolutions of storage modulus (G’) and phase angle (δ) during 45 minutes of rest. The phase angle (δ) calculated as tan⁻¹(G”/G’) can vary between 0° and 90°. The value of 0° corresponds to a perfect solid state (i.e. elastic), reflecting a no-delay between induced oscillatory strain and measured stress response. However, the value of 90° corresponds to a perfectly viscous structure (Mezger 2011).

The evolutions of G’ and δ at rest for various w/c ranging between 0.35 and 0.55 are shown in Figure 5.3. As can be observed, immediately after disruption, the investigated mixtures exhibited almost zero G’ and a value of δ higher than 45°, reflecting their negligible rigidity and a liquid-like state of the suspension, respectively. An increase in G’ was observed with rest time, indicating an increase in the rigidity of formed network. Simultaneously, the phase angle (δ) decreased until reaching a steady state. This behaviour reflects a transition from the liquid-like state to a solid-like state. As reported in a previous study, the evolution of angle δ may not be affected by the degree of hydration. As a consequence, its evolution can be used to describe the physical structuration at rest. Test results showed that the decrease in w/c from 0.55 to 0.35 resulted in a higher rate of decay in δ at rest, reflecting a faster formation of the elastic percolated network. The decrease in w/c resulted also in a higher rate of evolution of G’, hence reflecting a higher rate of gaining rigidity of formed network.
Figure 5.3 - Evolutions of a) Storage modulus and b) Phase angle at a shear strain of 0.001% and an angular frequency of 10 rad/s for cement mixtures proportioned with different \( \frac{w}{c} \)

Two independent indices can be determined to describe the kinetics of structural build-up of cement suspensions (Figure 5.3) (Mostafa and Yahia 2016). The first one is the percolation time \( t_{\text{perc.}} \), which represents the rest time needed to form the colloidal percolated network. This corresponds to the time required to reach the lowest and steady value of angle \( \delta \). The second index corresponds to the rigidification rate \( G_{\text{rigid.}} \), which describes the linear increase in \( G' \) after the formation of the percolated network. This expresses the growth of stress-bearing capacity of formed structure due to the chemical hydration of cement (Mostafa and Yahia 2016). The variations of \( t_{\text{perc.}} \) and \( G_{\text{rigid.}} \) indices with the change of \( \frac{w}{c} \) are presented in Figure 5.4.
As can be observed, the increase in \( w/c \) from 0.35 to 0.55 (i.e. less solid content) resulted in increasing \( t_{\text{perc.}} \) from 10 to 41 minutes and decreasing \( G_{\text{rigid.}} \) from 48 to 15 Pa/s.

In addition to the solid concentration, the variations of \( t_{\text{perc.}} \) and \( G_{\text{rigid.}} \) with the fineness of cement were also determined for different \( w/c \) of 0.45, 0.50, and 0.55 (Figure 5.5). As can be observed, the use of finer cement resulted in decreasing \( t_{\text{perc.}} \) and increasing \( G_{\text{rigid.}} \). For example, in the case of 0.55 \( w/c \) mixture, the use of GU-12000 (the highest fineness) allowed to form the elastic network in a very short time of 8 minutes compared to 41 minutes observed with GU-original cement. Additionally, the mixture prepared with GU-12000 resulted in a \( G_{\text{rigid.}} \) of 510 Pa/s, which is 35 times the \( G_{\text{rigid.}} \) value obtained with GU-original cement.

The variations of \( t_{\text{perc.}} \) and \( G_{\text{rigid.}} \) indices of 0.40 \( w/c \) mixture made with GU cement and tested at different temperatures of 3, 13, 23, and 33°C are summarized in Figure 5.6. The obtained results showed that the increase in temperature resulted in a higher kinetics of build-up. For example, for a temperature of 33°C, a short \( t_{\text{perc.}} \) of 9 minutes was obtained, compared to 13, 25 and 33 minutes obtained at 23, 13, and 3°C, respectively. In addition, for the highest temperature (33°C), a \( G_{\text{rigid.}} \) of 55 Pa/s was obtained compared to 16 Pa/s measured at the lowest temperature of 3°C.
Figure 5.5 - Variations of $G_{\text{rigid}}$ and $t_{\text{perc.}}$ indices for suspensions made with different $w/c$ and cement fineness values

Figure 5.6 - Variations of $G_{\text{rigid}}$ and $t_{\text{perc.}}$ indices with temperature

The variations of build-up indices ($t_{\text{perc.}}$ and $G_{\text{rigid}}$) of 0.35 $w/c$ mixtures made with LA cement and various percentages of Na$_2$SO$_4$ are shown in Figure 5.7. As can be observed, the additions of Na$_2$SO$_4$ led to a significant reduction in the rigidification of the network. For example, the
addition of 4.2% Na$_2$SO$_4$ resulted in lowering $G_{\text{rigid}}$ to 13% of its initial value, however, this addition resulted in increasing $t_{\text{perc}}$ from 8 to 28 minutes.

Figure 5.7 - Variations of $G_{\text{rigid}}$ and $t_{\text{perc}}$ indices with Na$_2$SO$_4$ percentage of LA cement suspensions

The obtained results highlighted the effect of cement content and fineness, alkali sulfate content, and temperature on the physical and chemical mechanisms of build-up of cement suspensions. In order to go a step further towards understating the dependency between build-up and mixture parameters, it will be interesting to correlate the observed variations of $t_{\text{perc}}$ and $G_{\text{rigid}}$ to the microstructural characteristics of cement suspension.

5.5.2 Physical consequences

Various forces govern the rheological and thixotropic behaviour of cement-based suspensions (Flatt 2004b). In the case of fresh cement pastes, where cement particles are in the colloidal range, the main forces dominating the structural build-up are the Brownian and surface forces, such as the electrostatic and van de Waals attractive forces (Flatt 2004b). The influence of varying the mixture parameters on the generated surface and Brownian interactions will be discussed in the following sections.
5.5.2.1 Surface interactions

As soon as cement particles are in contact with water, multivalent ions including cations (Ca^{2+}, K^+, Na^+) and anions (SO_4^{2-}, OH^-) dissolve in the pore solution. A few minutes after mixing, the solution becomes supersaturated and gives rise to the formation of ettringite-like compounds and precipitation of C-S-H at the surface of cement particles (Taylor 1997). At the same time, surface (inter-particle) forces are developed between cement particles allowing the formation of a colloidal network and modifying the kinetics of structural build-up of cement suspensions (Jiang et al. 1995; Roussel et al. 2012).

A) Mean field approach and DLVO theory

DLVO is the classic theory used to explain the interactions between charged particles in a liquid medium, hence their state of flocculation (Derjaguin and Landau 1941; Verwey and Overbeek 1948). This theory consists in a superposition of two opposing forces, the attractive van der Waals and the repulsive electrostatic forces. In the case of cement suspensions, the van der Waals attractive forces result from the summation of forces between individual molecules at the surface of cement particles (Flatt 2004a; Wallevik 2005). This attractive potential is effective at a short inter-particle distance and in the case of spherical particles, its value depends on both center-to-center distance between the particles and Hamaker constant (Flatt 2004a; Yang et al. 1997). The Hamaker constant depends on the optical properties of interacted particles and suspending medium (Flatt 2004a). The non-retarded value of Hamaker constant was estimated from AFM measurements for cement particles in water and found to be around 1.6 x 10^{-20} J (Flatt 2004a; Lomboy et al. 2011). On the other hand, the repulsive electrostatic force arises between similarly charged interfaces due to the pressure of the counter-ions cloud. The repulsive potential is maximum near the surface of particles and dramatically decreases with the separation distance until reaching zero value outside the charged atmosphere (i.e. electric double layer) (Hunter 2001). The repulsive potential is a function of both the thickness of the double layer (Debye length, $\kappa^{-1}$) and zeta potential ($\zeta$). The $\kappa^{-1}$ depends on the ionic strength and temperature of the bulk electrolyte, while $\zeta$ is a measure of the charge density at the shear plane (Ravina and Moramarco 1993). Indeed, increasing the number or valence of dissolved ions results in more counter-ions available to neutralize the charged cement particle, hence
comprising the double layer and minimizing the range of the repulsive potential. On the other hand, higher $\xi$ values mean higher charge density and higher repulsive potential (Flatt 2004b; Flatt and Bowen 2003; Ravina and Moramarco 1993; Yang et al. 1997). Therefore, one way to explore the changes in induced inter-particle interactions is to determine the variations of $\kappa^{-1}$ and $\xi$ for the investigated mixtures.

**Effect of mixture parameters on the electro-kinetic characteristics**

Zeta potential measurements were carried out on diluted cement suspensions proportioned with GU cement having various fineness levels and tested at different temperatures. Mixtures made with LA cement and different alkali sulfate percentages were also evaluated. The measured electro-kinetic parameters ($\xi$, $\kappa^{-1}$, pH, and conductivity) at an age of 30 minutes are presented in Figure 5.8 - Figure 5.10. As can be observed in Figure 5.8, the use of finer cement resulted in higher conductivity and pH values. This is due to the more dissolved ions stemming from the higher surface area of cement. The higher ionic strength can contribute in compressing the double layer, which results in decreasing $\kappa^{-1}$ (Figure 5.8-b). Moreover, the measured $\xi$ exhibited a positive sign, which is surprisingly opposite to the expected negative charge caused by the anionic SiO$_2^-$ groups of the formed C-S-H on cement surfaces (Jönsson et al. 2004; Lesko et al. 2001; Taylor 1997). In fact, this charge reversal is due to the accumulation of dissolved counter-ions, such as Ca$^{2+}$, and their physical adsorption on cement particles. The condensed Ca$^{2+}$ can, therefore, overcompensate the negative surface charge and leads to the appearance of apparently positive potential (Jönsson et al. 2004; Labbez et al. 2011; Nägele 1985). The use of cement with higher fineness can result in more calcium ions, thus more charge reversing and higher positive $\xi$ (Figure 5.8-b).

The measured electro-kinetic characteristics of suspensions tested at different temperatures revealed that suspensions with higher temperature showed higher pH and conductivity values (Figure 5.9). This is attributed to the higher dissolution kinetics that can take place at high temperature. The increase in dissolved ions and their compressing effect of the charged atmosphere was reflected by lower $\kappa^{-1}$ values. Furthermore, it is observed that the increase in temperature resulted in a slight increase in $\xi$ values. This can be related to the more accumulation of counter-ions on cement particles.
Figure 5.8 - Variations of electro-kinetic properties ($\zeta$, $\kappa^{-1}$, conductivity, and pH) with fineness of cement of suspensions (30% solid concentration)
Figure 5.9 - Variations of electro-kinetic properties (ξ, κ⁻¹, conductivity, and pH) with temperature of suspensions (30% solid concentration)

As can be observed in Figure 5.10, the increase in alkali sulfate did not result in a significant change in pH, but increased the conductivity (i.e. lower κ⁻¹ values). It is also observed that the addition of Na₂SO₄ decreased ξ which may be due to the lower apparent charge reversal (Labbez et al. 2006).
Figure 5.10 - Variations of electro-kinetic properties ($\xi$, $\kappa^{-1}$, conductivity, and pH) with percentage of Na$_2$SO$_4$, by mass of LA cement, of suspensions (30% solid concentration)

- **Comments on the changes in net inter-particle potential**

In the framework of DLVO theory and keeping in mind that the electrostatic repulsion energy is proportional to $\xi^2$, some assumptions can be deduced based on the results presented in Figure 5.8 - Figure 5.10. It seems that the use of finer cement or increasing temperature of the suspension does not result in decreasing the repulsive energy, hence it is not expected to increase
the inter-particle cohesion. On the other hand, the obtained results suggest that increasing the content of alkali sulfate can contribute in increasing the net attractive forces between cement particles (i.e. higher cohesion). However, this suggestion fails to explain, for example, the lower rigidity observed for cement mixtures incorporating various alkali sulfate contents (Figure 5.7). Moreover, it is worthy to note that the observed range of variations in both $\xi$ and $\kappa^{-1}$ values would result in a limited effect in changing the net interaction energy. Indeed, the change in properties of cement suspensions led to non-significant variations of $\xi$ between 4.01 and 1.65 mV and $\kappa^{-1}$ between 1.41 and 0.77 nm. It is well established that colloidal suspensions exhibiting a $\xi$ value lower than 5 mV will normally experience a rapid flocculation due to the relatively higher attractive van der Waals forces (Ravina and Moramarco 1993; Yang et al. 1997).

Although the concept of the mean field double layer model was applied to investigate the flocculation in cement suspensions (Nägele 1985; Nägele 1986; Yang et al. 1997), it could not explain the observed reductions in the kinetics of build-up of cement suspensions containing high percentages of alkali sulfates. Indeed, the adequacy of the mean field double layer model for neat cement suspensions has been vigorously challenged in the recent years (Flatt and Bowen 2003; Guldbrand et al. 1984; Labbez et al. 2006; Lesko et al. 2001). In these suspensions, neglecting the ions correlations between interacting particles is a major limitation of the mean field approach. In fact, cement suspensions are characterized by high ionic concentration, multivalent counter-ions, and high surface charge densities. At very small separation distances of few nanometers, correlations between unsymmetrical distribution of the counter-ions between interacted surfaces (i.e. ion-ion correlations) can result in additional electrostatic attractive forces (Pellenq et al. 1997). In highly correlated cement suspensions, these attractive ion correlations were found to arise between accumulated divalent calcium ions at the negatively charged C-S-H surfaces (Jönsson et al. 2004; Plassard et al. 2005). Proper assessment and understanding of the changes in the inter-particle surface forces necessitate taking into account this additional attraction.

**B) Ionic correlations and cohesion between cement particles**

An appropriate way to evaluate the inter-particle potentials in cement suspensions was developed and applied (Jönsson et al. 2005; Jönsson et al. 2004; Labbez et al. 2006; Pellenq et
A Monte Carlo simulation was performed in a primitive model, where dissolved ions were considered as charged hard spheres and solvent as a dielectric continuum. The interactions between cement particles were replaced by interactions between C-S-H nanoparticles, which are the main nucleating products due to cement hydration (Nachbaur et al. 2001; Taylor 1997). This can help to correlate the origin of cement cohesion to the forces between precipitated C-S-H on the surface of cement grains. The simulation modeled the interactions between C-S-H nanoparticles using two infinite parallel planar walls with homogeneous charge density. This was justified by the fact that precipitated C-S-H is in the form of small sheets with typical dimensions of 60 nm x 30 nm x 5 nm, which are considerably large compared to the inter-particle separation distance (Garrault et al. 2005). The total inter-particle force was deduced from the net osmotic pressure alone, omitting the contribution of van der Waals forces, which are negligible between two infinite plates. The net osmotic pressure included three components: entropic, correlation, and hard-core pressures (Jönsson et al. 2005; Jönsson et al. 2004).

In order to identify the acting inter-particle force taking into account the ions correlations, a simple free-energy model developed as a complement to the Monte Carlo simulations will be used (Jönsson et al. 2005; Jönsson and Wennerström 2004). This model can capture the main physical features of the charging cloud and it has the advantage of predicting the proper response to changes in the valence of counter-ions, added salt, such as alkali sulfate, dielectric properties of the solvent, and surface charge density (Jönsson et al. 2005).

- **Determination of ionic concentrations and surface charges**

One main parameter that controls the adequacy of predictions of the model is the concentration of mono- and divalent counter-ions in the pore solution. The concentrations of main dissolved ions, such as Ca\(^{2+}\), Na\(^+\), K\(^+\), SO\(_4\)\(^{2-}\), and OH\(^-\), in the pore solutions extracted from the investigated cement pastes after 30 minutes of age are summarized in Table 5.4. Concentrations of other ions, such as Al\(^{3+}\), Fe\(^{2+}\), and Mg\(^{2+}\) were found to be negligible. As can be observed, the decrease in w/c from 0.55 to 0.35 resulted in more dissolved alkali and sulfate ions and a non-significant increase in Ca\(^{2+}\), which overall led to a higher conductivity. In addition, the pore solution extracted from 0.55 w/c mixture proportioned using GU-12000 cement showed higher concentrations of dissolved ions and higher conductivity compared to those obtained with GU-original cement. On the other hand, the increase in temperature of 0.40 w/c mixtures from 3 to
33°C resulted in a slight decrease in Ca\(^{2+}\) content, an increase in the concentrations of alkali and sulfate ions, and a limited increase in the conductivity. The addition of alkali sulfate (Na\(_2\)SO\(_4\)) up to 4.2 %, by mass of cement, significantly increased the conductivity, Na\(^{+}\) and SO\(_4^{2-}\) ions, but a minor increase in Ca\(^{2+}\) and almost constant K\(^{+}\). Moreover, the pH value was slightly increased from 13.027 to 13.276.

Table 5.4 - The chemical potentials of dissolved ions in the pore solutions extracted from cement mixtures at an age of 30 minutes

<table>
<thead>
<tr>
<th>Description of mixtures</th>
<th>Ca(^{2+}) (mmol/l)</th>
<th>Na(^{+}) (mmol/l)</th>
<th>K(^{+}) (mmol/l)</th>
<th>SO(_4^{2-}) (mmol/l)</th>
<th>OH(^{-}) (mmol/l)</th>
<th>pH</th>
<th>Conductivity (mS/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-original, T = 23°C w/c 0.35</td>
<td>17.31</td>
<td>81.64</td>
<td>377.25</td>
<td>156.25</td>
<td>117.76</td>
<td>13.071</td>
<td>117</td>
</tr>
<tr>
<td>w/c 0.45</td>
<td>16.57</td>
<td>55.16</td>
<td>316.52</td>
<td>78.13</td>
<td>106.17</td>
<td>13.026</td>
<td>101</td>
</tr>
<tr>
<td>w/c 0.55</td>
<td>16.42</td>
<td>27.16</td>
<td>226.35</td>
<td>52.08</td>
<td>84.14</td>
<td>12.925</td>
<td>78</td>
</tr>
<tr>
<td>w/c = 0.55, T = 23°C Cement fineness GU-original,</td>
<td>16.42</td>
<td>27.16</td>
<td>226.35</td>
<td>52.08</td>
<td>84.14</td>
<td>12.925</td>
<td>78</td>
</tr>
<tr>
<td></td>
<td>GU-12000</td>
<td>18.52</td>
<td>67.94</td>
<td>375.97</td>
<td>208.33</td>
<td>13.091</td>
<td>112</td>
</tr>
<tr>
<td>GU-original, w/c = 0.40 T (°C)</td>
<td>3</td>
<td>19.97</td>
<td>61.2</td>
<td>287.43</td>
<td>52.08</td>
<td>110.92</td>
<td>13.045</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>18.25</td>
<td>64.84</td>
<td>351.99</td>
<td>104.17</td>
<td>117.22</td>
<td>13.069</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>17.11</td>
<td>65.92</td>
<td>355.28</td>
<td>117.3</td>
<td>112.46</td>
<td>13.051</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>17.58</td>
<td>66.69</td>
<td>373.09</td>
<td>130.21</td>
<td>115.35</td>
<td>13.062</td>
</tr>
<tr>
<td>LA, w/c = 0.35, T = 23°C Added</td>
<td>0</td>
<td>20.15</td>
<td>67.45</td>
<td>281.68</td>
<td>78.13</td>
<td>110.41</td>
<td>13.027</td>
</tr>
<tr>
<td>Na(_2)SO(_4) (%)</td>
<td>2.1</td>
<td>20.66</td>
<td>934.41</td>
<td>281.04</td>
<td>338.54</td>
<td>148.59</td>
<td>13.172</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>22.17</td>
<td>1820.66</td>
<td>275.28</td>
<td>677.08</td>
<td>188.80</td>
<td>13.276</td>
</tr>
</tbody>
</table>

The surface charge density of interacting C-S-H is another parameter affecting the accuracy of the free-energy model. Higher surface charge density can diminish the repulsive entropic pressure (gas pressure), hence dominating the interactions by a stronger attractive ion correlations forces (Jönsson et al. 2004). The charging mechanism of C-S-H plates depends on their structure and the degree of ionization of the surface silanols (SiOH) (Labbez et al. 2011; Taylor 1997). The estimation of the actual ionization fraction is challenging as its value depends on the pH, the counter-ions distribution, and the valency of co-ions (Jönsson et al. 2005; Labbez et al. 2006; Labbez et al. 2011). For example, the surface charge density of C-S-H increases with pH and is approximately 0.8 C/m\(^2\) at pH of 14, corresponding to nearly a complete ionization (i.e. 100% of the sites are ionized). However, at lower pH of 12, the degree of ionization was found to be around 75% for C-S-H immersed in a bulk solution containing 20 mmol/l of Ca\(^{2+}\). Furthermore, for a given pH, major increases in the relative concentration of mono- to divalent counter-ions could lead to decreasing the degree of ionization, hence result in
a lower surface charge density. The surface charge density values that have been measured in similar charging conditions were considered in this study (Jönsson et al. 2005; Labbez et al. 2006; Labbez et al. 2011).

**Predicting the cohesion between C-S-H plates**

In the simplified free-energy model, the system is modeled as one mobile counter-ion of valence (Z) moving along the separation distance (h) between two fixed point charges, representing the charged surfaces of C-S-H. The force acting on the fixed charges can be determined from the derivative of the free energy of the system according to Equation 5-1 (Jönsson et al. 2005):

\[
F = \frac{\partial (A(h)/k_B T)}{\partial S_1} = -\frac{7}{4(S_1 + (1/\sqrt{2\pi S_2}))^2} + \frac{1}{S_1}
\]

where, \( A(h) \) is the free energy of the system, \( k_B \) is Boltzmann’s constant, and \( T \) is the absolute temperature. \( S_1 \) and \( S_2 \) are dimensionless parameters representing rescaled wall-wall separation distance and surface charge density, respectively. The values of \( S_1 \) and \( S_2 \) were estimated according to Equation 5-2 and Equation 5-3, respectively (Guldbrand et al. 1984):

\[
S_1 = \frac{h}{Z^2 l_B^2}
\]

Equation 5-2

\[
S_2 = \frac{Z^2 l_B^2 \sigma}{e}
\]

Equation 5-3

where, \( h \) is the separation distance between charged plates, \( Z \) is the counter-ion valency, and \( e \) is the elementary charge. The Bjerrum length \( (l_B) \) was calculated using Equation 5-4:

\[
l_B = \frac{e^2}{4\pi \varepsilon_r \varepsilon_0 k_B T}
\]

Equation 5-4

where, \( \varepsilon_r \) and \( \varepsilon_0 \) are the relative dielectric permittivity of the liquid continuum and the vacuum, respectively.
In the case of cement suspensions, the bulk solutions contain both mono- and divalent counter-ions. Therefore, the force was estimated for each valence and then combined using Equation 5-5:

\[ F = K_{mo}F_{mo} + K_{di}F_{di} \]  

Equation 5-5

where, \( F_{mo} \) and \( F_{di} \) are the forces due to the mono- and divalent counter-ions, respectively. On the other hand, \( K_{mo} \) and \( K_{di} \) are the probability of mono- and divalent counter-ions in the confined solution, respectively. \( K_{mo} \) and \( K_{di} \) were calculated based on the concentration of mono- and divalent counter-ions in the bulk solution and their resulting free-energy difference in the confined solution as described by Jönsson et al. (Jönsson et al. 2005).

The variations of the predicted interaction between the two fixed charges with the change in \( w/c \), cement fineness, temperature, and the alkali sulfate percentages are shown in Figure 5.11. As can be observed, the model predicts a net attractive electrostatic interactions between charged surfaces for all investigated mixtures, which is in contrast to what was concluded from the mean field theory and zeta potential measurements. The range of this attraction is about few nanometers, which is in good agreement with the AFM measurements performed on C-S-H immersed in solutions of Ca(OH)\(_2\) at high pH (Plassard et al. 2005). The lowest estimated value of \((F/Z^2_{LB})\) in Figure 5.11 can be considered as an index of cohesion \((I_C)\). It is worthy to mention that the predicted data in Figure 5.11 did not take into account the additional attractive contribution of van der Waals attractive forces. Indeed, this is not expected to affect the nature of the interactions because it is relatively small compared to the experimentally measured force in case of infinite C-S-H plates (Jönsson et al. 2004). Furthermore, this minor contribution of van der Waals attractive forces is almost constant as it depends only on the value of Hamaker constant for a given separation distance between infinite plates.
Figure 5.11 - Continued on next page
Figure 5.11 - The predicted interaction between two fixed charges in the simplified free-energy model with the change in a) w/c; b) cement fineness; c) temperature; d) added Na$_2$SO$_4$ as a percentage of LA cement content

- **Effect of mixture parameters on the predicted cohesion**

As can be noted in Figure 5.11-a and Figure 5.11-b, changes in either the content or fineness of cement resulted in non-significant variations in the predicted cohesion. This is attributed to the fact that the resulting slight variations in the concentration of Ca$^{2+}$ and the relative ratio between mono- and divalent counter-ions (Table 5.4) did not lead to significant changes in the
distribution of the counter-ions through the confined double layer. Additionally, the changes in measured pH were negligible, hence resulting in similar induced surface charge densities.

In the case of increasing the temperature of cement suspensions from 3 to 33°C, a slight increase in cohesion was predicted as shown in Figure 5.11-c. This is likely to be related to the corresponding reductions in the relative dielectric permittivity of the solvent ($\varepsilon_r$), which in turn increase the Bjerrum length ($l_B$) and promote cohesion (Equation 5-4).

On the other hand, the addition of alkali sulfate resulted in a marked decay in the predicted cohesion. Indeed, the addition of 4.2% of Na$_2$SO$_4$ resulted in decreasing the attractive range and intensity by almost 30%. This is could be attributed to the major increase in the concentration of Na$^+$ counter-ions in the bulk solution (Table 5.4). Both Monte Carlo simulations and experimental data have shown that for a given concentration of Ca(OH)$_2$, the considerable increase in Na$^+$ ions in the bulk solution can promote their adsorption at the C-S-H/solution interface (Jönsson et al. 2005; Labbez et al. 2011). In this case, the monovalent counter-ions (Na$^+$ and K$^+$) compete the divalent Ca$^{2+}$ ones for the charged surface. As a result, more monovalent counter-ions are allowed to enter the electric double layer (i.e. the confined solution), hence increasing the repulsive entropic pressure and leading to weakening the cohesion. Additionally, it was found that the replacement of di- by monovalent ions in the double layer leads to decreasing the degree of ionization, thus lowering the surface charge density (Labbez et al. 2006). Furthermore, the observed higher concentration of dissolved SO$_4^{2-}$ co-ions in the bulk solution can provide an additional source of weakening the cohesion. Indeed, the formation of a co-ions layer (i.e. sulfate adsorption) around the double layer favor the Ca$^{2+}$ exchange with the monovalent counter-ions, hence promoting the reduction in degree of ionization of the silanol groups (Labbez et al. 2006; Labbez et al. 2011). The addition of sulfate ions and its effect on decreasing cohesion was confirmed by AFM between C-S-H surfaces (Medala et al. 2009).

Interestingly, and in contrary to what was expected according to DLVO theory and zeta measurements, the decay in cohesion with the addition of Na$_2$SO$_4$ can explain the lower rigidity measured for cement mixtures proportioned with high concentrations of alkali sulfate (Figure 5.7). Furthermore, this lower cohesion may also allow a weaker arresting of the small particles
in the attractive atmosphere (Mewis and Wagner 2012). This may contribute in increasing the percolation time, which was also observed in Figure 5.7.

Overall and according to the ICP results and the predictions of the free-energy model, it seems that increasing either the content or fineness of cement may have non-significant enhancements of cohesion. However, the increase in the temperature may result in slightly higher cohesion. On the other hand, the presence of high concentrations of alkali sulfate could lead to a weaker cohesion, thus negatively affecting the structural build-up of cement-based suspensions.

5.5.2.2 Brownian interactions

In quiescent cement suspensions and immediately after disruption, colloidal cement particles are free to randomly move within the continuum media due to their Brownian energy, as long as they do not approach each other too closely (Coussot and Ancey 1999; Einstein and Fürth 1956; Mewis and Wagner 2012). This random motion contributes in transporting the particles to positions where their surrounding attraction clouds can encounter each other. This results in a “perikinetic” flocculation of cement particles, which can shorten the rest time needed to form the structural network ($t_{perc}$) (Chang et al. 2006; Valioulis and John List 1984). The rate of this type of flocculation is promoted by a higher frequency of collisions between the Brownian particles.

A) Estimation of the frequency of collisions

An expression to estimate the frequency of collisions of Brownian hard spheres was originally developed by Smoluchowski (Smoluchowski 1917). Thereafter, this model was modified to represent the real colloidal flocculation by including the effects of inter-particle and hydrodynamic forces. The modified model is given in Equation 5-6 (Abel et al. 1994; Fuchs 1934; Honig et al. 1971; Mewis and Wagner 2012; Prieve and Ruckenstein 1980; Spielman 1970):

$$f_c = 8\pi DaC^2 \cdot \frac{1}{W}$$

Equation 5-6
where, $f_C$ represents the frequency of collisions (i.e. the rate of Brownian flocculation), $a$ is the particle radius, and $C$ is the concentration or density of Brownian particles in a given volume of suspension. The coefficient $D$ is the Stokes-Einstein diffusivity, which describes the intensity of the Brownian motion as a balance between induced thermal movement and viscous resistance (Einstein and Fürth 1956; Holthoff et al. 1996). For a spherical colloid, $D$ can be estimated using Equation 5-7:

$$D = \frac{k_B T}{6\pi \eta_0 a^3}$$  \hspace{1cm} \text{Equation 5-7}$$

where, $k_B$ is the Boltzmann constant, $T$ is the absolute temperature, $\eta_0$ is the viscosity of the suspending medium.

In Equation 5-8, $(1/W)$ represents the fraction of successful collisions, where $W$ is known as the stability ratio. In the case of hard spheres, all collisions would be successful (i.e. $W = 1$). However, in real colloidal systems, the frequency of collisions will vary depending on the hydrodynamic and inter-particle interactions. For example, higher hydrodynamic forces result in less frequency of successful collisions because of difficulty in draining liquid between approaching particles. On the other hand, net attractive inter-particle forces would enhance the collision efficiency, while stabilizing forces, such as the electrostatic repulsive force, would diminish it. An approximate value of the stability ratio can be calculated (Prieve and Ruckenstein 1980):

$$W = W_\infty + 0.25\left(e^{\Phi_{\text{max}}/k_B T} - 1\right)$$  \hspace{1cm} \text{Equation 5-8}$$

where, $W_\infty$ is the stability ratio in the absence of any stabilizing forces and $\Phi_{\text{max}}$ is the potential energy at the energy barrier. In the case of the investigated neat cement suspensions, a net attractive potential is obtained (i.e. $\Phi_{\text{max}} = \text{zero}$), hence $W$ leads to $W_\infty$. The value of $W_\infty$ depends upon the competition between accelerating attractive potential and retarding hydrodynamic effects, which was correlated to the value of $A/k_B T$ (Prieve and Ruckenstein 1980). The Hamaker constant $(A)$ is around $1.6 \times 10^{-20}$ J for C3S and $1.8 \times 10^{-20}$ J for cement (Flatt 2004a; Lomboy et al. 2011), while $k_B T$ is $4.1 \times 10^{-21}$ J at 23ºC. Therefore, $A/k_B T$ can take a value between 4 and 4.5. The correlation of $A/k_B T$ with $W_\infty$, resulted in a value of $W_\infty$ equals 1. By
replacing D (Equation 5-7) in Equation 5-6 and substituting W with $W_\infty = 1$, a formula for estimating the frequency of collisions of Brownian cement particles can be established:

$$f_c = \frac{4k_BT}{3\eta_0}C^2$$

Equation 5-9

- **Determining number density of the Brownian particles**

In Equation 5-9, the number density of Brownian particles (C) should be estimated for the fine particles experiencing weak gravitational compared to Brownian forces. Therefore, the Péclet number (Pe) describing the ratio between gravitational to Brownian forces for a spherical particle was used to estimate the diameter of Brownian cement particles. The Péclet number (Pe) is defined as follows (Benes et al. 2007; Melik and Fogler 1984):

$$Pe = \left(\frac{4\pi}{3}\right)\frac{\Delta \rho ga^4}{k_BT}$$

Equation 5-10

where, $\Delta \rho$ is the density difference between the particle and suspending medium, and g is the acceleration of gravity. In the case of cement, the density is around 3.15 g/cm$^3$ and the value of Pe will equal unity when the particle diameter (2a) equals to 0.94 $\mu$m. Accordingly, cement particles characterized by size less than 0.94 $\mu$m are those responsible for controlling the frequency of collisions due to their higher diffusivity to convection effects.

In order to identify the number of Brownian particles (i.e. < 0.94 $\mu$m) in a reference volume of 100 $\mu$m$^3$ or 0.315 nanograms of various GU and LA cements, their number-particle distributions were estimated from the measured volume distribution (Figure 5.12). The number distributions were established assuming a spherical geometry of cement particles and a given density of 3.15 g/cm$^3$. As can be seen, LA and GU-4000 showed a similar number distribution to that of GU-original. On the other hand, further grinding at 8000 and 12000 resulted in higher number of cement particles in a given cement volume of 100 $\mu$m$^3$. It is also observed that all cement types exhibited comparable modal number-based diameters of almost 0.55 $\mu$m, where the majority of particles are smaller than 5 $\mu$m.
The estimated characteristic particle sizes were compared with those observed under microscopy. The 0.50 w/c mixtures were prepared using GU-original and GU-8000 cements and placed in sealed capsules, where SEM images could be obtained using a technique described in (Venkiteela and Sun 2010). The obtained SEM images for GU-original and GU-8000 are shown in Figure 5.13. As can be seen, the SEM images confirm the relatively limited number of cement particles larger than 5 μm with respect to the total number of cement particles. Furthermore, the comparison between these two images reveals that grinding cement resulted in promoting the presence of Brownian particles smaller than 0.94 μm.
The number of Brownian particles, as well as their percentage with respect to the total number of particles in 100 μm³ of cement, were estimated from the number-particle distributions and summarized in Table 5.5. As can be observed, both GU-original and GU-4000 showed almost a constant number of Brownian particles, while further grinding resulted in a higher number of Brownian particles. It is worthy to mention that despite the fact that the volume of the Brownian portion is limited between 4.7 to 9.4% of the total volume, the number of Brownian particles is more than 80% of the total number of particles. The volume occupied by the Brownian particles can be visualized as the physically active portion of the cement matrix. To facilitate the numerical calculations of the number density (C) in Equation 5-9, the modal number-based
diameter (0.55 μm, Figure 5.12) was used. The estimated equivalent number of Brownian cement particles in (100 μm³ or 0.315 nanograms) of cement are summarized in Table 5.5. Hence, using the measured densities of cement mixtures, the numbers of Brownian particles in a 1000 μm³ of cement paste (i.e. the number density, C) were estimated and given in Table 5.6.

Table 5.5 - Characteristics of the Brownian portion in (100 μm³ or 0.315 ng) of cement powders

<table>
<thead>
<tr>
<th>Type of cement</th>
<th>Number of Brownian particles ( &lt; 0.94 μm)</th>
<th>Relative number of Brownian particles (%)</th>
<th>Relative volume of the Brownian portion (%)</th>
<th>Equivalent number of mono-Brownian particles (d = 0.55 μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-original</td>
<td>33.8</td>
<td>85.6</td>
<td>4.7</td>
<td>53.9</td>
</tr>
<tr>
<td>GU-4000</td>
<td>33.7</td>
<td>85.3</td>
<td>4.7</td>
<td>53.9</td>
</tr>
<tr>
<td>GU-8000</td>
<td>46.0</td>
<td>88.0</td>
<td>6.3</td>
<td>72.3</td>
</tr>
<tr>
<td>GU-12000</td>
<td>69.6</td>
<td>82.8</td>
<td>9.4</td>
<td>107.9</td>
</tr>
<tr>
<td>LA</td>
<td>35.2</td>
<td>85.2</td>
<td>4.8</td>
<td>55.1</td>
</tr>
</tbody>
</table>

Table 5.6 - Number densities of equivalent mono-Brownian particles in 1000 μm³ of paste

<table>
<thead>
<tr>
<th>Description of mixtures</th>
<th>Density of paste (g/cm³)</th>
<th>Number density (10⁻³ μm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-original, T = 23°C</td>
<td>w/c</td>
<td>0.35, 0.40, 0.45, 0.50, 0.55</td>
</tr>
<tr>
<td>w/c = 0.55, T = 23°C</td>
<td>Cement fineness</td>
<td>GU-original, GU-4000, GU-8000, GU-12000</td>
</tr>
<tr>
<td>GU-original, w/c = 0.40</td>
<td>T (°C)</td>
<td>3, 13, 23, 33°C</td>
</tr>
<tr>
<td>LA, w/c = 0.35, T = 23°C</td>
<td>Added Na₂SO₄ (%)</td>
<td>0, 2.1, 4.2%</td>
</tr>
</tbody>
</table>

- **Determining viscosity of the suspending pore solutions**

The frequency of collisions is also affected by the viscosity of the continuum media. Indeed, higher viscosity of the solvent leads to a higher resistance to movement of Brownian particles, hence decreasing their velocity and rate of collisions (Jia et al. 2007). Therefore, the variations in the viscosity of the pore solutions of cement mixtures were determined using equivalent
electrolytes at different temperatures. Ordinary and concentrated electrolyte solutions were prepared by dissolving a mixture of Na$_2$SO$_4$, Ca(OH)$_2$, and NaOH in a distilled water. The ordinary electrolyte was made to obtain ionic concentrations corresponding to the average of those measured for cement mixtures without the addition of alkali sulfates based on data reported in Table 5.4. On the other hand, the concentrated electrolyte was prepared to simulate a high ionic concentrations comparable to those determined for the pore solution in the case of adding 4.2% alkali sulfates. The estimated ionic concentrations for the two prepared electrolytes are summarized in Table 5.7.

Table 5.7 - Ionic concentrations of prepared electrolytes simulating the extracted pore solutions

<table>
<thead>
<tr>
<th>Ions</th>
<th>Ionic concentration (mmol/l)</th>
<th>Ordinary pore solution</th>
<th>Concentrated pore solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$^+$</td>
<td>344</td>
<td>1862</td>
<td></td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>20</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>141</td>
<td>880</td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>103</td>
<td>151</td>
<td></td>
</tr>
</tbody>
</table>

The variations of measured dynamic viscosity of ordinary and concentrated electrolytes as well as the distilled water with temperature are shown in Figure 5.14.

Figure 5.14 - Variations of dynamic viscosity of equivalent electrolytes with temperature
As can be observed, the increase in temperature resulted in decreasing the electrolyte’s viscosity, regardless of the ionic strength of the pore solution. Furthermore, for a given temperature, the presence of dissolved ions was shown to increase the viscosity of the solvent, which can reduce the collision frequency.

**B) Effect of mixture parameters on the frequency of Brownian collisions**

Once the number densities of Brownian particles (C) and viscosities of the solvent media (\(\eta_0\)) are known, the frequency of collisions (\(f_C\)) of investigated mixtures can be estimated using Equation 5-9. The variations of estimated frequencies of collisions per 1000 \(\mu\)m\(^3\) of cement paste with the change in \(w/c\), cement fineness, temperature, and added alkali sulfate percentages are presented in Figure 5.15. As can be observed, the increase in \(w/c\) resulted in a lower frequency of collisions due to the smaller number of Brownian particles in a given volume of cement paste. This was reflected by the longer percolation times observed for higher \(w/c\). Furthermore, grinding cement increased the number of Brownian particles, and thus resulting in a considerable increase in the rate of collisions and faster rate of structuration (i.e. less \(t_{perc}\)). This situation is similar to the case where silica fume is used as a partial replacement of cement particles. This can result in increasing the number of Brownian particles hence, decreasing the percolation time (Mostafa and Yahia 2016). On the other hand, the increase in temperature enhanced the rate of diffusion and decreased the solvent viscosity, which eventually increased the rate of collisions. This can explain the shorter percolation time measured at higher temperature. The addition of alkali sulfate led to a lower frequency of collisions due to the increase in solvent viscosity. This is in good agreement with the increase in percolation time observed for cement mixtures with high alkali sulfate contents. Overall, it could be concluded that increasing cement content, fineness, and the temperature of suspension can enhance the rate of Brownian flocculation. Conversely, great ionic additions, such as the case of high additions of \(Na_2SO_4\), can diminish it.
Figure 5.15 - Continued on next page
In addition to the perikinetic Brownian flocculation, it should be kept in mind that the Brownian diffusion may induce an opposite effect by extracting the attached small particles from the attractive atmosphere after their agglomeration. This process was found to be minor in the case of flocculated cement suspensions where attractive forces dominate the Brownian ones (Coussot and Ancey 1999; Roussel et al. 2010).
5.5.3 Cement hydration and nucleation intensity

After the percolation period, non-significant movement is expected for the colloidal particles forming the structural network. Assuming that the attractive cohesion does not vary during the induction period, the observed rigidification (increase in $G'$) after the percolation time can be due to the chemical aging (Jiang et al. 1995; Roussel 2012). The rate of rigidification for a given network is proportional to the quantity of formed hydrates at the contact zones between cement particles (Mostafa and Yahia 2016; Roussel et al. 2012). The formation of cement hydrates originates due to nucleation and growth processes (Bullard et al. 2011; Thomas et al. 2011). In these processes, the bulk solution becomes saturated and cause the precipitation of nucleus of C-S-H at the cement surface and the following growth along and outward the surface of the particles (Garrault-Gauffinet and Nonat 1999; Garrault and Nonat 2001; Jiang et al. 1995; Taylor 1997).

5.5.3.1 Effect of mixture parameters on the heat flow

The chemical hydration of the investigated mixtures can be identified using calorimetric measurements. The calorimetry results determined during 24 hours after mixing are presented in Figure 5.16. As can be observed, the heat curves exhibited the main kinetic features of cement hydration (Aïtcin 2007; Bullard et al. 2011; Taylor 1997). The increase in w/c from 0.35 to 0.45 and 0.55 at a constant temperature of 23°C resulted in comparable induction periods and slight variations in both time and maximum value of the second peak (Figure 5.16-a). On the other hand, for a given w/c of 0.55 (Figure 5.16-b), the use of finer cement resulted in a considerable increase in the heat flow during both the induction period and the second peak of hydration. This is related to the larger surface area of particles in contact with water, hence resulting in a higher release of heat of hydration (Bentz et al. 1999; Bentz and Haecker 1999; Taylor 1997). The heat flow of 0.40 w/c mixtures hydrated at 23 and 33°C are presented in Figure 5.16-c. The calorimetry values of 3 and 13°C mixtures were not measured due to the difficulty in lowering the ambient temperature where the calorimetry is installed. As can be observed, cement paste hydrated at 33°C exhibited a shorter induction period and shifting the second peak to an earlier time as well as releasing a higher rate of heat compared to the mixture tested at 23°C. This expected result is due to the acceleration of the dissolution and precipitation processes during
cement hydration (Escalante-Garcia and Sharp 2000). Furthermore, the addition of Na₂SO₄ (up to 4.2%, by mass of LA cement) resulted in higher rate of heat release (Figure 5.16-d). These results are in good agreement with data available in the literature, where the increase in alkali content was found to enhance the rate of cement hydration (Jawed and Skalny 1978). On the other hand, the increased sulfate content was shown to have a little effect on altering the hydration process (Halaweh 2007).

Figure 5.16 - Continued on next page
Figure 5.16 - Heat flow curves during cement hydration for various mixture parameters a) w/c; b) cement fineness; c) temperature; d) added Na$_2$SO$_4$ as a percentage of LA cement content

5.5.3.2 Nucleation and growth rate constants (BNG model)

The measured isothermal calorimetric profiles of cement hydration are the result of several processes which may operate in series and/or parallel such as dissolution, diffusion, growth and nucleation, complexation, etc. (Bullard et al. 2011). The kinetics of nucleation-growth processes and microstructure development can be determined using the boundary nucleation and growth (BNG) model (Thomas 2007). The BNG model has been successfully used to describe the
hydration kinetics of cement and C₃S in which nucleation is assumed to occur due to the formation of C-S-H at random sites on the surface of cement particles (Thomas 2007; Zhang et al. 2010). This model has the advantage to account for the changes in powder’s surface area and solid content.

The application of the BNG model in this study was based on two assumptions. First, the recorded heat of hydration is mainly due to C₃S hydration (Aïtcin 2007). Although for the same amount, C₃A releases higher heat than C₃S, the C₃A content in GU and LA cements are much smaller than that of C₃S. Therefore, the occurred nucleation and growth kinetics can be mainly related to C₃S. Second, the nucleation and growth were assumed to start at the time of mixing and continue during the induction period. This was observed and confirmed experimentally for cement and C₃S pastes using AFM and SEM measurements (Garrault et al. 2005; Garrault and Nonat 2001; Venkiteela and Sun 2010). According to the BNG model, the volume fraction of formed hydrates at a given time (X (t)) can be identified from Equation 5-11 (Thomas 2007):

\[
X(t) = 1 - \exp\left[ -2O_v^B \int_0^t \left( 1 - \exp\left( -Y^e \right) \right) dy \right] \tag{Equation 5-11}
\]

where, \( Y^e = \begin{cases} 
\frac{\pi}{3} I_B G^2 t^3 \left( 1 - \frac{3y^2}{G^2 t^2} + \frac{2y^3}{G^3 t^3} \right) & (t > y/G) \\
0 & (t \leq y/G) 
\end{cases} \) \tag{Equation 5-12}

where, \( I_B \) is the nucleation rate per unit area of cement surface (describing the frequency of generating nucleus per unit area of cement particles during a given time), and \( G \) is the 3-D isotropic growth rate of each nucleus. The \( O_v^B \) represents the area of cement particles per unit volume of paste and is related to the specific surface area of cement (\( S_{\text{BET}} \)) and \( w/c \) as follows (Scherer et al. 2012):

\[
O_v^B = \frac{S_{\text{BET}}}{(w/c)/\rho_w + (1/\rho_c)} \tag{Equation 5-13}
\]

where, \( \rho_w \) and \( \rho_c \) are the densities of water and cement, respectively.
Two independent rate constants ($K_B$ and $K_G$), each with units of inverse time, combining the three physical parameters $I_B$, $G$, and $O_V^B$ were proposed to describe the kinetics of nucleation and growth processes (Thomas 2007):

$$K_B = \left(I_B O_V^B\right)^{0.25} G^{0.75}$$
Equation 5-14

$$K_G = O_V^B G$$
Equation 5-15

where, $K_B$ describes the rate of covering the surface of cement particles with hydration products in a unit volume of paste, and $K_G$ indicates the rate of filling the pore space between particles in a unit volume of paste.

5.5.3.3 Effect of mixture parameters on the nucleation and growth rate constants

The values of $O_V^B$, summarized in Table 5.8, were estimated for the various investigated cement mixtures using Equation 5-13.

<table>
<thead>
<tr>
<th>Description of mixtures</th>
<th>$O_V^B$ (μm$^{-1}$)</th>
<th>$I_B$ (μm$^2$ h$^{-1}$)</th>
<th>$G$ (μm/h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GU-original, $T = 23°C$</td>
<td>$w/c$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.35</td>
<td>1.98</td>
<td>16.639</td>
</tr>
<tr>
<td></td>
<td>0.45</td>
<td>1.72</td>
<td>14.828</td>
</tr>
<tr>
<td></td>
<td>0.55</td>
<td>1.52</td>
<td>12.505</td>
</tr>
<tr>
<td>$w/c = 0.55, T = 23°C$</td>
<td>Cement fineness</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>GU-original</td>
<td>1.52</td>
<td>12.505</td>
</tr>
<tr>
<td></td>
<td>GU-4000</td>
<td>1.65</td>
<td>6.953</td>
</tr>
<tr>
<td></td>
<td>GU-8000</td>
<td>2.55</td>
<td>3.081</td>
</tr>
<tr>
<td></td>
<td>GU-12000</td>
<td>3.57</td>
<td>6.865</td>
</tr>
<tr>
<td>GU-original, $w/c = 0.40$</td>
<td>$T$ (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>1.84</td>
<td>11.884</td>
</tr>
<tr>
<td></td>
<td>13</td>
<td>1.84</td>
<td>14.11</td>
</tr>
<tr>
<td></td>
<td>23</td>
<td>1.84</td>
<td>16.569</td>
</tr>
<tr>
<td></td>
<td>33</td>
<td>1.84</td>
<td>19.242</td>
</tr>
<tr>
<td>LA, $w/c = 0.35, T = 23°C$</td>
<td>Added Na$_2$SO$_4$ (%)</td>
<td>2.21</td>
<td>11.828</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>2.21</td>
<td>22.14</td>
</tr>
<tr>
<td></td>
<td>2.1</td>
<td>2.21</td>
<td>23.817</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>2.21</td>
<td></td>
</tr>
</tbody>
</table>
The heat flow was defined as \( S(dX/dt) \), where \( S \) is a scaling constant that converts measured heat flow into a fractional rate of transformation. Then, the best fitting criterion was used to determine the \( S \), \( K_B \), and \( K_G \) values using the measured heat flow data. The obtained values of the rate constants (\( K_B \) and \( K_G \)) were used to calculate the values of \( I_B \) and \( G \) according to Equation 5-14 and Equation 5-15. The variations of \( K_B \) and \( K_G \) with \( w/c \), cement fineness, temperature, and alkali sulfate content are presented in Figure 5.17, while the estimated values of \( I_B \) and \( G \) are given in Table 5.8. An Arrhenius-type dependence was reported between the rate constants and the absolute temperature (\( \ln K \) versus \( 1/T \)) with a slope representing the activation energy (Thomas 2007; Zhang et al. 2010). Therefore, the activation energy was calculated from the rate constants determined at 23 and 33°C and then used to estimate the values of \( K_B \) and \( K_G \) at 3°C and 13°C.

![Figure 5.17 - Continued on next page](image-url)
Figure 5.17 - Variations of the nucleation and growth constants \( K_B \) and \( K_G \) for various mixture parameters a) \( w/c \); b) cement fineness; c) temperature; d) added Na\(_2\)SO\(_4\) as a percentage of LA cement content

As can be seen in Figure 5.17-a, the change of \( w/c \) from 0.35 to 0.55 resulted in comparable values of the fitted rate constants (\( K_B \) and \( K_G \)). Indeed, the BNG model predicts that the increase in \( w/c \) can lead to decreasing \( I_B \) (i.e. less number of generated nucleus per hour per \( \mu m^2 \) of cement) and increasing \( G \) (i.e. a higher rate of 3-D growth of each generated nuclei) (Table 5.8). Furthermore, the increase in \( w/c \) reduced the area of cement per unit volume of paste (\( O_V^{B} \)). Consequently, the total effect of these variations was reflected by almost similar rates of
covering cement particles ($K_B$) and filling the pore spaces ($K_G$) with hydration products in a unit volume of paste.

On the other hand, the use of finer cement resulted in higher values of $K_B$ and $K_G$ (Figure 5.17-b). Thus, higher rates of covering particles and filling the capillary pores with hydrates. This is due to the more available surface area for nucleation in a unit volume of paste ($O_{V}^{B}$).

Furthermore, the increase in temperature of 0.40 w/c mixtures from 3 to 13, 23, and 33°C resulted in considerable enhancements in the nucleation and growth kinetics (Figure 5.17-c). This is related to the increase in both the growth rate and number of nucleating sites at the same age per unit volume of paste (Table 5.8). As a consequence, this suggests that higher temperature of suspension can lead to less time needed to cover the cement particles, as well as an intensive growth of hydration products in the pore space between cement particles.

The addition of alkali sulfates resulted in increasing the frequency of generating nuclei ($I_B$) and a minor effect on their rate of growth ($G$) (Table 5.8). This was reflected by an increase of the nucleation rate constant ($K_B$) and non-significant variations in the growth rate constant ($K_G$) (Figure 5.17-d).

Based on the nucleation rate constant ($K_B$) which is thought to be a dominant parameter controlling the chemical bridging between cement particles during the induction period, it could be concluded that changes in cement content (i.e. w/c) result in slight variations in the rate of covering cement grains with hydrates. On the other hand, increasing the fineness of cement, temperature of suspension, or alkali sulfates content can significantly enhance the nucleation kinetics, hence resulting in a stronger bridging for a given pseudo contact distance between cement particles.

### 5.6 Modelling the kinetics of structural build-up

The kinetics of structural build-up of cement suspensions at rest, expressed by $t_{perc.}$ and $G_{rigid.}$ indices, can be modeled by taking into consideration the previously discussed microstructural characteristic, such the inter-particle cohesion ($I_C$), frequency of Brownian collisions ($f_C$), and nucleation rate constant ($K_B$).
5.6.1 Modelling of the percolation time (t_{perc.})

The variations of t_{perc.} are supposed to inversely proportional to both f_{C} and I_{C}. Indeed, higher frequency of collisions will result in a higher construction rate of the colloidal network. In addition, higher intensity of cohesion can densify the network locally and contributes in arresting flocculated particles (Mewis and Wagner 2012; Trappe et al. 2001). On the other hand, t_{perc.} is expected to be proportional to the separation distance between particles immediately after the disruption. Indeed, this separation distance represents the span cut by the particle until reaching its equilibrium position. A simplified average separation distance (S_{d}) was estimated from the mean distance between centers of two neighboring particles in the case of a stable system (b) according to literature (Coussot and Ancey 1999; Larrard 1999):

\[ b = d_{50V} (\phi/\phi_{m})^{1/3} \]  
Equation 5-16

where, \( \phi \) is the solid fraction calculated as \([1 + 3.15 (w/c)]^{-1} \), and \( \phi_{m} \) is the maximum packing fraction. The value of \( \phi_{m} \) can be estimated from a semi-empirical correlation proposed by Hu and de Larrard (Hu and de Larrard 1996) as follows:

\[ \phi_{m} = 1 - 0.45 \left( \frac{d_{min}}{d_{max}} \right)^{0.19} \]  
Equation 5-17

where, \( d_{min} \) and \( d_{max} \) are the diameters of the smallest and largest particles in the system, respectively. In this study, the values of \( d_{min} \) and \( d_{max} \) were taken as \( d_{10V} \) and \( d_{90V} \), respectively (Table 5.2).

After several trials, the correlation between \( t_{perc.} \) and \( f_{C} \), \( I_{C} \), and \( S_{d} \) was found to be exponential function as follows:

\[ t_{perc.} = A e^{B \cdot \alpha} \]  
Equation 5-18

\[ \alpha_{t} = \frac{S_{d}^{n_{1}}}{I_{C}^{n_{2}} \cdot f_{C}^{n_{3}}} \]  
Equation 5-19

\( A^\prime, B^\prime, n_{1}, n_{2}, \) and \( n_{3} \) are fitting constants that can be determined by regression. The obtained results are given in Equation 5-20 and Equation 5-21 and plotted in Figure 5.18.
\[ t_{\text{perc.}} = 7.1 \times 10^{3.9 \alpha_t} \]  
Equation 5-20

\[ \alpha_t = \frac{S_d^{0.81}}{I_c^{1.77} \cdot f_C^{1.39}} \]  
Equation 5-21

In this model, \( t_{\text{perc.}} \) is in minutes, while \( S_d \), \( I_c \), and \( f_C \) are in Å, Å\(^{-1}\), and \( 1/\text{s.} \times 10^3 \) μm\(^3\) of paste, respectively.

![Figure 5.18 - Measured and predicted \( t_{\text{perc.}} \) as function of microstructural parameters (\( \alpha_t \))](image)

5.6.2 Modelling of the rigidification rate (\( G_{\text{rigid.}} \))

The rigidification rate of the formed colloidal network (\( G_{\text{rigid.}} \)) is anticipated to increase with the nucleation rate constant (\( K_B \)) and the number of contacts between particles in a unit volume of paste. The number of contacts is mainly affected by both the size and polydispersity of particles. For example, for a given solid fraction (\( \phi \)), smaller particle size and/or broad size distribution can provide a higher number of contact points. Therefore, the number of contact points will be assumed to vary as a function of \( \phi/d_{50} \), while \( d_{50} \) will be taken as the surface average diameter (\( d_{50S} \)). The surface average diameter was shown to well characterize the effects of both particle size and polydispersity on the yield stress response of flocculated suspensions (Zhou et al. 1999).
Additionally, for a given rigidification point, it is expected that higher intensity of cohesion can lead to a stronger converge between attracted particles, which will result in a higher rigidification impact for a given nucleation rate. This situation is important to capture, for example, the effect of alkali sulfates additions. Indeed, despite that higher amounts of added Na$_2$SO$_4$ resulted in a higher chemical nucleation (Figure 5.17-d), reductions in the measured $G_{\text{rigid}}$ were observed (Figure 5.8). This suggests that the reductions in $I_C$ can induce a larger pseudo contact distance, hence lowering the rigidification rate.

The $G_{\text{rigid}}$ was found to be well correlated exponentially with $\alpha_G$, where $\alpha_G$ is a function of $K_B$, $\phi/d_{50S}$, and $I_C$ as follows:

\[
G_{\text{rigid}} = A^* e^{B^* \alpha_G} \quad \text{Equation 5-22}
\]

and,

\[
\alpha_G = \frac{I_C^{m_1} \cdot K_B^{m_2} \cdot \phi^{m_3}}{d_{50S}^{m_4}} \quad \text{Equation 5-23}
\]

$A^*$, $B^*$, and $m_1$ to $m_4$ are constants to be determined by fitting the estimated and measured rigidification rates. The relationship between experimental and model prediction for $G_{\text{rigid}}$ are presented in Figure 5.19, where:

\[
G_{\text{rigid}} = e^{54.8 \alpha_G} \quad (A^* = 1) \quad \text{Equation 5-24}
\]

and,

\[
\alpha_G = \frac{I_C^{0.74} \cdot K_B^{0.28} \cdot \phi^{1.47}}{d_{50S}^{1.04}} \quad \text{Equation 5-25}
\]

where, $G_{\text{rigid}}$ is in Pa/s and $I_C$, $K_B$, and $d_{50S}$ are in Å$^{-1}$, h$^{-1}$, and μm, respectively.
5.6.3 Accuracy of the proposed model

Three additional cement mixtures were prepared to evaluate the accuracy of proposed model to predict $t_{perc.}$ and $G_{\text{rigid.}}$. One cement mixture was proportioned with a $w/c$ of 0.40 using HE cement and tested at 23°C. On the other hand, the two other mixtures were prepared using GUL cement and two different $w/c$ (0.40 and 0.50) and tested at temperatures of 3 and 13°C. The build-up measurements were performed to determine the $t_{perc.}$ and $G_{\text{rigid.}}$ values for the three mixtures. The microstructural parameters, including $I_C$, $f_C$, $S_d$, $K_B$, $\phi$, and $d_{50S}$, were determined and summarized in Table 5.9. The proposed model was then used to predict the values of $t_{perc.}$ and $G_{\text{rigid.}}$. The measured and predicted values of the build-up indices are presented in Figure 5.20. As can be observed, a good agreement between the measured and predicted build-up indices is obtained. Although, the model was developed based on the properties of GU and LA cement mixtures, it showed a good accuracy to predict $t_{perc.}$ and $G_{\text{rigid.}}$ of other mixtures made with different cement types (HE and GUL). Overall, the attempt of the model to capture the main parameters controlling the structuration kinetics is very encouraging as it can allow better control of the kinetics of structural build-up of neat cement suspensions.

Figure 5.19 - Measured and predicted $G_{\text{rigid.}}$ as function of microstructural parameters ($\alpha_G$)
Table 5.9 - Microstructural parameters of the mixtures used for validation

<table>
<thead>
<tr>
<th>Microstructural parameters</th>
<th>Cement mixtures</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HE, ( w/c = 0.40, 23^\circ C )</td>
</tr>
<tr>
<td>( I_C ) ( (\AA^{-1}) )</td>
<td>2.83</td>
</tr>
<tr>
<td>( f_C ) ( (10^{-3} \text{ } \mu m^3.s^{-1}) )</td>
<td>503</td>
</tr>
<tr>
<td>( S_d ) ( (\mu m) )</td>
<td>1.294</td>
</tr>
<tr>
<td>( K_B ) ( (h^{-1}) )</td>
<td>0.1014</td>
</tr>
<tr>
<td>( \phi ) (-)</td>
<td>0.442</td>
</tr>
<tr>
<td>( d_{50s} ) ( (\mu m) )</td>
<td>3.584</td>
</tr>
</tbody>
</table>

Figure 5.20 - Comparison between the predicted and measured build-up indices

5.6.4 Significance of the microstructural parameters

A parametric study has been performed using the proposed model to evaluate the significance of the microstructural parameters on the kinetics of build-up. The values of \( t_{perc.} \) and \( G_{rigid.} \) were estimated for a reference mixture corresponding to the average values of measured microstructural parameters in this study (Table 5.10). Then, \( t_{perc.} \) was estimated with the variation of each microstructural parameter, including the viscosity of suspending medium (\( \eta_0 \)), \( d_{50V} \) and \( d_{10V}/d_{90V} \) of cement, solid content (\( w/c \)), volume of the Brownian portion (\( V_{Brownian} \)), and the intensity of cohesion between cement particles (\( I_C \)). The microstructural parameters used
for the reference mixture as well as the boundaries of investigated range of each parameter are listed in Table 5.10. In order to facilitate the comparison between the microstructural parameters, their range of variation was rescaled between -1 and +1 representing the lower and higher examined boundaries, respectively. Similarly, $G_{\text{rigid}}$ was estimated for different $w/c$, $I_C$, $d_{50S}$, and nucleation rates ($K_B$). The characteristics of the reference mixture and the range of variation of each microstructural parameter are summarized in Table 5.11. The estimated $t_{\text{perc}}$ and $G_{\text{rigid}}$ with the variation of each microstructural parameter are shown in Figure 5.21.

Table 5.10 - The reference mixture and the range of microstructural parameters used to estimate $t_{\text{perc}}$.

<table>
<thead>
<tr>
<th>Microstructural parameters</th>
<th>$w/c$</th>
<th>$d_{10V}/d_{90V}$</th>
<th>$d_{50V}$</th>
<th>$I_C$</th>
<th>$V_{\text{Brownian}}$</th>
<th>$\eta_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference mixture</td>
<td>0.45</td>
<td>0.10</td>
<td>8</td>
<td>2.4</td>
<td>6.8</td>
<td>0.0013</td>
</tr>
<tr>
<td>Scaled range (-1)</td>
<td>0.35</td>
<td>0.05</td>
<td>3</td>
<td>2.0</td>
<td>4.5</td>
<td>0.0008</td>
</tr>
<tr>
<td>Scaled range (+1)</td>
<td>0.55</td>
<td>0.15</td>
<td>13</td>
<td>2.8</td>
<td>9.0</td>
<td>0.0018</td>
</tr>
</tbody>
</table>

Table 5.11 - The reference mixture and the range of microstructural parameters used to estimate $G_{\text{rigid}}$.

<table>
<thead>
<tr>
<th>Microstructural parameters</th>
<th>$w/c$</th>
<th>$K_B$</th>
<th>$d_{50S}$</th>
<th>$I_C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference mixture</td>
<td>0.45</td>
<td>0.09</td>
<td>3.35</td>
<td>2.4</td>
</tr>
<tr>
<td>Scaled range (-1)</td>
<td>0.35</td>
<td>0.04</td>
<td>2.10</td>
<td>2.0</td>
</tr>
<tr>
<td>Scaled range (+1)</td>
<td>0.55</td>
<td>0.14</td>
<td>4.60</td>
<td>2.8</td>
</tr>
</tbody>
</table>

As can be observed in Figure 5.21-a, the volume of the Brownian portion seems to be a predominant parameter affecting the percolation time. For a given $w/c$ of 0.45, the increase in $V_{\text{Brownian}}$ from 4.5 to 9% resulted in decreasing $t_{\text{perc}}$ from 27 to 8 minutes. It is also observed that the variations of $t_{\text{perc}}$ with $V_{\text{Brownian}}$ is nonlinear, where the increase in $V_{\text{Brownian}}$ beyond a certain amount resulted in less reduction rate in $t_{\text{perc}}$. On the other hand, it is noted that for a given cement content and $d_{50S}$, the changes in $d_{10V}/d_{90V}$ did not result in significant variations of $t_{\text{perc}}$. Furthermore, for a given volume of the Brownian portion, the $w/c$, $d_{50V}$, $\eta_0$, $I_C$ showed almost comparable influence on the percolation time. Indeed, their variations resulted in differences in $t_{\text{perc}}$ between 14 and 8 minutes.
The value of $G_{\text{rigid}}$ is shown to be highly sensitive to the variations in $d_{50S}$ of used cement (Figure 5.21-b). For a given $w/c$ and nucleation rate ($K_B$), the decrease in $d_{50S}$ from 4.6 to 2.10 μm (i.e. higher number of rigidification points) resulted in increasing $G_{\text{rigid}}$ by three orders of magnitude. Similarly, the increase in cement content (i.e. lower $w/c$) is shown to significantly increase $G_{\text{rigid}}$. Furthermore, for a given number of contact points, the increase of $K_B$ and $I_C$ have resulted in comparable enhancements of the rigidification rate.
Based on the sensitivity of $t_{\text{perc.}}$ and $G_{\text{rigid.}}$ to the microstructural parameters, it can be concluded that for a given w/c mixture, smaller percolation times can be ensured by using cement with a relatively high volume of particles smaller than approximately 1 $\mu$m (or adding Brownian particles such as silica fume). Alternatively, keeping a minimum concentration of mono-valent ions and promoting the presence of multi-valent ions in the pore solution. Also, maintaining the viscosity of the suspending medium as low as possible can allow a faster structuration of the elastic network. On the other hand, a high rigidification rate of a given w/c mixture can be secured by using a fine cement with a relatively small median surface-based diameter. A second option is to promote the nucleation kinetics by allowing a higher temperature of the mixture or incorporating set-accelerators. Additionally, increasing the intensity of cohesion can result in a higher rigidification impact.

5.7 Conclusions

The physico-chemical kinetics of structural build-up ($t_{\text{perc.}}$ and $G_{\text{rigid.}}$) were measured and correlated to the microstructural changes of various neat cement suspensions. Based on the obtained results, the following conclusions can be pointed out:

1. Higher cement content, fineness, and temperature of the suspension can result in shorter times to form the elastic network as well as higher rates of gaining rigidity with time. On the other hand, the increase in alkali sulfate content can lead to longer percolation times and lower rigidification rates.

2. The structural build-up measurements confirmed the inadequacy of zeta potential concept and mean field approach to describe the structuration of neat cement suspensions, particularly those incorporating a high amount of alkali sulfates.

3. The increase in either the content or fineness of cement does not influence the cohesion, while the increase in the temperature can slightly increase it. On the other hand, the presence of high concentrations of alkali sulfate could lead to a weaker cohesion, thus negatively affecting the structural build-up of cement-based suspensions.
4. The increase in cement content, fineness, and temperature of the suspension can enhance the rate of Brownian flocculation. Conversely, great ionic additions, such as the case of high additions of Na₂SO₄, can reduce it.

5. The changes in cement content result in slight variations in the nucleation rate. On the other hand, increasing the fineness of cement, temperature, or alkali sulfates content can significantly enhance the nucleation kinetics and the rate of covering cement particles with hydrates, hence resulting in a stronger bridging for a given pseudo contact distance between cement particles.

6. A semi-empirical model to predict the percolation time and rigidification rate as a function of the microstructural parameters is developed and validated. The model showed a good accuracy to predict the t_{perc.} and G_{rigid.} of mixtures prepared with various cement types and tested at different temperatures.

7. For a given cement content, volume of the Brownian portion as well as the median volume-based diameter of used cement, intensity of cohesion between particles, and viscosity of the suspending medium have significant effects on the percolation time of neat cement suspensions. On the other hand, at a given nucleation rate, the median surface-based diameter of cement plays a key effect of G_{rigid.}.

5.8 References


CHAPTER 6: CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

The main objective of this work was to use dynamic rheometry to provide a deeper insight into the physical and chemical kinetics of build-up of cement suspensions as well as identifying the key factors affecting this phenomenon. The research program undertaken in this study was carried out in three phases. A performance evaluation of the various shearing procedures that can be applied to obtain a well-dispersed state for cement suspensions (Chapter 3). Developing new build-up indices that can be used to quantify the physical and chemical kinetics of structuration of cement suspensions (Chapter 4). The roles of mixture parameters of neat cement suspensions on the kinetics of build-up and their dependency on the microstructural characteristics (Chapter 5). Based on the obtained results, the following conclusions can be pointed out:

6.1.1 Performance evaluation of disruptive shears

- In the case of flocculated cement suspensions, the use of disruptive rotational shear rate lower than 150 s\(^{-1}\) may not be enough to achieve a well-dispersed state. An efficient dispersion can be obtained by applying a shear rate corresponding to the transition shear rate, where the rate of decrease in the apparent viscosity becomes slight and linear. In the case of 0.35 and 0.50 w/c mixtures, this value is around 225 s\(^{-1}\). Applying higher values of disruptive shear rates resulted in higher levels of recovered storage modulus after shearing where the restored structure can be formed due to the interactions between smaller, but stronger individual elements.

- The large amplitude oscillatory shear (LAOS) at a high frequency of 100 rad/s can be applied to disperse flocculated cement suspensions. This should be done at shear strain near the crossover value corresponding to the maximum damping factor (i.e. maximum
liquid state). The use of strain beyond the crossover value has resulted in a less efficient
dispersion due to the strain-thickening effects. The value of the crossover strain was
found to be around 3.5% for 0.35 w/c suspension

- The application of LAOS at the crossover strain resulted in a higher dispersion degree
compared to that measured after shearing cement suspension at the transition shear rate.
In the case of 0.35 w/c suspension, the use of an oscillatory disruptive shear at 3.5%
strain was shown to reduce the viscosity by 70 times compared to 5 times obtained with
a rotational shear at 225 s⁻¹.

- The dispersion efficiency of rotational shear performed at shear rates lower than the
transitional value can be enhanced by applying a post-oscillatory shear at strain around
the crossover value. The combination of (rotational shear + LAOS) was found to achieve
comparable dispersion degrees for shear strain and shear rate values different than the
optimum ones (i.e. cross over shear strain and transitional shear rate).

- The application of a disruptive oscillatory shear before the rotational one was not
effective in enhancing the dispersion degree of flocculated cement suspension.

6.1.2 Quantifying the physical and chemical kinetics of build-up

- The value of the critical shear strain defining the linear viscoelastic domain (LVED) of
cement suspensions is affected by the colloidal stability of the suspension. For
flocculated cement suspensions, this value was found to be around 0.0025% and
increases with the presence of HRWR up to 0.2%.

- The evolutions of both storage modulus (G’) and phase angle (δ) at rest can be used to
describe the kinetics of structuration of cement suspensions. The evolution of δ is not
affected by the degree of hydration and can be used to describe the rate of formation of
the internal percolated elastic network, thus reflecting the physical structural changes at
rest. On the other hand, the evolution of G’ at rest can represent the increase in stress-
bearing capacity of formed colloidal structure.
Two independent build-up indices can be identified from the evolutions of $G'$ and $\delta$ at rest. The percolation time ($t_{perc}$), corresponding to the time when the phase angle reaches its lowest and steady value, represents the resting period needed for colloidal particles to reach their favourable and equilibrium positions. The linear increase of $G'$ after the network formation ($G_{rigid}$) can, on the other hand, be used to describe its rigidification rate due to the nucleation of cement hydrates. The $t_{perc}$ and $G_{rigid}$ indices are proved to be efficient and sensitive to quantify the structural build-up of cement suspensions proportioned with various water-to-cement ratios, superplasticizer dosages, and silica fume replacement contents.

The faster rate of internal network formation does not necessarily mean higher rigidity of formed network. For example, although the incorporation of HRWR results in lower rigidification rates, its presence was shown to enhance the formation of the elastic network, reflected by decreasing $t_{perc}$. This was attributed to the structural arrest “caging” of dispersed particles.

A combined index of build-up ($G_{rigid}/t_{perc}^{1/2}$) was proposed and found to have a good correlation with the decay in the lateral pressure of various cement suspensions. The correlation between $G_{rigid}/t_{perc}^{1/2}$ and lateral pressure showed a better trend compared to those obtained with $A_{thix}$ and modified $A_{thix}$.

### 6.1.3 Role of mixture parameters on the kinetics of build-up

The evolutions of the viscoelastic properties at rest, expressed by $t_{perc}$ and $G_{rigid}$, showed that increasing cement content, fineness, and temperature of the suspension can result in shorter times to form the elastic network as well as higher rates of gaining rigidity with time. On the other hand, the increase in alkali sulfate content can lead to longer percolation times and lower rigidification rates.

The structural build-up measurements confirmed the inadequacy of zeta potential concept and the mean field approach to describe the structuration of neat cement suspensions, particularly those incorporating a high amount of alkali sulfates.
The predictions of the free-energy model have shown that increasing either the content or fineness of cement does not influence the cohesion, while increasing the temperature can slightly increase it. On the other hand, the presence of high concentrations of alkali sulfate can lead to a weaker cohesion, thus negatively affecting the structural build-up of cement-based suspensions.

The increase in cement content and fineness promotes the rate of Brownian collisions due to the availability of a higher number of Brownian particles in a given volume of cement paste. On the other hand, the increase in temperature enhanced the rate of diffusion and decreased the solvent viscosity, which eventually increased the rate of collisions. The addition of alkali sulfate led to a lower frequency of collisions due to the increase in solvent viscosity.

The changes in cement content resulted in slight variations in the nucleation kinetics. On the other hand, increasing the fineness of cement, temperature, or alkali sulfates content can significantly enhance the nucleation kinetics and the rate of covering cement particles with hydrates, hence resulting in a stronger bridging for a given pseudo contact distance between cement particles.

A semi-empirical model to predict the percolation time and rigidification rate as a function of the microstructural parameters was developed and validated (Equations 6.1 and 6.2). The model showed a good prediction ability for mixtures prepared with various cement types and different temperatures.

\[ t_{\text{perc.}} = 7.1e^{3.9a_t} \quad \text{and,} \quad a_t = \frac{S_d^{0.81}}{I_C^{1.77} \cdot f_C^{1.39}} \]  
\hspace{1cm} (6.1)

where, \( t_{\text{perc.}} \) is in minutes, while the separation distance (\( S_d \)), the intensity of cohesion (\( I_C \)), and the frequency of collisions (\( f_C \)) are in Å, Å\(^{-1}\), and 1/s, respectively.

\[ G_{\text{rigid.}} = e^{54.8a_G} \quad \text{and,} \quad a_G = \frac{I_C^{0.74} \cdot K_B^{0.28} \cdot \phi^{1.47}}{d_{50S}^{1.04}} \]  
\hspace{1cm} (6.2)
where, $G_{\text{rigid}}$ is in Pa/s, while the intensity of cohesion ($I_C$), the nucleation rate constant ($K_B$), and the median surface-based diameter ($d_{50S}$) are in Å$^{-1}$, h$^{-1}$, and μm, respectively. $\Phi$ is the solid fraction.

- For a given cement content, volume of the Brownian portion as well as the median volume-based diameter of cement, intensity of cohesion between particles, and viscosity of the suspending medium have significant effects on the percolation time of neat cement suspensions. On the other hand, at a given nucleation rate, the median surface-based diameter of cement plays a key role in affecting $G_{\text{rigid}}$.

### 6.2 Future work

Results of this study present a promising step toward the implantation of dynamic rheology to allow a better quantifying, understanding, and controlling of the kinetics of structural build-up of cement-based suspensions. This study has mainly focused on neat cement pastes. Additional research is recommended based on the findings of the current study to cover the following points:

- Results showed that using the small amplitude oscillatory shear (SAOS) can provide further data on the kinetics of build-up at rest. However, Build-up can also occur when low shear rates are applied due to other causes such as the “Orthokinetic flocculation”. Therefore, it is recommended to investigate the possibility of using the large amplitude oscillatory shear (LAOS) to simulate the low shearing conditions, while measuring the changes in the viscoelastic properties. The possibility of using the LAOS in studying the kinetics of breakdown of cement suspensions should be also investigated. This can allow, thereafter, finding if a dependency exists between the kinetics of build-up and breakdown.

- The use of dynamic rheometry can allow inducing different shear strains and angular frequencies. This may be used to simulate the mechanical vibrators, and for example, investigating the effect of vibrations on the rheological properties of cement suspensions as well as the fiber orientations.
• Within this study, it was assumed that the C-S-H is the primary nucleation product controlling the rigidification rate. However, further studies investigating the contribution of each type of the hydration products on the build-up will be interesting.

• The strain sweep measurements performed on various cement suspensions showed many interesting stresses, such as the one corresponding to the critical shear strain, at the flow point, and the peak value of the stress-strain curve. These points describe structural changes at the microstructural scale. Further investigations to explore the changes in the microstructure at these stresses will be valuable. Such study would require the incorporation of light scattering techniques to visualize the microstructural changes. Coupling the dynamic rheology with the light scattering can provide a direct way to better understand the origins of static yield stress.

• It is recommended to perform additional investigations on the viscoelastic properties and the kinetics of build-up of self-consolidating pastes where various chemical and mineral admixtures can be used. Indeed, it was shown that the incorporation of HRWR can enhance the formation of the elastic network at rest. Therefore, it is recommended to investigate the role of type, dosage, and molecular weight of the superplasticizer on the kinetics of build-up, particularly the rate of forming the elastic network, and explore the impact of this on the overall build-up performance in field applications. Furthermore, this study can help in developing models to predict the percolation time and rigidification rates for the case of stabilized cement systems.

• It is recommended to use the microstructural parameters controlling the kinetics of build-up to perform a computational modeling and simulation of structuration process of cement suspensions at rest.

• The use of dynamic rheometry allowed a better understanding of the structuration kinetics of cement pastes. As far as the gap of the measuring assembly of the rheometer is tiny (1.126 mm), the oscillatory testing of cement mixtures containing fine aggregate, such as mortar, was not possible through this study. However, it is interesting to investigate the effect of aggregate characteristics on the viscoelastic properties of cement suspensions. This can be used to perform further investigations to correlate the kinetics
of build-up of paste with mortar and concrete. Laboratory tests, such as the resonant column test, the ultrasonic pulse test, the piezoelectric bender element test, and Piezoelectric rings-actuators technique may be help in evaluating the storage modulus of mortar suspensions at low strains.

6.3 Conclusions en français

L'objectif principal de ce travail était d'utiliser un rhéomètre dynamique pour mieux comprendre de la cinétique physique et chimique de la structuration de suspensions de ciment, ainsi que l'identification des principaux facteurs influant sur ce phénomène. Le programme de recherche entrepris dans cette étude a été réalisée en trois phases. Une évaluation de la performance des différentes procédures de cisaillement qui peuvent être appliquées pour obtenir un état bien dispersé pour des suspensions de ciment (chapitre 3). Le développement de nouveaux indices d'accumulation qui peuvent être utilisés pour quantifier la cinétique physiques et chimiques de structuration de suspensions de ciment (chapitre 4). Les rôles des paramètres de mélange de suspensions de ciment pur sur la cinétique de la structuration et de leur dépendance à l'égard des caractéristiques microstructurales (chapitre 5). Sur la base des résultats obtenus, les conclusions suivantes peuvent être soulignés :

6.3.1 Évaluation de la performance des cisaillements perturbateurs

- Dans le cas de suspensions de ciment floculés, l'utilisation de taux de cisaillement perturbateur de rotation inférieur à 150 s\(^{-1}\) peut ne pas être suffisant pour atteindre un état bien dispersé. Une dispersion efficace peut être obtenue en appliquant un taux de cisaillement correspondant à la vitesse de cisaillement de transition, où le taux de diminution de la viscosité apparente est faible et linéaire. Dans le cas des mélanges de rapport E/L de 0,35 et 0,50, cette valeur est de l'ordre de 225 s\(^{-1}\). L’application des valeurs plus élevées des taux de cisaillement disruptifs a donné lieu à des niveaux supérieurs de module de stockage récupéré après cisaillement lorsque la structure restaurée peut être formée en raison des interactions entre les plus petits, mais les plus forts éléments individuels.
• Une grande amplitude d'oscillation de cisaillement (LAOS) à une haute fréquence de 100 rad/s peut être appliquée pour disperser des suspensions de ciment floculées. Cela devrait être fait à une déformation de cisaillement proche de la valeur de croisement correspondant au facteur d'amortissement maximum (état liquide maximum). L'utilisation de la déformation au-delà de la valeur de croisement a donné lieu à une dispersion moins efficace en raison des effets épaississants des contraintes. On a trouvé une valeur 3.5% pour la déformation de croisement pour une suspension de E/L de 0,35.

• L'application de LAOS à la déformation de croisement conduit à un degré de dispersion plus élevé par rapport à celle mesurée après cisaillement de la suspension de ciment à un taux de cisaillement de transition. Dans le cas d'une suspension de E/L de 0,35, l'utilisation d'un cisaillement oscillatoire perturbateur à une déformation de 3,5% a réduit la viscosité de 70 fois comparé à 5 fois obtenus avec un cisaillement en rotation à 225 s⁻¹.

• L'efficacité de la dispersion de cisaillement de rotation qui a été réalisée à des vitesses de cisaillement inférieures à la valeur de transition peut être améliorée en appliquant un cisaillement post oscillatoire à une déformation autour de la valeur de recouvrement. La combinaison du cisaillement de rotation et du LAOS a été trouvée être plus efficace pour atteindre des degrés de dispersion comparables pour la déformation de cisaillement et des valeurs de taux de cisaillement différentes des valeurs optimales (à savoir la déformation de cisaillement de croisement et le taux de cisaillement de transition).

• L'application d'un cisaillement oscillatoire perturbateur avant celui de rotation n'était pas efficace pour améliorer le degré de la dispersion de suspension floculée de ciment.

6.3.2 Quantification des cinétiques physiques et chimiques de la structuration

• La valeur de la déformation de cisaillement critique définissant le domaine viscoélastique linéaire (LVED) des suspensions de ciment est influencée par la stabilité colloïdale de la suspension. Pour les suspensions floculées de ciment, sa valeur a été
estimée à environ 0,0025% et augmente avec l’utilisation d’un réducteur d’eau de haute gamme jusqu’à 0,2%.

- L’évolution des deux modules de stockage (G’) et de l’angle de phase (δ) au repos peuvent être utilisés pour décrire la cinétique de structuration des suspensions de ciment. L’évolution de δ n’est pas affectée par le degré d’hydratation et peut être utilisé pour décrire le taux de formation du réseau élastique percolé interne, reflétant ainsi les changements structurels physiques au repos. D’autre part, l’évolution de G’ au repos peut représenter l’augmentation de la capacité d’encaissement des contraintes de la structure colloïdale formée.

- Deux indices d'accumulation indépendants peuvent être identifiés à partir d'évolution de G’ et δ au repos. Le temps de percolation (tperc.), correspondant au temps où l'angle de phase atteint sa valeur la plus basse et stable, représente la période de repos nécessaire pour les particules colloïdales à atteindre leurs positions favorables et d'équilibre. D'autre part, l'augmentation linéaire de G’ après la formation du réseau (Grigid.) peut être utilisé pour décrire le taux de rigidification dû à la germination des hydrates de ciment. Les indices tperc. et Grigid. se sont révélés être efficaces et sensibles pour quantifier la structuration des suspensions de ciment proportionnés avec différents rapports eau-ciment, dosages de superplastifiants, et fumée de silice en remplacement.

- Le développement plus rapide de la formation du réseau interne ne signifie pas nécessairement une plus grande rigidité du réseau formé. Par exemple, l’incorporation des résultats de superplastifiants HRWR à des taux de rigidification plus faibles, a favorisé la formation du réseau élastique, reflétée par une diminution de tperc. Ceci a été attribué à l'arrêt structurel "encagement" de particules dispersées.

- Un indice combiné de la structuration (Grigid./tperc.\(^{1/2}\)) a été proposé et on a constaté une bonne corrélation avec la décroissance de la pression latérale de diverses suspensions de ciment. La corrélation entre Grigid./tperc.\(^{1/2}\) et la pression latérale a montré une meilleure tendance par rapport aux valeurs obtenus avec Athix et Athix modifié.
6.3.3 Rôle des paramètres de mélange sur la cinétique de la structuration

- Les évolutions des propriétés viscoélastiques au repos, exprimé par $t_{perc}$ et $G_{rigid}$, ont montré que l'augmentation de la teneur en ciment, la finesse et la température de la suspension peut résulter en des temps plus courts pour former le réseau élastique ainsi que des taux plus élevés pour gagner en rigidité avec le temps. D'autre part, l'augmentation de la teneur en sulfate alcalin peut conduire à des durées plus longues de percolation et des taux inférieures de rigidification.

- Les mesures de structuration ont confirmé l'inadéquation du concept de potentiel zêta et l'approche du champ moyen pour décrire la structuration des suspensions de ciment soignées, en particulier ceux incorporant une grande quantité de sulfates alcalins.

- Les prédictions du modèle d'énergie libre ont montré que l'augmentation du contenu ou de la finesse du ciment n'a pas d'influence sur la cohésion, tout en augmentant la température qui peut légèrement l'augmenter. D'autre part, la présence de concentrations élevées de sulfate alcalin peut conduire à une plus faible cohésion, ce qui affecte négativement la structuration de suspensions à base de ciment.

- L'augmentation de la teneur en ciment et sa finesse favorise le taux de collisions Browniens en raison de la disponibilité d'un plus grand nombre de particules Browniens dans un volume donné de la pâte de ciment. D'autre part, l'augmentation de la température a amélioré la vitesse de diffusion et a diminué la viscosité du solvant, qui a finalement augmenté le taux de collisions. L'addition de sulfate alcalin conduit à une fréquence inférieure des collisions en raison de l'augmentation de la viscosité du solvant.

- Les changements de la teneur en ciment ont donné lieu à de légères variations dans la cinétique de nucléation. D'autre part, l'augmentation de la finesse du ciment, de la température ou de la teneur en sulfates alcalins peut améliorer de façon significative la cinétique de la nucléation et le taux de recouvrement des particules de ciment avec des hydrates, d'où résulte une transition solide pour une pseudo distance de contact entre les particules de ciment.
Un modèle semi-empirique pour prédire le temps de percolation et le taux de rigidification en fonction des paramètres microstructuraux a été développé et validé (équations 6.1 et 6.2). Le modèle a montré une bonne capacité de prédiction pour les mélanges préparés avec différents types de ciment et différentes températures.

\[ t_{\text{perc.}} = 7.1e^{3.9a}, \quad \text{et,} \quad \alpha_i = \frac{S_d^{0.81}}{I_C^{1.77} \cdot f_c^{1.39}} \]  
(6.1)

où \( t_{\text{perc.}} \) est en minutes, tandis que la distance de séparation (\( S_d \)), l'intensité de la cohésion (\( I_C \)), et la fréquence des collisions (\( f_c \)) sont en Å, Å\(^{-1}\) et 1/s. \( 10^3 \mu m^3 \) de pâte, respectivement.

\[ G_{\text{rigid.}} = e^{54.8a_G}, \quad \text{et,} \quad \alpha_G = \frac{I_C^{0.74} \cdot K_B^{0.28} \cdot \phi^{1.47}}{d_{50S}^{1.04}} \]  
(6.2)

où \( G_{\text{rigid.}} \) est exprimé en Pa/s, l'intensité de la cohésion (\( I_C \)), la constante de vitesse de nucléation (\( K_B \)), et le diamètre médian en surface (\( d_{50S} \)) sont exprimés en Å\(^{-1}\), h\(^{-1}\), et μm, respectivement. \( \phi \) est la fraction solide.

Pour une teneur en ciment donné, le volume de la partie Brownienne, ainsi que le diamètre médian en volume de ciment, l'intensité de la cohésion entre les particules, et la viscosité du milieu de suspension ont des effets significatifs sur le temps de percolation des suspensions de ciment pur. D'un autre côté, à une vitesse de nucléation donné, le diamètre médian en surface du ciment joue un rôle clé en affectant \( G_{\text{rigid.}} \).

### 6.4 Recommandations pour des travaux futurs

Les résultats de cette étude présentent une étape prometteuse vers l'utilisation de rhéologie dynamique pour permettre une meilleure quantification, compréhension et un contrôle de la cinétique de la structure d'accumulation de suspensions à base de ciment. Cette étude a porté principalement sur les pâtes pures de ciment. De futurs travaux seront recommandés sur la base des résultats de l'étude en cours afin de couvrir les points suivants :
• Les résultats ont montré que l'utilisation d'une faible amplitude de cisaillement oscillatoire (SAOS) peut fournir des données supplémentaires sur la cinétique de la structuration au repos. Cependant, la structuration peut également se produire lorsque des taux de cisaillement faibles sont appliquées en raison d'autres causes telles que la "floculation orthocinétique". Par conséquent, il est recommandé d'étudier la possibilité d'utiliser un cisaillement oscillatoire de grande amplitude (LAOS) pour simuler les conditions de cisaillement faibles tout en mesurant les variations des propriétés viscoélastiques. La possibilité d'utiliser le LAOS dans l'étude de la cinétique de décomposition (rupture) des suspensions de ciment devrait également être étudiée. Cela peut permettre, par la suite, de trouver si une dépendance existe entre la cinétique de la structuration et la décomposition.

• L'utilisation du rhéomètre dynamique peut permettre d'induire différentes déformations de cisaillement et les fréquences angulaires. Ceci peut être utilisé pour simuler les vibreurs mécaniques, par exemple étudier l'effet des vibrations sur les propriétés rhéologiques des suspensions de ciment, ainsi que les orientations des fibres.

• Dans le cadre de cette étude, on a supposé que le gel C-S-H est le produit de la nucléation primaire contrôlant le taux de rigidification. Toutefois, d'autres études portant sur la contribution de chaque type de produits d'hydratation sur la structuration pourraient être intéressante.

• Les mesures de déformation par balayage effectués sur diverses suspensions de ciment ont montré de nombreuses contraintes intéressantes, telles que celle correspondant à la déformation de cisaillement critique au point d'écoulement, et la valeur de pic sur la courbe contrainte-déformation. Ces points décrivent des changements structurels à l'échelle de la microstructure. D'autres recherches pour explorer les changements dans la microstructure à ces contraintes seront précieuses. Une telle étude nécessiterait l'intégration des techniques de diffusion de la lumière pour visualiser les changements microstructuraux. Le couplage des techniques de la rhéologie dynamique avec la diffusion de la lumière peut fournir une manière directe pour comprendre mieux les origines de la limite d'élasticité statique.
Il est recommandé d'effectuer des investigations complémentaires sur les propriétés viscoélastiques et la cinétique de la structuration de pâtes auto-consolidées où divers adjuvants minéraux et chimiques peuvent être utilisés. En effet, il a été montré que l'incorporation de l'un HRWR de type polycarboxylate peut améliorer la formation du réseau élastique au repos. Par conséquent, il est recommandé d'étudier le rôle du type, le dosage, et le poids moléculaire du superplastifiant sur la cinétique de la structuration, en particulier le taux de formation du réseau élastique, et d'explorer l'impact de cette situation sur la performance globale de la structuration dans les applications sur le terrain. En outre, cette étude peut aider à développer des modèles pour prédire le temps de percolation et les taux de rigidification pour le cas des systèmes stabilisés au ciment.

Il est recommandé d'utiliser les paramètres microstructuraux contrôlant la cinétique de la structuration pour réaliser une modélisation informatique et une simulation des processus de structuration des suspensions de ciment au repos.

L'utilisation d'un rhéomètre dynamique a permis de mieux comprendre la cinétique de structuration des pâtes de ciment. Dans la mesure où l'écart de l'ensemble de mesure effectuées avec le rhéomètre est très petit (1.126 mm), l'essai de cisaillement oscillatoire de mélanges de ciment contenant des granulats fins comme un mortier, était inapplicable. Cependant, il est intéressant d'étudier l'effet des caractéristiques globales sur les propriétés viscoélastiques des suspensions de ciment. Ceci peut être utilisé pour effectuer des investigations supplémentaires pour établir une corrélation entre la cinétique d'accumulation de la pâte avec le mortier et le béton. Les essais de laboratoire, tels que l'essai la colonne de résonance, l'essai d'impulsions ultrasoniques, l'essai de des bilames piézoélectriques « Bender Element » et la technique des anneaux-actionneurs piézoélectriques peuvent être aider à évaluer le module stockage des suspensions de mortier à de faibles déformation.