Fall 2018

Sensitivity of rheological properties of cement paste with SCC consistency

Azadehalsadat A. Asghari

Department: Civil, Architectural and Environmental Engineering

Recommended Citation

Asghari, Azadehalsadat A., "Sensitivity of rheological properties of cement paste with SCC consistency" (2018). *Doctoral Dissertations*. 2717.
https://scholarsmine.mst.edu/doctoral_dissertations/2717

SENSITIVITY OF RHEOLOGICAL PROPERTIES OF CEMENT PASTE WITH SCC CONSISTENCY

by

AZADEHALSADAT ASGHARI

A DISSERTATION

Presented to the Faculty of the Graduate School of the

MISSOURI UNIVERSITY OF SCIENCE AND TECHNOLOGY

In Partial Fulfillment of the Requirements for the Degree

DOCTOR OF PHILOSOPHY

in

CIVIL ENGINEERING

2018

Approved by

Dr. Dimitri Feys, Advisor
Dr. Aditya Kumar
Dr. Cesar Mendoza
Dr. Thomas Schuman
Dr. Jeffrey D. Smith

PUBLICATION DISSERTATION OPTION

This dissertation has been prepared in the style such that the individual sections will be submitted for publication.

Paper I (pages 39-75) is a manuscript entitled “Which parameters, other than the water content, influence the robustness of cement paste with SCC consistency?” This manuscript was published in the Journal of Construction and Building Materials, published by ELSEVIER, Volume 124, pp. 95-103.

Paper II (pages 76-109) is a manuscript entitled “Mix design factors of self-consolidating cement paste affecting the magnitude of variations in rheological properties induced by the addition time of PCE-superplasticizer” This manuscript was published in the Journal of Construction and Building Materials, published by ELSEVIER, Volume 159, pp. 269-276.

Paper III (pages 110-143) is a manuscript entitled “On How the Evolution of Rheological Properties with Time of Cement Pastes with SCC Consistency is affected by Mix Design and Mixing Procedure Factors” and Accepted for publication in ACI Materials Journal.

Paper IV (pages 144-177) is a manuscript entitled “Influence of maximum applied shear rate on the rheological properties of flowable cement pastes” and is submitted to the Cement and Concrete Research Journal.

ABSTRACT

Robustness, which is defined as the capacity of a mixture to tolerate small variations in constituent elements, mixing parameters or temperature that are inevitable with production at any significant scale, is a key property to expand the practical implementation of self-consolidating concrete (SCC). At the first step, the effect of different amount of water, amount of superplastizer, mixing time, mixing speed and the addition time of superplastizer on the rheological properties of cement pastes with SCC consistency, has been evaluated. Two different SCC mix design concepts, the powder-type and VMA-type were selected for this research. The results show that the selected powder-type mix design is more robust than the VMA-type to a change in addition time of SP. Then, an experimental study was conducted to evaluate different mix design parameters by varying the binder combination, the type of PCE-SP and the addition of viscosity-modifying agent (VMA) to determine which particular parameters cause the largest difference in rheological behavior due to a variation in adding time of SP. In third step, the robustness of the "loss of workability" of flowable cement pastes, which is mainly affected by variations in the water content and the adding time of the superplasticizer, was evaluated. A comparison study was performed to develop a more accurate vision on robustness of cement paste, and also concrete, by taking into account the time-dependency of the rheological properties. Furthermore, the change in rheological properties of well-dispersed cement pastes subjected to different maximum shear rates has been conducted. It was shown that the choice of maximum shear rate during the rheological measurements is critical for the values of the rheological properties.

ACKNOWLEDGMENTS

I would like to extend my sincere appreciation and gratitude to my mentor and graduate advisor, Dr. Dimitri Feys for years of advice, support and encouragement, . All his advice and recommendations helped to improve the overall quality of my work. I would like to thank my advisory committee members Prof. Thomas Schuman, Prof. Jeffrey D. Smith Dr. Aditya Kumar and Dr. Cesar Mendoza, for their constructive comments.

I would like to gratefully acknowledge the many individuals and organizations that made this research project possible. I would like to acknowledge the financial support provided by Missouri Department of Transportation (MODOT) as well as the RE- CAST (Research on Concrete Applications for Sustainable Transportation) Tier-1 University Transportation Center (UTC) at Missouri University of Science and Technology. I would like to express my full appreciation to the staff in the Center for Infrastructure Engineering Studies namely: Professor Kamal H. Khayat, Dr. Soo Duck Hwang, Jason Cox and Abigayle Sherman. I would thank my colleagues: Zach Russel, Farid Van Der Vurst, Aida Ley Hernandez, Iman Mehdipour and Meyyada Alabdulhady for your wonderful collaboration, constructive comments and emotional support.

In the last but not least, I would like to express my sincere appreciation and gratitude to my supportive husband, Soheil, who has enlightened my life with his support and love and inspiring me to follow my dreams. My Precious Daughter, Saina, who came through this journey from the day first and with her big smiles and LOVE help me go through hard days. I would like to extent my deepest appreciation to my parents, sister, and brother for their love, encouragement, and supports all through all my educational life.

TABLE OF CONTENT

Page

SECTION

PAPER

SECTION

LIST OF ILLUSTRATIONS

Page

SECTION

PAPER I

PAPER II

PAPER III

PAPER IV

LIST OF TABLES

Page

SECTION

PAPER I

PAPER II

PAPER III

PAPER IV

1. INTRODUCTION

1.1. BACKGROUND

Self-Consolidating Concrete (SCC) is a new type of a high-performance concrete demonstrating low flow resistance and sufficient stability of the constituent elements. In this way, high fluidity and deformability is ensured, enabling the concrete to flow through congested reinforcement or in formworks that induce difficult casting conditions. The initial use of SCC in Japan in the late 1980s was intended to improve the construction speed, ease its placement, eliminate the need for vibration, all resulting in an increase in durability of concrete structures.

SCC is though more sensitive to small changes in mix design and in the mixing procedure, compared to conventional vibrated concrete. Therefore, robustness is an important aspect when studying and optimizing rheological properties and workability of SCC. The robustness of concrete (or cement-based materials in general) is defined as the capacity of a mixture to retain its performance despite variations in the quantity and properties of the raw materials and mixing procedures that are inevitable when producing on any significant scale.

Extensive research on SCC has been performed in the last decades, but robustness of SCC is still one of the main shortcomings limiting practical implementation. Typically, small variations in the water content, through inaccuracies of the balances in the concrete production plant or small mistakes in the determination of the water content of the fine aggregate, is the most investigated parameter in robustness studies.

Therefore, there is a need to better understand the robustness of cement-based materials by varying a number of parameters, including the water and superplasticizer (SP) contents, mixing procedure (mixing time, mixing speed) and the addition time of superplasticizer. The robustness can be measured by variations in the rheological properties of the material, which can be performed immediately after mixing, and with increased elapsed time.

1.2. OBJECTIVE AND SCOPE OF WORK

The initial workability, thixotropy and workability loss over a certain period of time have significant effect on the construction process, and as a consequence, on the mechanical properties and the durability of hardened cement-based material. The workability of cement-based materials is related to the rheological properties of the fresh cement paste (FCP), mortar or concrete, which are highly controlled by the water-to-cement (W/C) ratio, the presence of supplementary cementitious materials and chemical admixtures, temperature, and aggregate quantities and properties.

The objective of this research is to evaluate the influence of the mixing (or shearing) procedure on the rheological properties of cement pastes with SCC consistency: both the initial properties and the evolution with time. Two flowable cement pastes are extracted from self-consolidating concrete mixtures proportioned according to two different design strategies: the powder type (more popular in Europe) and the VMA type mix designs, more popular in North America. The reasoning behind selecting paste and not concrete or mortar is to reduce material consumption, enhance the accuracy of the measurements and the ability to control temperature of the sample inside the rheometer.

The main purpose of the research is to understand the mechanisms governing how paste mix design factors (mainly water content and dispersing agent content), and mixing procedure (adding time of the admixtures, mixing speed (or applied shear rate) and mixing time), affect the rheological properties. In addition, during phase 1 of this research, it has been observed that delaying the addition of the SP in the VMA-type mix design has a larger effect on the yield stress and plastic viscosity than a change in water equivalent to 10 l/m^3 in the corresponding concrete. This change in water content is considered a tolerance limit for SCC in the European guidelines for SCC. A part of this research on the initial rheological properties was devoted to the sensitivity of cement paste mixtures to a delayed addition of SP, in which the influence of the type of supplementary cementitious materials or mineral fillers, w/cm, presence or absence of VMA and two different types of SP was investigated.

The second part of the research focuses on the workability loss of flowable cement pastes. Similarly to the initial rheological properties, the sensitivity of the time-variation of these rheological properties has been investigated. A similar set of parameters was employed as for the investigation on the initial rheological properties.

The third part of the research looks at the dependency of the rheological properties of cement paste with SCC consistency on the applied shear rate. The maximum applied shear rate has been increased from 12.5 s^{-1} to 25 s^{-1}, 50 s^{-1} and 100 s^{-1} to clarify the behavior observed during mixing and pumping. The relationship between plastic viscosity and yield stress subjected to different pre-shear values was investigated and different models have been evaluated.

1.3. RESEARCH SIGNIFICANCE

Self-Consolidating Concrete (SCC) is a relatively new type of high performance concrete which does not need any consolidation, allowing contractors to enhance construction speed and to re-allocate labors to other phases in the project. However, SCC has not yet applied significantly in the construction industry, partly due to its fresh properties sensitivity to small variations in the mix design and the mixing procedure (for example an unnoticed change in sand moisture content), especially compared to normal concretes. In collaboration with Ghent University in Belgium, the researchers evaluated the methods to enhance the robustness of SCC: i.e. to reduce the sensitivity of the properties to small changes in mix design and mixing procedure. While Ghent University investigated several moisture regulating additions (such as super-absorbent polymers), Missouri S&T researchers were investigating the influence of the mixing procedure on the properties of cement pastes with SCC consistency.

To determine the influence of the mixing procedure, the fresh properties of cement pastes with SCC consistency were confirmed by means of rheology. Rheology is defined as the science of flow of materials, and cement-based materials are usually identified by two parameters: the yield stress, which is the stress needed to start the flow, and the plastic viscosity, which indicates the stress needed to accelerate the flow. By varying amount of water, superplasticizer dosage, the mixing time, the mixing speed, the time of addition of the admixtures the most significant aspects of the mixing procedure influenced the rheology of cement pastes with SCC consistency has been investigated.

Combining the results from Missouri S&T and Ghent University, the research teams aim to develop guidelines for mix designs and mixing procedures to enhance the robustness of SCC. Thus the construction industry has more support to successfully develop and apply Self-Consolidating Concrete as an infrastructure material, either in the pre-cast or ready-mix industry, for new projects and repair applications. These results can be used in the construction, maintenance and repair of transportation infrastructure in both parts of the world.

1.4. OUTLINE OF THE DISSERTATION

The research results of parts 1 and 2 of the project are published (or accepted) in three journal publications. Results of the third phase are submitted. The dissertation is divided into four sections: introduction, literature review, results and discussion (as published), and conclusions and recommendations.

INTRODUCTION: this section presented a brief introduction to the research topics and explains the need for this research project and the scope of this research project.

LITERATURE REVIEW: A comprehensive literature review is presented on rheology and hydration of cement-based materials and on specific topics of interest towards the results and discussion.

RESULTS AND DISCUSSION: this section includes the content of four technical papers on the evaluation of different parameters affected on rheological robustness of the cement paste with SCC consistency. The initial rheological properties, the workability loss over time and effect of the maximum applied shear rate on rheology for cement pastes with SCC consistency have been evaluated. In addition, influence of the addition time of SP on robustness of cement pastes with SCC consistency on the robustness of rheological properties extensively has been investigated.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS: this section summarizes the relevant key findings of all research works, as well as recommendations for future research.

1.5. LIST OF PUBLICATIONS/SUBMISSIONS

Peer-reviewed Journal Articles

1. Asghari, A. A., Ley Hernandez, A. M., Feys, D., & De Schutter, G. (2016), “Which Parameters, Other than the Water Content, Influence the Robustness of Cement Paste with SCC Consistency?”, Construction and Building Materials, 124, pp. 95-103.
2. Asghari, A. A., Feys, D., De Schutter, G. (2018), “Mix Design Factors of Self-Consolidating Cement Paste Affecting the Magnitude of Variations in Rheological Properties Induced by the Addition Time of PCE-Superplasticizer”, Construction and Building Materials, 159, pp. 269-276.
3. Asghari, A. A., Feys, D., De Schutter, G. (2018), “Time Evolution of Rheology of Cement Pastes Affected by Mix Design and Mixing Procedure”, Accepted for publication in ACI Materials Journal.
4. Asghari, A. A., Feys, D. (2018), “Influence of Maximum Applied Shear Rate on the Rheological Properties of Flowable Cement Pastes”, Submitted to Cement and Concrete Research.

Conference Proceedings

1. Asghari, A. A., Feys, D., De Schutter, G. (2017), "Sensitivity of Workability Loss of Flowable Cement Paste to Small Changes in Constituent Elements and Mixing Procedure ", ACeRS, Atlanta, Georgia.
2. Asghari, A. A., Feys, D., "Influence of applied maximum shear rate on rheological properties of cement-paste with SCC consistency", Washington DC, USA 15-18 May 2016 Edited by Kamal H. Khayat, 473.
3. Asghari, A. A., Feys, D., De Schutter, G. (2014), "Influence of the Addition Time of Superplasticizer on the Rheological Properties of Self-Consolidating Cement Paste", 5th Advances in Cement Based Materials, Cookeville, Tennesse

2. LITERATURE REVIEW

Self-Consolidating Concrete (SCC) is known as a highly flowable concrete: the concrete of the future which spreads into place under its own weight, reaches proper consolidation without vibration, and, at the same time, presents a sufficiently homogeneous material that resists segregation. The SCC mix design is typically characterized by high binder content; use of SCMs and/or fillers and low ratio of water-to-cementitious materials (w/cm), when comparing to more conventional concrete mixtures.

Three mix design methods have been presented for SCC, which combine such high fluidity with an adequate stability:

- Powder type SCC (popular in Europe), in which a superplasticizer (SP) produces the proper fluidity and a high amount of SCM or fillers (typically 550 to 650 kg/m3) prevents the static segregation of the aggregates. Static segregation of aggregate known as vertical separation of Cement paste and coarse aggregate while the concrete is at rest before setting
- Viscosity Modifying Admixtures (VMA) type SCC, in which superplasticizers disperse the cement particles to establish the sufficient fluidity. The powder content of a VMA type SCC is around 350 to 450 kg/m^3, but the addition of VMA to the mixture creates the segregation resistance. Segregation in concrete determined as separation of some size groups of aggregates from cement paste by American Society for Testing and Materials

- Combination type SCC (popular in North America), in which intermediate powder content (450 to 550 kg/m^3) is combined with the use of a VMA and superplasticizers in order to acquire a mixture with the proper fresh and hardened properties.

Unlike normal concrete, SCC properties are no longer related to the consolidation quality or the labor skills. But instead, the fresh properties of SCC are more sensitive to small variations in mix design, properties of the constituent elements, the mixing procedure and casting process. This can have significant consequences on the final performance of the concrete. SCC technology is mainly being applied in the pre-cast industry. However, in the ready-mix industry, the application of SCC is slowed down due to an increased number of variables that can have a significant influence on the flowability of the concrete being delivered, which are mainly enhanced transportation time and exposure to high or low temperatures. This research project investigates the robustness of SCC mixtures subjected to variations in mixing procedure and addition sequence of the materials.

Based on the mentioned parameters (mixture design and selection of material constituents), which can significantly affect the robustness of SCC, an extensive literature review undertaken in this thesis consists of:

- Reviewing the different aspects that can affect the workability of cement pastes with SCC consistency by considering the fundamental aspects of rheology of colloidal and non-colloidal suspensions, their interactions, and their dispersion properties.
- Reviewing the hydration of cement clinkers in the early age and the effect of different SCM such as silica fume and fly ash on the cement compounds hydration.

. Addressing parameters such as mix design, mixing procedure and material properties influencing robustness of initial rheological properties of flowable cement pastes and workability loss of flowable cement paste over time.

2.1. RHEOLOGY OF SUSPENSIONS

2.1.1. Introduction to Colloid Science and Rheology. Colloid generally references to the dispersed phase of two-component system that are noticed by an optical microscope hardly. In addition, thermal forces influence their motion. Hunter (1981) mentioned the ancient Egyptians and Chinese used lampblack and natural polymer mixtures as inks that is a first case of manmade colloidal dispersions.

Macosko (1994) suggested a size range from $\sim 1\ nm$ (10^{-9} m) to – 1 μm (10^{-6} m) for colloidal particles. While the smaller size limit is required to consider the suspending medium as a continuum on the time and length scale of colloidal motion, the upper size limit is critical to observe thermal forces in defining the colloidal particles motion.

2.1.1.1. Individual colloids forces. Mewis et al. (2012) demonstrated the fundamental unit of energy in the colloidal is Thermal energy. The thermal energy has been defined as the $k_B T$, where k_B is Boltzmann's constant (1.381×10^{-23} JK^{-1}) and T is the absolute temperature (K).

The colloidal particle forces considered as Brownian force, is defined in terms of the thermal energy as

$$F^B = k_B T/a \qquad (2.1)$$

For a particle with radius a =1 μm, the colloidal particle force is on the order of 4×10^{-15} N.

Perrin (1916) evaluated the motion of Colloidal particles (also named Brownian particles). The colloidal particles move permanently in a random pattern because of Brownian force. As particle size decreases, Brownian motion plays more important role compared to other forces.

2.1.1.2. Colloidal interactions. Hiemenz et al. (1997) investigated the effect of fluctuating polarization on the colloidal particles. The electron cloud polarization of one atom by the fluctuating electron cloud of another atom lead to dispersion forces that is the interaction between atoms and molecules. An attractive force between the atoms has been induced by this fluctuation polarization, most of the time. The similar effect has been observed in Colloidal particles whereby the atoms of one colloid particle create polarization in the atoms of another colloidal particle. The fluctuating polarization influence is described as the London-van der Waals force between the particles. A plot of the London-van der Waals force is shown in Figure 2.1 (dashed line).

For two spherical colloidal particles with radii a_1 and a_2, with separation *r* between particle centers, the potential (London-van der Waals force) is presented as:

$$\phi^d(r) = -\frac{A}{6}\left(\frac{2a_1a_2}{r^2-(a_1+a_2)^2}+\frac{2a_1a_2}{r^2-(a_1-a_2)^2}+\ln\frac{r^2-(a_1+a_2)^2}{r^2-(a_1-a_2)^2}\right) \qquad (2.2)$$

The Hamaker constant, the coefficient A, is a function of the particles material as well as that of the suspending medium (and, in the full theory, can also related to the separation distance). Limits range from about 30×10^{-20} J, for gold particles in water, to an amount of the order of 1×10^{-20} J or less, for inorganic and polymeric particles. Flatt et al. (2003) presented that the Hamaker constant for tricalcium silicate, C_3S, a major component of Portland cements of 4.55 x 10-6 J/mol.

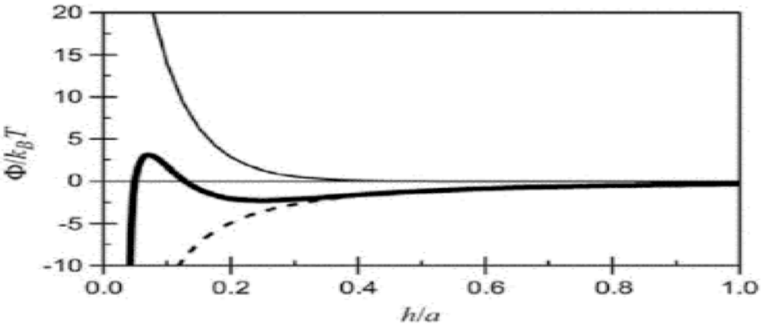


Figure 2.1.Interaction (DLVO) force for spherical colloid particles. The total force present as solid line, constitue of the London-van der Waals force (dashed line) plus the electrostatic force, (thin line)(Mewis et al. (2012)).

Hiemenz et al. (1997) described the electrostatic potential in colloidal particles. A double layer of positively charged counter ions covering a negative charges surface have been illustrated in Figure 2.2. The thick line in Figure 2.2 presents the electrostatic potential.

The two colloidal particles interact in close distance where their respective electrostatic fields overlap (Figure 2.3). Each colloidal particle considers electro-neutral with its associated counter-ions. In solution, the osmotic repulsion increases because of the excess number of ions in the surrounding double layer. This osmotic pressure neutralizes this overconcentration of counter-ions and the colloidal particles will be repelled from each other

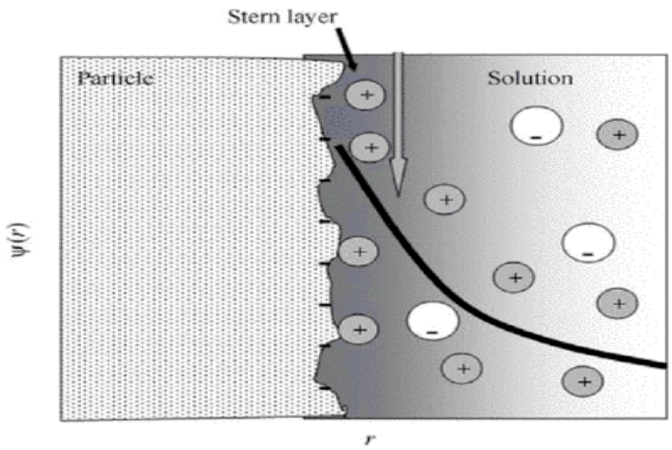


Figure 2.2. A double layer schematic in solution at the surface of a colloidal particle [Hiemenz et al. (1997)].

Derjaguin et al. (1941) and, independently, Verwey aet al. (1948) discovered the linear addition of the dispersion attraction potential to the electrostatic repulsion potential to describe the complicated behavior of colloidal dispersions. Figure 2.1 depicts the combined potential, the DLVO potential $\phi^{DLVO} = \phi^{d} + \phi^{el}$, for a typical system. The combined curve displays, with enhancing separation distance, an initial minimum, an electrostatic barrier, and a secondary minimum. Particles that are originally separated experience a long-range attraction. The particles will flocculate if the secondary minimum is adequately deep. This secondary flocculation is reversible, by means of shear.

Maranzano et al. (2000) investigated the steric repulsions induced by grafted or adsorbed polymers. It shown that grafted polymers can provide thermodynamic stability

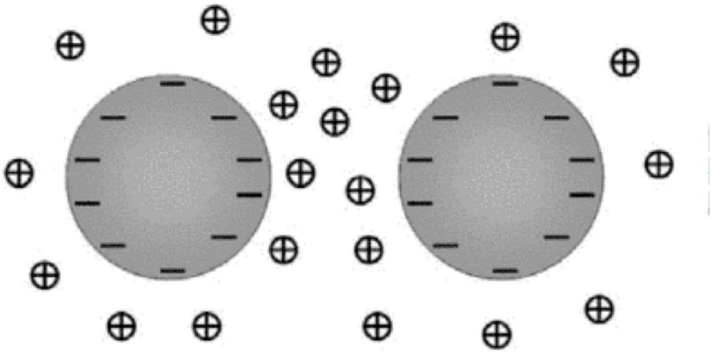


Figure 2.3. The corresponding ion distribution presented in two similar colloidal particles

to dispersions. Conceptually, an end-grafted polymer brush as an end-grafted polymer brush system, depicted in Figure 2.4. With sufficient graft density and molecular weight, particles can be prevented from aggregating by the steric repulsion. The absolute value of the potential induced by the polymers is not a uniform reduction function of the inter-particle distance. In contrast to the van der Waals forces and the electrostatic repulsion potentials, steric hindrance presents a more abrupt change from its characteristic value near the particle surface, to zero at a particle distance equal to the effective length of the polymers and is a purely geometrical phenomenon.

2.1.2. Hydrodynamic Effects. Hydrodynamic interactions have been described as follow: when the Particles move, they involved in a fluid excite flows, and similarly move in reaction to fluid motion.

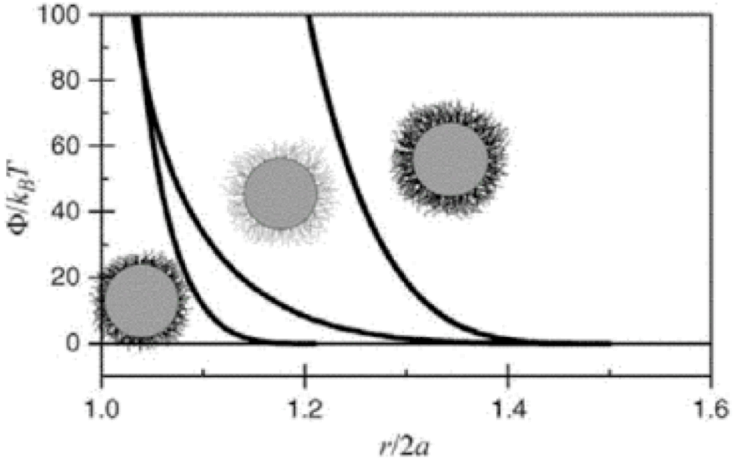


Figure 2.4. Potential of interaction because of steric repulsion between grafted polymer brushes of different length and different graft density. (Maranzano et al. (2000).)

By creating and reacting to a fluid's local velocity, particles undergo hydrodynamic interactions with each other and with the walls of their container. Hydrodynamic effects observe in both colloidal and non-colloidal particles. Non-colloidal particles have been characterized in dimensions of a few micrometers or more. In suspensions of non-colloidal particles, the contributions to the suspension stress from Brownian motion and from interparticle forces such as electrostatic interactions can be neglected.

2.1.2.1. Viscosity of dilute suspensions. The existence of particles distorts the flow field and hence can be expected to enhance the energy decadence during flow, and therefore the increase in the viscosity. In suspension rheology, evaluating a dilute suspension of spherical particles is the easiest problem.

Einstein (1956) calculated the energy dissipation in a sphere of radius R around the particle, as R→∞ by equation 2.3. Only the flow field close to the surface of the particles requires to be known to calculate the additional energy dissipation created by the presence of particles. This equation can be applied to other heterogeneous systems.

$$\eta = \eta_m(1 + 2.5\,\phi) \qquad (2.3)$$

The suspension viscosity is in proportion to the viscosity of the suspending medium. As the system is dilute and particles do not interact together, the contributions of the individual particles are additive and the viscosity is linear in particle concentration. Only the particle volume fraction enters the equation while the size of the particles is not relevant because absolute length scales do not enter the equation. The factor 2.5, calculated by Einstein (1906) is only valid for special conditions: no slip at the particle surface, spherical particles, and absence of particle interactions.

2.1.2.2. Semi-dilute suspensions. The principle of dilute suspensions and Equation (2.3) is only applied as long as interactions between particles can be neglected, which is the case with very low volume fractions (lower than 0.05). Consequently, this equation cannot be applied to most commonly used suspensions, which in general have much higher particle concentrations (up to a volume fraction of 0.1 to 0.12). The average distance between particles is approximately equal to their average diameter at particle volume fractions of about 0.1. A second particle placed within one particle diameter of the original particle will face a distorted flow field because of the presence of the reference particle. In fact, the flow field around both particles will be dramatically changed, and this acts to alter the energy dissipation rate. Batchelor et al. (1972)

presented that the influence related to the interaction between couple of particles is proportional to the square of the particle concentration or volume fraction:

$$\eta_r = 1 + 2.5\,\phi + c_2\phi^2 + c_3\phi^3 + \cdots \qquad (2.4)$$

The coefficient c_2 of the quadratic term depends on not only contributions from hydrodynamic particle interactions, but also the direct interparticle forces.

2.1.2.3. Concentrated suspensions. Mewis (2012) considered spherical particles with volume fractions of more than 0.15 as concentrated suspension. Enhancing the volume fraction results to a more rapid increase in viscosity and, finally, the formation of a paste or solid.

Concentrated systems of non-colloidal particles are a complicated problem due to evaluation of many-body hydrodynamic interactions.. In order to resolve the many-body hydrodynamic interactions, different researchers perform particle simulations using various levels of approximation, from Stokesian by Brady et al. (1988) and Sierouand (2001), lattice Boltzmann by Lad (1994) and Chen et al. (1998) or dissipative particle dynamics by Martys (2005), through to extremely intensive methods employing boundary integral representations by Kim et al. (1991)

Brady et al. (1997) presented particle simulations to evaluate the trajectories of a relatively small number of particles by solving the equations of motion concluding hydrodynamic interactions. By eliminating Brownian motion, Simulations present hydrodynamic forces is a singularity Ball et al. (1995) demonstrated by increasing the particle volume fraction, the particles dramatically cluster together. Dratler et al. (1996) simulated a short-range repulsive force to exist between the particles to avoid clustering. . In fact, a type of shear ordering at high packing fractions has been observed in simulations for non-Brownian suspensions of spheres. Sierou et al. (2002) reported a flow-induced string formation at volume fractions above 0.50.

Chong et al. (1971) presented the viscosity in concentrated suspensions as a maximum volume fraction. Viscosities increase rapidly when increasing the volume fraction. Maximum volume fraction ϕ_{max} is a good scaling factor for the viscosity-concentration curves of suspensions as has been shown in Figure 2.5 .The actual value of ϕ_{max} depends on shape, size distribution, and packing protocol. The maximum volume fraction range from 0.524 by Shapiro et al. (1992) to 0.71.by De Kruif et al. (1986) for colloidal particles.

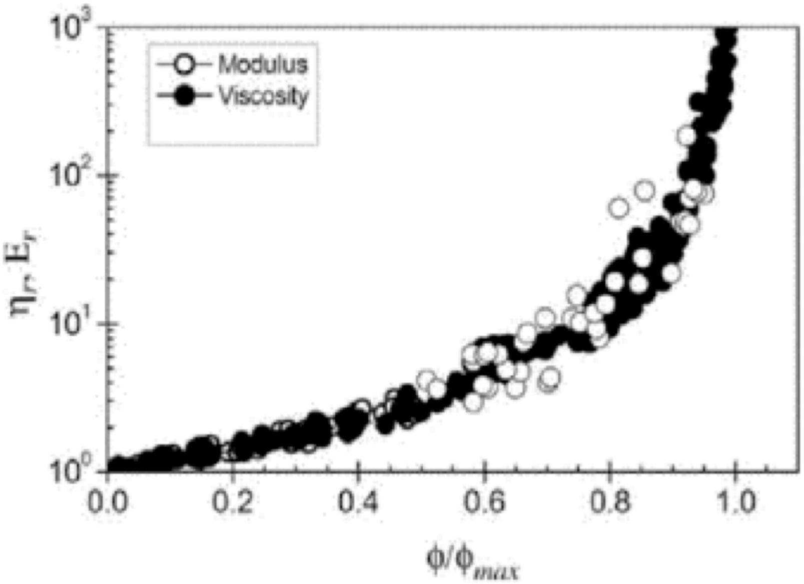


Figure 2.5. Reduction of the concentration dependence of the relative viscosity η_r and the relative elasticity modulus E_r, using the maximum packing (Chong et al. (1971)).

Scott et al. (1969) and Torquato et al. (2000) computed the Random close packing (RCP) for identical spheres. RCP is a good measurement to estimate realistically the highest volume fraction that still flows. By compacting particles and by computations a value of approximately 0.64 is presented for random close packing of identical spheres. Doney et al. (2004) presented that the densest packing density can't be obtained for monodisperese particles with spherical particles

Brady et al. (2001) explained the physical mechanism behind the strong increase in viscosity with volume fraction. It has been attributed to lubrication hydrodynamics acting between particles in close proximity. At high volume fractions, many-body interactions become more and more important, but are more difficult to calculate.

2.1.3. Shear Thickening. Williamson et al. (1931) presented the "Inverse plasticity" concept. Inverse plasticity was a term applied to explain a common property of coatings, such as paints and inks, where increasing the rate of shear results in an enhancement of the viscosity of the dispersion. Figure 2.6 is an example of industrial data on cornstarch, where Newtonian, "plasticity" and "inverse plasticity" behaviors are observed. Results for curves labeled V–IX present a shear thickening of material that, pass a certain critical rate or applied load, simply flow slower. Early work identified conditions (such as suspending media and starch concentrations) required to realize this response and their influence on the supposed critical rate of flow at the onset of the limiting response.

Bossis (1989) investigated the viscosity of concentrated dispersions as a function of Péclet number. The relative viscosity was divided into the hydrodynamic and thermodynamic (Brownian) part, as a function of the Péclet number, shown in Figure 2.7, The Péclet number, given in equation 2.5,expresses the relative influence of hydrodynamic forces to Brownian forces.

$$P_e = \frac{\eta_s . \dot{\gamma} . a^3}{k_B . T} \qquad (2.5)$$

Where $\dot{\gamma}$ presents shear rate (1/s), η_s is suspending medium apparent viscosity (Pa s), a is radius of particle (m), k_B is Boltzmann's constant and T presents the temparature (K).

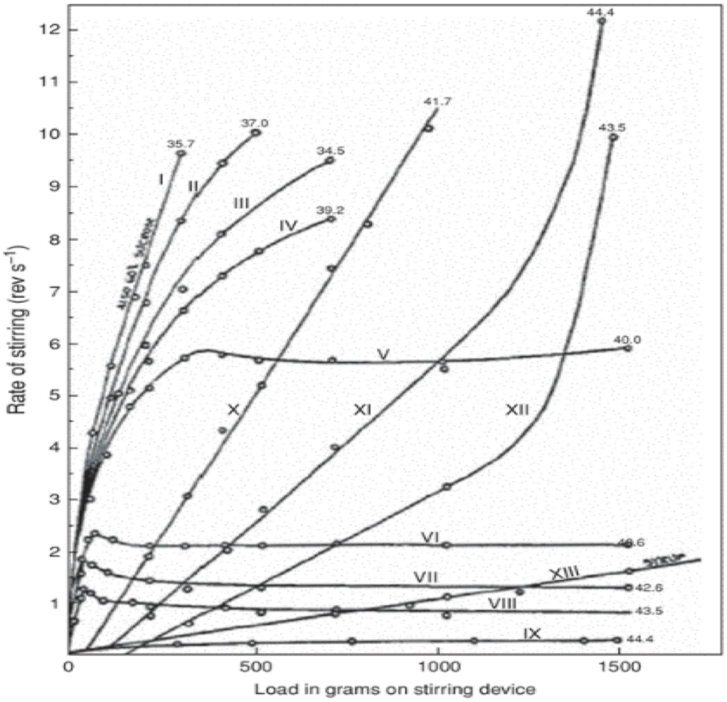


Figure 2.6. Viscous curves for cornstarch (Williamson et al. (1931))

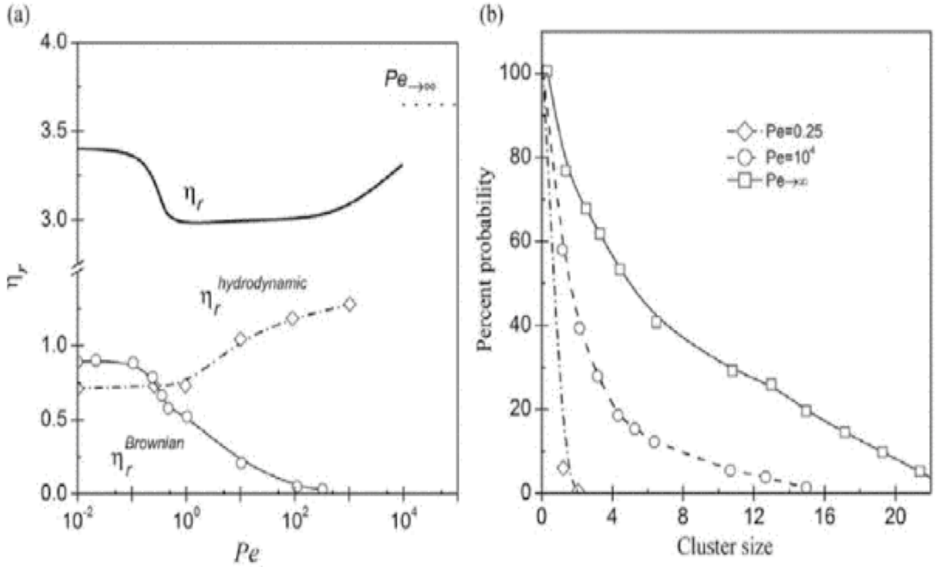


Figure 2.7. (a) The shear viscosity as a function of P_e; (b) particles percentage in clusters with a specific number of particles (Bossis (1989)).

Particularly, at $P_e \sim (1)$, the sample demonstrates shear-thinning behavior, while with increasing the shear rate; the viscosity increases to an amount higher than its low shear amount. Three sets of results have been shown that the shear thickening viscosity is controlled by the hydrodynamic component of the viscosity in P_e higher than 1, while the low $P_e$viscosity is controlled by the Brownian forces.

Laun (1984) investigated the effect of particle concentration on rheological behavior of colloidal dispersions. At low concentrations, the dispersion viscosity is nearly independent of shear stress [Figure 2.8] while increasing particle concentration influences both the low and high shear rheology of colloidal dispersions, but in various ways. While colloidal interactions result in enhancing high shear viscosity, application of low shear

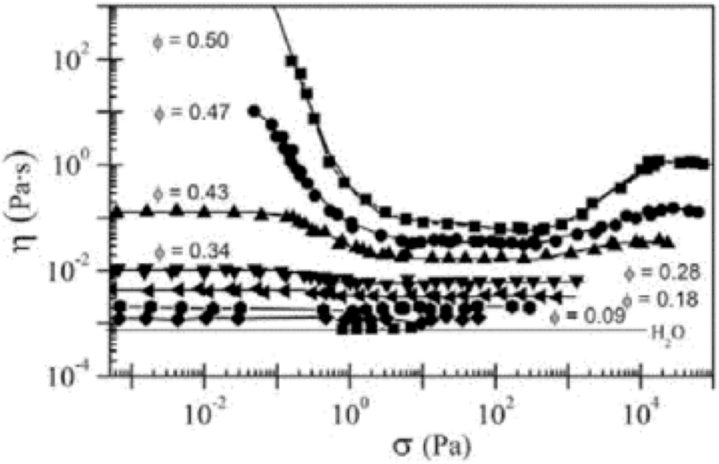


Figure 2.8. Shear viscosity of colloidal latex particles in water versus applied shear stress as a function of particle volume fraction (Laun (1984)).

stress results in shear thinning as the distortion of the equilibrium structure by flow leads in fewer particle interactions (collisions).

Mewis et al. (2012) illustrated the colloidal microstructural change in different shear rate in Figure 2.9 where the particles are organized and flow with fewer interparticle encounters. However, shear thickening happens when the shear forces become adequate and particle motion get strongly correlated as particles get in close proximity.

Maranzano et al. (2001) recognized these new correlated categories of particles as hydrodynamic clusters or “hydroclusters” for short. This self-organized or flow-organized microstructure is the consequence of the lubrication hydrodynamic interactions. The hydroclusters are not aggregates or coalesced particles.

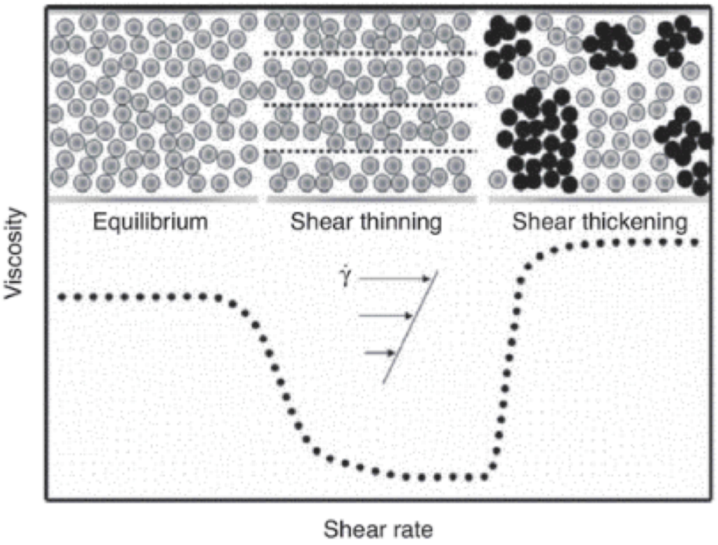


Figure 2.9. The connection between colloidal microstructure and shear viscosity. The dark particles demonstrate hydroclusters. (Mewis et al. (2012).

2.1.4. Diffusion or Migration. Ramachandran et al. (2007) demonstrated the particle migration in an inhomogeneous flow field established in viscous suspensions. One type of migration happens when a difference in shear rate has been observed. This event presents an important issue in both rheological measurements and the actual processing of suspensions. Gadala-Maria et al. (1980) observed that, the apparent viscosity of a suspension with non-colloidal particles, slowly reduced by time during shearing during viscosity measurements in a coaxial cylinder rheometer. Leighton et al. (1987) described that particles migrated to the bottom of the cup, where the suspension was almost static. The apparent reduction in viscosity is caused by the decrease of the particle concentration in the annular gap. This shear-induced migration was observed, by

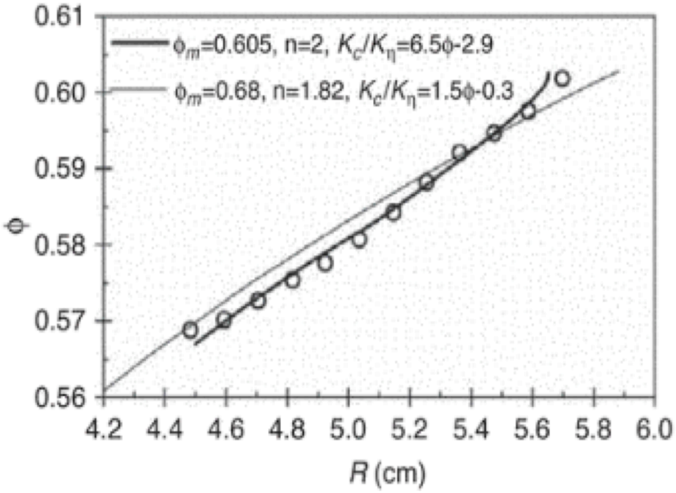


Figure 2.10. Comparison of measured concentration profiles in Couette flow (circles) (Ovarlez et al. (2006)).

Sinton (1991) and Hampton et al. (1997) in pipe flow, Lyon et al. (1998) in channel flow, Chow et al. (1994) in parallel plates and Tetlow et al. (1998) and Shapley et al. (2002) in coaxial cylinders. Ovarlez et al. (2006) investigated the migration induced by shear. As shown in Figure 2.10, the particles migrate from the zones of high shear rate to low shear rate, which creates a concentration gradient. Thus particle migration has to be considered in measurements of suspensions including non-Brownian particles.

2.1.5. Inertial Effects. Mewis et al. (2012) presented that Fluid inertia can be neglected in the flow where the Reynolds number is sufficiently small. For any fluid, including suspensions, a global Reynolds number can be defined as:

$$R_e = \rho \, V \, D/\eta \qquad (2.6)$$

Where V is a characteristic velocity of the system (usually the average velocity) and D is a characteristic dimension of the flow geometry, e.g., the pipe diameter in case of pipe flow or the depth of a two-dimensional channel.

In the case of suspensions, the slow flow condition also has to be satisfied at the particle length scale, which implies a sufficiently small particle Reynolds number that defined as:

$$Re_p = \frac{\rho_s . \dot{\gamma} . a^2}{\eta_s} \qquad (2.7)$$

Where Re_p is Particle Reynolds number (-), ρ_s presents the density of the suspending medium (kg/m^3), $\dot{\gamma}$ is the applied shear rate (1/s), a is radius of particle (m) and $\eta_s$is the suspending medium's apparent viscosity (Pa s).

Segree et al. introduced the tubular pincher Segre-Silberberg effect. Inertia results in additional migration effects. Particles that flow parallel to walls can be subjected to a side (or "Lift") force that leads them to move away from the wall. For a dilute suspension in pressure-driven tube flow, this event causes to the so-called tubular pincher Segre-Silberberg effect [71] which all particles in tube gathered on a ring with radius 0.6*R*, where *R* is the tube radius. Matas et al. (2014) reported that by enhancing Reynolds number, the ring of high concentration alters towards the wall, and the appearance of a second, inner ring has been observed.

2.1.6. Sedimentation. Nguyen et al. (2005) investigated the sedimentation of suspension at low Reynolds number. Under gravity, particles denser than the suspending medium settled and induced difference in particle concentration. A single particle, or particles in a dilute suspension, can settle with a velocity given by Stokes' law:

$$V_{s,0} = \frac{2a^2 \Delta\rho g}{9\eta_m} \qquad (2.8)$$

Where $\Delta\rho$ is the difference between the densities of particle and fluid and g is the gravitational constant. A particle Reynolds number $Re_p << 1$ is assumed in this equation.

Nguyen et al. (2005) concluded that the sedimentation results are sensitive to some parameters of the system, such as particle size distribution and the settling instrument geometry and size.

2.2. HYDRATION

2.2.1. Tricalcium Silicate Hydration. Kurdowski et al. (2014) mentioned the importance of the tricalcium silicate hydration. More than 60% of Portland cement clinker constitute of tricalcium silicate Furthermore, the tricalcium silicate hydration model considered as a fine model of cement reaction with water.

During reaction of tricalcium silicate with water the calcium silicate hydrate (C–S–H) and calcium hydroxide (CH) is formed. This reaction is presented by the following equation:

$$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH \qquad (2.9)$$

Jawed et al. (1983) demonstrated a microcalorimetric curve of C_3S in isothermal conditions, the calcium ions concentration and the hydrated phases (Figure 2.11). The following stages determined on the calorimetric curve, specifically: the pre–induction (I), induction (II), Increase of hydration rate (III), reduction of hydration rate (IV) and small hydration rate (V) respectively**.**

The following hypotheses are presented to describe the incident of the induction period:

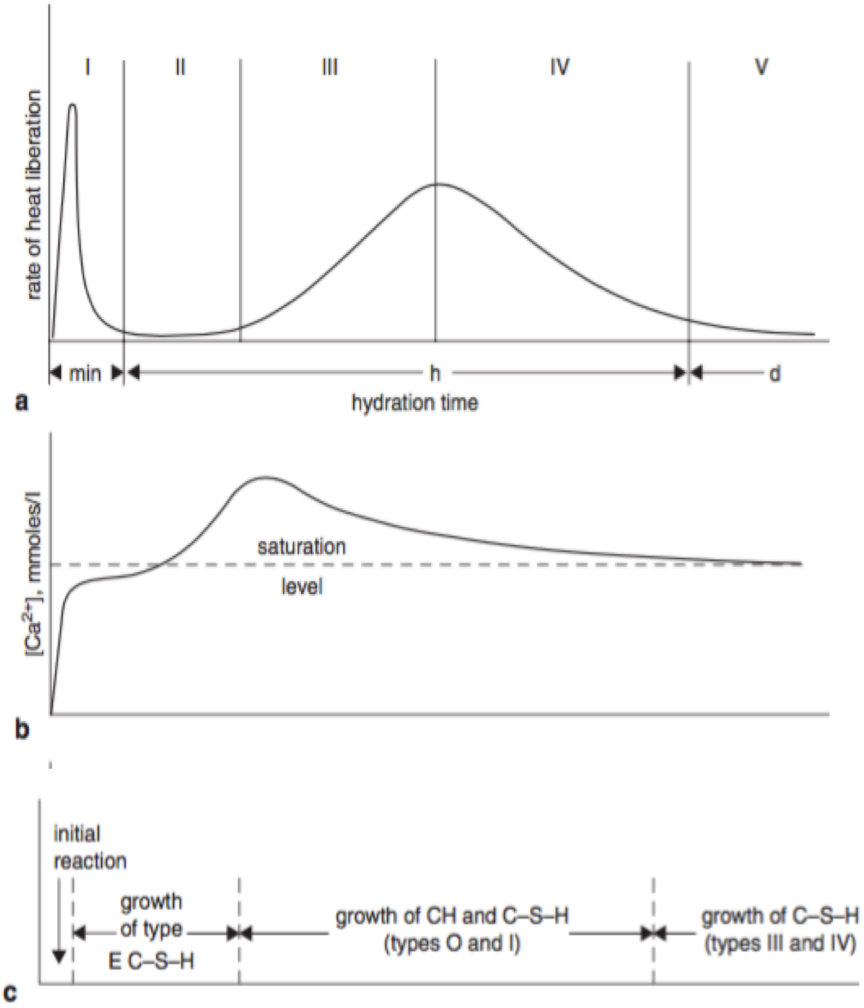


Figure 2.11. (a) Microcalorimetric curve of C_3S (**b**), varation of Ca^{2+} ions concentration in the water (**c**) hydrates development (Jawed et al. (1983)).

- Calcium hydroxide and calcium silicate hydrate Nucleation,
- Deficiently permeable calcium silicate hydrate layer Formation,
- Solution Supersaturation related to calcium hydroxide.

- Barret et al. (1980) and Kurdowski et al. (1986) have shown that the calcium silicate hydrate nucleation happens very fast because of the quick decrease of silica concentration in solution. Acceleration of C-S-H nucleation because of the addition of CH nuclei, does not eliminate the induction period.

De Jong et al. (1967) proposed the hypothesis regarding the induction period. Induction period, the low permeable C–S–H layer that has a gel structure precipitated on the surface of C_3S..In addition, Fuji et al. (1974) and Ménétrier et al. (1979) observed the C–S–H layer on the C_3S surface. At first the nuclei reveal in spherical forms (primary C_3SH hydrate) that thereafter altered to the C–S–H II made the barrier layer. Finally the secondary C-S-H changed to the low C/S ratio hydrate (C/S= 0.8–1.5). In the lower C/S ratio, hydrate is more penterable and concluded to end of induction period. Double et al. (1980) investigated the osmotic pressure as a factor for finishing the induction period. As shown in Figure 2.12, the impermeable layer of C-S-H broke up under osmotic pressure complete the induction period stage.

Kurdowski (2014) reported hydration of a few percent of C_3S at the end of induction period. The enhanced reaction rate that begins after the induction period is strongly related to the sample fineness and the defects degree in C_3S structure. Ménétrier et al. (1979) reported the varying forms of C-S-H phase (Table 2.2). With concurrent change of C–S–H II to C–S–H I (fibers), The hydration of tricalcium silicate begins at high speed. CH reveals both on the C_3S surface and in the pores.

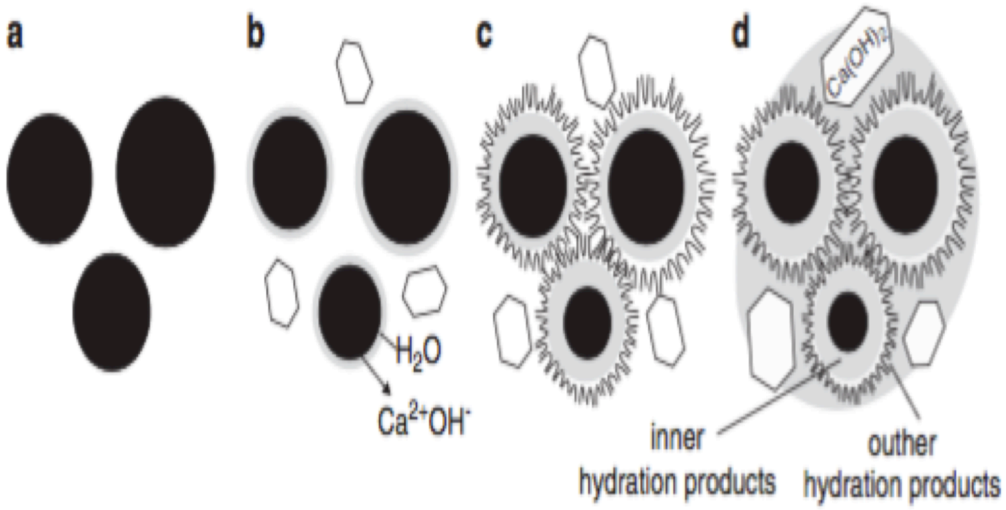


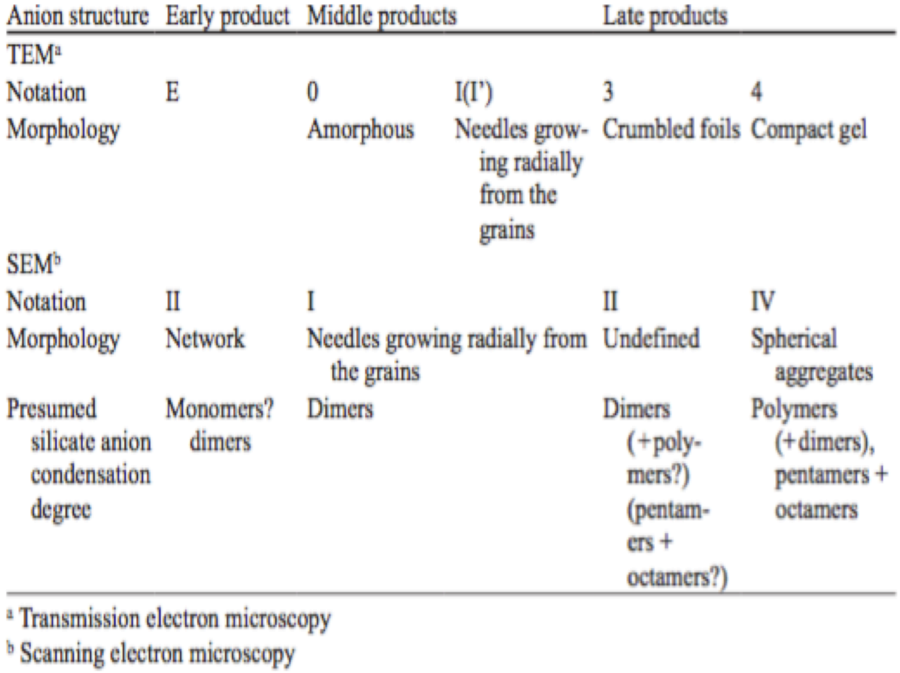
Figure 2.12. The cement hydration scheme (Double et al. (1980)): (**a**) cement particles in water, (**b**) formation of gel structure on cement particles, (**c**) gel structure break by the osmotic pressure and the development of C–S–H II gel, (**d**) pores in the paste occupied by gel formation.

2.2.2. Dicalcium Silicate Hydration. Kurdowski (2014) determined that the hydration of C_2S happens analogously and can be presented as follow:

$$2\ C_2S + 4H \rightarrow C_3S_2H_3 + CH \qquad (2.10)$$

Benstead et al. (1983) explained that the rate of C_2S hydration is substantially slower compared to C_3S while the mechanism of reaction is similar to C_3S. After 24 h hydration, the C_2S surface is similar to the C_3S surface after 5 min hydration. The different C_3S and C_2S structures caused the low hydration rate in C_2S. As a consequence, the large calcium hydroxide crystals observed, even though the calcium silicate hydrate morphology is the same as C_3S

Table 2.1 C–S–H phases (Ménétrier et al. (1979).



Anion structure	Early product	Middle products		Late products	
TEM[a]					
Notation	E	0	I(I')	3	4
Morphology		Amorphous	Needles growing radially from the grains	Crumbled foils	Compact gel
SEM[b]					
Notation	II	I		II	IV
Morphology	Network	Needles growing radially from the grains		Undefined	Spherical aggregates
Presumed silicate anion condensation degree	Monomers? dimers	Dimers		Dimers (+polymers?) (pentamers + octamers?)	Polymers (+dimers), pentamers + octamers

[a] Transmission electron microscopy

[b] Scanning electron microscopy

2.2.3. Hydration of Tricalcium Aluminates. Kurdowski (2014) reported that the highest rate of reaction with water among the clinker phases belongs to tricalcium aluminate. As a consequence, tricalcium aluminate affects the initial rheological properties of cement paste. The gel products are produced very quickly and thereafter crystallize as a mixture of the two phases: H_8 and C_4A H_{13} respectively. These products have covered the C_3A grains and further hydration happens as a consequence of diffusion of ions through this layer.

Jawed et al. (1983) showed the microcalorimetric curve and the mechanism of this process schematically in Figure 2.13. An induction stage is poorly distinguishable in the calorimetric curve after a rapid reaction with water. Ramachandran (1973) attributed this event to the hexagonal hydrates layer formation. When the hexagonal hydrates layer break down during changing to the cubic $C_3A\ H_6$, C3A hydration no longer was interrupted by the hexagonal hydrates layers. This process related to the high heat of C_3A reaction with water and as consequently the paste temperature increase immediately.

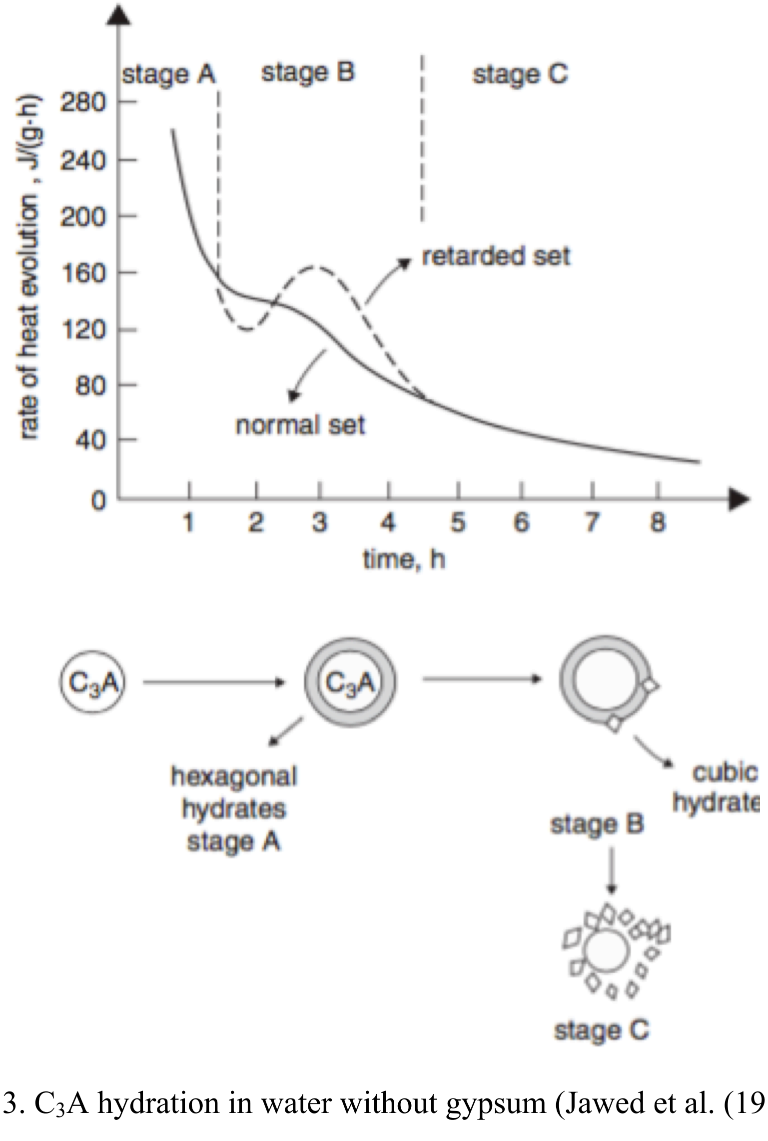


Figure 2.13. C_3A hydration in water without gypsum (Jawed et al. (1983)).

2.2.4. Effect of Calcium Carbonate. Stober et al. mentioned that the application of limestone in cement production was popularize in France and in Poland at first. Pollmann (1989) Pollmann et al. (1997) performed a substantial amount of research to evaluate the influence of calcium carbonate on hydration of cement. Glasser et al. (1985) examined the, limestone as inert filler; nevertheless, calcium carboaluminate hydrates formation verified the reaction between calcium carbonate and aluminates. Brown et al. discussed the consequence of low $CaCO_3$ dissolution rate. The consequences are the existence of reaction products in the narrow interface area and the reduction of induction period.

2.2.5. Consequence of Fly Ash on the Cement Clinkers Hydration. Takemoto et al. (1980) reported that the hydration of fly ash with the C_3S is complicated. It observed the delays of the C_3S hydration at stages I and II with presence of fly ash and acceleration of the C_3S hydration at stage III and later. Mohan et al. investigated the effect of fly ah on hydration of C_3S. The hydration of C_3S in presence of 30 % fly ash, investigated at a W/C ratio of 0.5. The XRD method applied to determine hydration degree of C_3S. The hydration degree of C_3S without fly ash after 24 hours was 35 %, while the blends with fly ash shown a hydration degree of 45%. It can be concluded that including fly ash increase the C_3S hydration at stage III. Skalny et al. (1980) and Plowman et al. (1984) reported that the hydration of C_3A has been delayed by fly ash. The retardation degree can mostly be related to the amount of sulphate in fly ash and potential of calcium adsorption.

2.2.6. Influences of Silica Fume on Cement Components Hydration. Stein et al (1964) reported the acceleration of the C_3S hydration in the cement-silica mixture with

20% by weight of silica fume. fine amorphous silica with a Brunauer–Emmett–Teller (BET) surface area of close to 200 m^2/g decreases the dormant length and enhances the magnitude of the second peak in the calorimetric curve because of the reduction of Ca^{2+} and OH$^-$ concentration in the water dispersion and the pastes. Beedle et al. (1989) identified the decrease of induction stage in cement-silica fume mixtures with silica fume a range of 50–380 m^2/g specific surface area. When the silica fume with smaller surface area near 19 m^2/g was applied, the induction period did not decreased. Figure 2.14 presents that at first; the second peak magnitude enhanced by enhancing the silica fume fineness, while is reduced at very high surface areas.

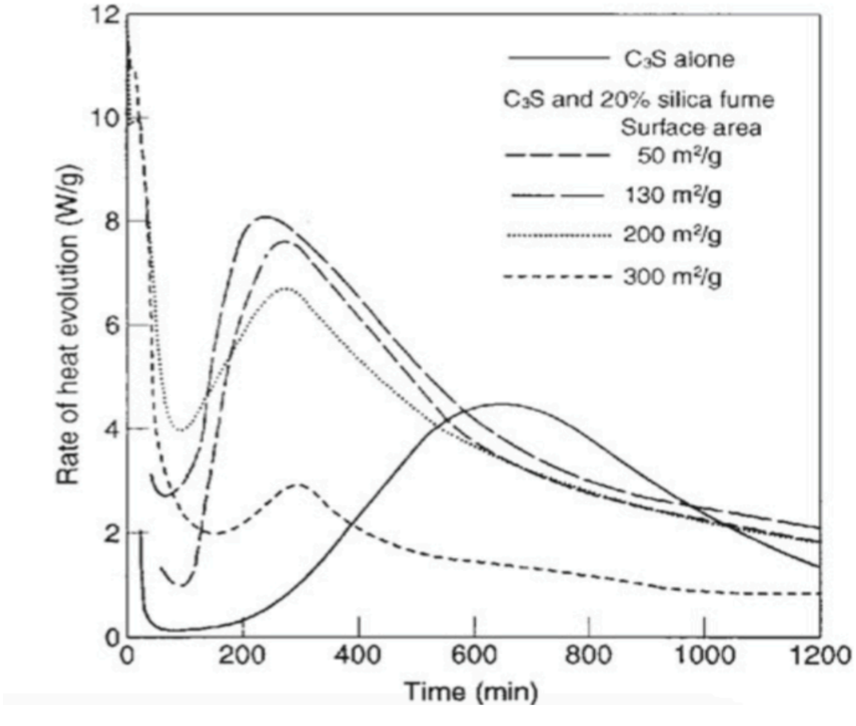


Figure 2.14. Calorimetric curves for the C_3S in presence of silica fume, comparing different surface area (Beedle et al. (1989)).

2.3. RHEOLOGY OF FRESH SCC

2.3.1. Robustness of Initial Rheological Properties of Flowable Cement Pastes. The robustness is defined as the capacity of a mixture to tolerate changes and variations in materials and procedures, including temperature, that are inevitable when producing on any significant scale, and to retain its fresh properties until placing. Robustness of SCC depends on the mix design, the mixing procedure and the use of the concrete.

2.3.1.1. Material proportions. Fluctuations in the water content appear to dominate robustness. According to Li and Kwan divided the water in fresh concrete into two parts: the filling water which fills the voids between the solid particles, and the excess water which forms a water film on the surface of the solid particles and contributes to the fluidity of fresh concrete. Billberg (2011) reported that As the amount of excess water in a mixture increases with a higher water-to-cement ratio (w/cm) or the use of a less water-demanding powder, the robustness of a mixture increase. Krieger (1972) developed the Krieger-Dougherty model that explain this observation: as the amount of excess water increases, the packing density decreases and hence the inclination of the Krieger- Dougherty curve decreases, which corresponds to a lower sensitivity to changes in the amount of excess water. However, Kwan et al. (2009) reported an increase in w/cm cause a decrease in robustness, which contradicts the theory explained above. Billberg et al. (2008) used two different w/cm in two powder-type SCC mix designs and Kwan et al. (2009) used three w/cm in two powder-type SCC mix compositions.

2.3.1.2. Material properties. Naji et al. (2011) and Haldenwang et al. (2011) stated that the use of a different SP or VMA type, or changing admixture producer, could have a major impact on the robustness of a mix composition. Billberg et al. (2008) reported that some types of VMA are more efficient in improving the robustness than others and some types of VMA even decrease the robustness of the mix design. Differences in the chemical purity, physical properties, and molecular sizes of SP and VMA's in between different deliveries probably also have a major impact on the fresh properties of SCC, but less information about this subject is available in literature.

Kubens (2010) reported that when the same SCC mix design is made with different cement deliveries, the produced mixtures will have large fluctuations in their fresh properties. Wallevik et al. (2007) reported that the usage of SP increases the sensitivity of the fresh properties to the cement properties. According to Nunes et al. (2011), the variations in fluidity are mainly caused by differences in cement fineness and the sulfate content of cement. These properties affect the adsorption equilibrium, and ratio of the adsorbed amount of SP to the surface area of the cement particles.

2.3.1.3. Mixing procedure. Besides a higher sensitivity of the workability and rheology to changes in material proportions and properties, SCC is also more sensitive to variations in the mixing procedure. The effect of different mixing procedures (mixing time, addition time of the superplasticizer, mixing speed) on fresh properties has been investigated. Lowke et al. (2005) and Schiessl et al. (2007) examined the influence of mixing time on the fresh properties of SCC mixtures. The results have revealed that, with an increase in mixing energy, the slump flow increased due to the formation of fluid bonds with increased dispersion. After reaching maximum deformability (dispersion of water and SP maximized and a homogenous material is obtained), the slump flow decreased due to over-mixing. As the rheology of SCC is sensitive to the mixing procedure, further work is essential to better understand the effect of mixture procedure influencing SCC rheological properties. In concrete batching plants, the mixing procedure is relatively well controlled, but in truck mixing operations, the procedure fully depends on the truck driver, who may not have the necessary knowledge to assure consistent mixing energy.

The type and the time of addition of organic admixtures affect the deformability of fresh cement pastes. Uchikawa et al. (1995) reported that delayed addition enhances the flow for naphtalene sulfonate and aminosulphonic SP, does not affect the flow when using lignin sulfonic acid-based SP and is reported to decrease with polycarboxylate superplasticizer types. Some researchers report that delaying the addition time of SP for a few minutes, an improvement of the rheological properties is observed. Aiad et al. (2002, 2003) demonstrated the influence of delayed added timing (by 1, 3, 6, 10, and 13 min) of two different SP on the rheological properties. The result show an enhancement of the efficiency of the SP up to 10 min delay (add SP 10 min after adding water), but after that, an increase in apparent viscosity has been observed. Another effect of the addition time of SP on rheology has been reported by Altable et al. (2006) where mixtures in which the polycarboxylate-based superplasticizer (PC) was added with water demonstrate a higher apparent viscosity, compared to a delayed addition of the SP. Faltt et al. (2011) divided the superplasticizer added to a cement suspension into three parts. The first part of added superplasticzier is consumed by chemical reactions; especially within the first minutes during the formation of AFt and C-S-H. Thus, this fraction of SP does no longer exist for dispersing cement agglomerates. The second part of added SP is adsorbed onto the surface of cement particles and is most important part for dispersion. The distinction between adsorbed polymers from those in OMP is complicated by available analytical models so adsorbed SP cannot be measured easily. The third part consists of the excess superplasticizer, which remains dissolved in the aqueous phase. Thus, at equal amount of SP, cement with a higher consumption degree (Part 1) could have a lower surface coverage and hence worse workability (for cements otherwise equal: specific surface, composition, etc.).

2.3.2. Workability Loss of Flowable Cement Paste Over Time by Varying Different Parameters. Petit et al. (2006) determined that workability loss over time could be induced by two factors: physical factors (such as coagulation and restructuring of the microstructure) and chemical factors (cement hydration and decrease in free water content). Kong et al. (2013) reported that cement hydration, mixture composition, and the interaction between the binder particles and chemical admixtures are dominant parameters that influence the workability loss over time. In addition, Kreppelt et al. (2002) and Zhang et al. (2015) reported that the variations in the amount of superplasticizer influence the cement hydration process and thus change the workability loss on their turn. The correlations between mixture compositions and the initial rheological properties of the cementitious system and the development of rheological properties over time have been investigated in many projects. Golaszewski et al. (2004) reported that the rheological properties of cement mortars are strongly influenced by superplasticizer types and dosages, w/cm, and cement type. Struble et al. (1995) quantitatively described the relationship between viscosity and concentration of Portland cement pastes by using the Krieger–Dougherty (K–D) equation. In addition, Flatt et al. (2007, 2008) extended a model of yield stress (so-called Yodel) to anticipate the relationship of yield stress on the volume fraction of solids phase in cement materials system. Wallevik (2009) presented a rheological material model to describe time-dependent behavior of cement paste with different types of admixtures. The model is called the Particle Flow Interaction Theory, or the PFI- theory and can describe transient effects often observed in cement pastes. A good agreement is observed between the predictions with experimental data collected during complicated shear flow for all the experiments. The results have been highlighted that combination of coagulation, dispersion and re-coagulation of the cement particles (giving a thixotropic behavior) in combination with breaking of chemically formed linkages between the particles (giving a structural breakdown behavior) control the time-dependent behavior of cement paste.

PAPER

I. WHICH PARAMETERS, OTHER THAN THE WATER CONTENT, INFLUENCE THE ROBUSTNESS OF CEMENT PASTE WITH SCC CONSISTENCY?

Azadehalsadat A. Asghari[1], Aida Margarita Ley Hernandez[1], Dimitri Feys[1,*], Geert De Schutter[2]

ABSTRACT

Robustness is the capacity of cement-based mixtures to tolerate small variations in constituent elements, mixing parameters or temperature. It is an important reason slowing down the practical implementation of self-consolidating concrete (SCC). Especially the sensitivity of fresh SCC properties to a small variation in water content can be found in literature. The influence of the mixing sequence and mixing procedure on the robustness of SCC mixtures is not extensively reported.

The present paper evaluates the effect of mixing time, mixing speed and the addition time of superplasticizer on the rheological properties of cement pastes with SCC consistency, which can be related to SCC mixtures. By means of rheology, the changes induced by the variations in mixing procedure are compared to the changes induced by the variations in water and superplasticizer content. The results indicate that changing the water content is the main factor influencing rheology of cement pastes with low water-to-powder ratio (w/p). However, with increased water content in the paste mix design, other factors, such as adding time of the superplasticizer and mixing speed have equal or even superior importance as changing the water content. Dependent on the mix design, it may thus be necessary to use variables other than the water content to study robustness.

Keywords: Cement paste, Delayed addition, Mixing, Rheology, Robustness.

1. INTRODUCTION

Self-Consolidating Concrete (SCC), which has been developed in Japan to solve the durability problem of concrete structures [1], is a high-performance concrete demonstrating high flowability and sufficient resistance to segregation to ensure flow through congested reinforcement or in complex formwork shapes [2]. Extensive research on SCC has been performed in the last decades, but robustness of SCC is still one of the main shortcomings limiting practical implementation. The robustness is defined as the capacity of a mixture to tolerate changes and variations in materials and procedures, including temperature, that are inevitable when producing on any significant scale, and to retain its fresh properties until placing [3]. Robustness of SCC depends on the mix design, the mixing procedure and the use of the concrete. Fluctuations in the water content appear to dominate robustness. According to Li and Kwan [4], the water in fresh concrete can be divided into two parts: the filling water which fills the voids between the solid particles, and the excess water which forms a water film on the surface of the solid particles and contributes to the fluidity of fresh concrete. As the amount of excess water in a mixture increases with a higher water-to-cement ratio (w/cm) or the use of a less water-demanding powder, the robustness of a mixture is reported to increase [5]. These observations could be explained using the Krieger-Dougherty model [6]: as the amount of excess water increases, the packing density decreases and hence the inclination of the Krieger-Dougherty curve decreases, which corresponds to a lower sensitivity to changes in the amount of excess water. However, an increase in w/cm is also reported to cause a decrease in robustness [7], which contradicts the theory explained above. Billberg and Westerholm [5] used two different w/cm in two powder-type SCC mix designs and Kwan and Ng [7] used three w/cm in two powder-type SCC mix compositions.

Different authors state that the use of a different superplasticizer or VMA type, or changing admixture producer, can have a major impact on the robustness of a mix composition [8-16]. Polynaphthalene sulfonate (PNS) and polyphosphonic (PPh) based superplasticizers could result in more robust SCC mixtures than polycarboxylate ether (PCE) based superplasticizers [9, 13,16]. Many different products are referred to as viscosity-modifying agents (VMA), however not all VMA types have the same influence on the robustness: some types of VMA are more efficient in improving the robustness than others [5, 8, 11-14], and some types of VMA even decrease the robustness of the mix design [8]. Differences in the chemical purity and physical properties of chemical admixtures probably also have a major impact on the fresh properties of SCC, but less information about this subject is available in literature.

When the same SCC mix design is made with different cement deliveries, the produced mixtures will have large fluctuations in their fresh properties [17-19]. The usage of superplasticizers increases the sensitivity of the fresh properties to the cement properties [19]. According to Nunes et al. [18], the variations in fluidity are mainly caused by differences in cement fineness and the sulfate content of cement. These properties affect the adsorption equilibrium, and ratio of the adsorbed amount of superplasticizers to the surface area of the cement particles [20-23].

Besides a higher sensitivity of the workability and rheology to changes in material proportions and properties, SCC is also more sensitive to variations in the mixing procedure. The effect of different mixing procedures (mixing time, addition time of the superplasticizer, mixing speed) on fresh properties has been investigated. Lowke et al. and Schiessl et al. [24, 25] examined the influence of mixing time on the fresh properties of SCC mixtures. The results have revealed that, with an increase in mixing energy, the slump flow increased due to the formation of fluid bonds with increased dispersion [26]. After reaching maximum deformability (dispersion of water and SP complete and a homogenous material is obtained [26]), slump flow decreased due to over-mixing [24, 25]. The type and the time of addition of chemical admixtures affect the deformability of fresh cement pastes: delayed addition enhances the flow for naphtalene sulfonate and aminosulphonic SP, it does not affect the flow when using lignin sulfonic acid-based SP and it is reported to decrease with polycarboxylate superplasticizer types [27]. Some researchers report that delaying the addition time of SP for a few minutes, an improvement of the rheological properties is observed. Aiad et al. [28-29] demonstrated the influence of delayed added timing (by 1, 3, 6, 10, and 13 min) of two different SP on the rheological properties [28]. The result show an enhancement of the efficiency of the SP up to 10 min delay (add SP 10 min after adding water), but after that, an increase in apparent viscosity has been observed. Another effect of the addition time of SP on rheology has been reported by Altable [30] where mixtures in which the polycarboxylate-based superplasticizer (PC) was added with water demonstrate a higher apparent viscosity, compared to a delayed addition of the SP. As the rheology of SCC is sensitive to the mixing procedure, further work is essential to better understand the effect of mixing procedure influencing SCC rheological properties. In concrete batching plants, the mixing procedure is relatively well controlled, but in truck mixing operations, the procedure fully depends on the truck driver, who may not have the necessary knowledge to assure consistent mixing energy.

The objective of this paper is to evaluate the influence of the mixing procedure on the rheological properties of cement pastes with SCC consistency. The reasoning behind selecting paste and not concrete or mortar is to reduce material consumption, enhance the accuracy of the measurements and the ability to control temperature of the sample inside the rheometer. As aggregates amplify the rheological properties of the paste, the results are deemed applicable to SCC [31-36]. However, the influence of mixing time and mixing energy may need to be re-evaluated on concrete scale, as the applied shear rates on the paste are different in concrete. The main purpose of the paper is to give an indication on the relative importance of the addition time of the SP and the mixing time and speed, relative to a change in w/p (water-to-powder ratio, as limestone is used as filler), or in SP content on the variations in rheological properties.

2. EXPERIMENTAL PROGRAM

2.1. MATERIALS

ASTM C 150 Type I/II Ordinary Portland cement (OPC) was utilized. Limestone filler, consisting of more than 98% $CaCO_3$, was used as mineral filler for specific mixtures, while silica fume (SF) and class C fly ash (FA) were used as supplementary cementitious materials (SCM) in other mixtures. The cement, limestone filler, silica fume and class C fly ash are commercial products available on the local market.

For all mixtures, a polycarboxylate ether (PCE)-based superplasticizer (SP) was used. One of the SPs (SP 2) had relatively long workability retention, while SP 1 was more efficient but showed a larger decrease in slump flow with time. Both SPs are commercial products from two different manufacturers. The choice of the SP manufacturer corresponds to the mix design type, as the powder-type and VMA-type cement paste mix designs were chosen based previous experiences with corresponding SCC mix designs (see section 2.3). The VMA-type mixture logically required the addition of a VMA to assure stability. To avoid compatibility issues, the VMA was chosen from the same manufacturer as the superplasticizer added to the mixture. No air-entraining agents were used in this research project.

2.2. RHEOLOGICAL TESTING

The Anton Paar MCR 302 Rheometer (Figure 1) is a rheometer based on the principle of coaxially rotating cylinders. The inner cylinder rotates at different velocities, while the outer cylinder remains stationary. The resulting torque is registered at the inner cylinder. Two sets of coaxial cylinders were used on cement-paste scale: the smooth cylinders and the sandblasted cylinders. The sandblasted cylinders have the advantage of reducing slip or the formation of a lubricating layer. Except for the cement pastes with low water contents, the smooth and sandblasted cylinders deliver similar results. Over the course of the research project, the measurements were first performed on the smooth geometry, followed by the sandblasted version. For the smooth inner and outer cylinders, the inner cylinder radius (R_i) measures 13.39 mm, the outer cylinder radius (R_o), 14.56 mm and the height (h) is 40.00 mm. The sandblasted configuration has the following dimensions: R_i = 13.33 mm, R_o = 14.56 mm, and height h = 40.00 mm. The sample size for the rheometer was approximately 20 ml. A small cup was used to sample the paste from the middle of the mixing bowl.

The rheological properties of each cement paste are determined using the following testing procedure. At the start of each test, the cement paste is pre-sheared for 60 s at the maximum shear rate employed during the test, which is 100 s^{-1}. This time period has been proven to be sufficient in most cases to eliminate the effect of thixotropy from the results. After the pre-shearing period, the cement paste is subjected to a stepwise decrease in shear rate from 100 to 10 s^{-1} in 10 steps. Each step takes 5 seconds. It should be noted that the imposed rotational velocity, corresponding to the intended shear rate, has been determined by the software of the rheometer. Verification after the measurements has revealed that the applied shear rate is very close to 100 s^{-1}, calculated from the applied stress and the rheological properties of the material.

The rheological properties of cement-based materials are usually characterized with the Bingham model (eq. 1) [37]:

$$\tau = \tau_0 + \mu_p \dot{\gamma} \qquad (1)$$

For this equation, τ is the shear stress (Pa), τ_0 is the Bingham yield stress (Pa), μ_p is the Bingham plastic viscosity (Pa s), and $\dot{\gamma}$ is the shear rate (s^{-1}). The yield stress is the stress needed to start the flow. The plastic viscosity is the resistance of the material to an increase in flow rate once the yield stress is exceeded.

When the rheological measurement is performed with a coaxial cylinders rheometer, torque (T) and rotational velocity (N) are measured. Shear stress and shear rate data must be derived from the torque and rotational velocity data. When the torque is in equilibrium at each shear rate step, the rheological properties can be calculated by means of the Reiner-Riwlin equation [38-39]. If the torque was not in equilibrium at a certain step, the respective data point was eliminated from the results. The Reiner-Riwlin equation transforms the parameters G and H (T = G + H N), defining a linear relationship between torque (T) and rotational velocity (N), into the Bingham parameters [38]. This assumes a laminar, stable flow and no particle movements in the horizontal or vertical direction and all material in the entire gap must be sheared. In all performed experiments, the shear stress at the outer radius for the lowest rotational velocity applied was larger than the yield stress, proving that the sample was entirely sheared.

For most of the powder-type cement-pastes with SCC consistency, non-linear, shear-thickening rheological behavior has been observed, leading to the application of the modified Bingham model [40-41] (eq. 2):

$$\tau = \tau_0 + \mu_p \dot{\gamma} + c\dot{\gamma}^2 \qquad (2)$$

For this equation, τ is the shear stress (Pa), τ_0 is the Bingham yield stress (Pa), μ is the linear term of the modified Bingham model (Pa s), $\dot{\gamma}$ is the shear rate (s^{-1}) and c is the second order term of modified Bingham model (Pa s^2). A modified version of the Reiner-Riwlin equation (see [42]) can be used to calculate the rheological properties.

One of the consequences of applying a non-linear rheological model is that the viscosity is not a unique value. To solve this problem, the reported viscosity values in this paper are differential viscosity values, meaning they describe the inclination of the rheological curve at a fixed shear rate, which is chosen at 50 s^{-1}. For the Bingham model, the inclination of the line is the plastic viscosity (μ_p), while for the modified Bingham model, the inclination is μ + 100 c at a shear rate of 50 s^{-1}.

2.3. MIX DESIGN

Three different self-consolidating cement pastes were investigated in this research project. The mix designs were derived from standard powder-type and VMA-type SCC mixtures used in Europe and North-America (see Table 1a). Mix designs 1 and 3 are based on the powder-type approach, produced with admixtures from manufacturer 1. The main difference between mixtures 1 and 3 is the amount of water and the water-to-powder ratio (w/p), which is, for cement paste, the mass of water divided by the mass of all solids. Mixture 2 is based on the VMA-type approach, made with admixtures from manufacturer 2. The mix proportions for 1.5 liter of cement paste are listed in Table 1b. For all three reference cement pastes, the amount of SP was determined to obtain a mini-slump flow value of 330 ± 10 mm at 20 °C and 7 min after mixing, ensuring SCC consistency. The mini slump cone [43, 44] has a diameter of 70 mm at the top, 100 mm at the bottom and a height of 50 mm.

2.4. MIXING PROCEDURE

2.4.1. Reference Mixing Procedure. The preparation of the cement pastes was performed in a small Hobart mixer which was in compliance with ASTM C305-14. All mixing occurred at the lowest speed available and the contact time between cement and water was taken as the reference time (t_0). The reference mixing procedure consisted of homogenizing the dry materials (cement, SCM and/or fillers) for 30 s, mixing with water for 1 min, scraping the bowl of the mixer for 1 min and mixing for an additional 30 s. The SP was added (100% delayed) and the paste was mixed for 2 additional minutes, followed by some minor scraping (30 s) and everything was homogenized during the final minute (see Table 2). The total mixing duration was 6.5 minutes, of which 6 minutes occurred after contact with water. This mixing procedure deviates from the standardized procedure in ASTM C305-14 to enable homogenizing the cement and SCMs or limestone powder and to add the SP after the incorporation of the water. Also the scraping time was significantly extended to assure that a minimum of particles was stuck on the surface of the bowl.

The reference mixing procedure was employed to investigate the repeatability of the mixture and the mixing procedure, the influence of water (corresponding to a variation of 5 and 10 l/m^3 in concrete), and SP variations (±5% and ±10%). Rheological measurements were performed at 15 min at constant temperature of 23°C.

2.4.2. Variations in Mixing Energy. The change in mixing energy of the cement pastes has been investigated by varying the mixing time or the mixing speed. For the short mixing time, at the lowest speed, every mixing step longer than 30 s was halved, while for the long mixing time, all mixing steps in the reference procedure longer than 30 s were doubled. The details can be found in Table 2. The reference mixing procedure was also executed with increased mixing speed from step 5 on (high speed column in Table 2). The mixing energy is related to the total number of the rotations of the paddle. From the manufacturer, it is known that at the low speed, the paddle rotates at 2.27 rps, and at 4.68 rps at intermediate speed. The total number of revolutions after cement-water contact is also included in Table 2.

2.4.3. Variations in Adding Time of the Superplasticizer. In this project, the superplasticizer has been added to the mixtures in two different ways. In the reference mixing procedure, all SP was delayed by 2 min (100% delayed). To investigate the influence of SP adding time, the SP was also added at t_0, physically mixed in the water. If VMA was used, it was added to the mixture with a delay of 2 min after cement-water contact, regardless of the addition time of the SP. The amount of SP or VMA was not changed when investigating the influence of the water amount, mixing energy or adding time of the SP.

3. RESULTS AND DISCUSSIONS

3.1. REPEATABILITY OF MIXTURES

Before starting the variations in constituent elements and measuring the responses of the rheological properties, confidence intervals were established for the rheological properties based on the repetitive production of cement pastes 1 and 3. For each mix design, a 90% confidence interval was established for yield stress and plastic viscosity, based on 4 repetitions. A summary of the confidence interval for all mixtures, measured at 15 min, is shown in Table 3. Due to changes in cement delivery, confidence limits for mix design 2 could not be established.

Repeatability can give a first indication on the robustness of the mixtures. The variations in constituent elements, mix design and mixing procedure are very small, but the larger the confidence interval, the less robust the mixture. The defined 90% confidence intervals include the errors due to small variations in constituent material properties, mixing procedure, sampling as well as the rheological measurements. If due to an induced variation in mix design or mixing procedure the rheological properties are outside the confidence interval, the probability is large that the variation is significant. As can be seen in Table 3, mix design 3 appears to be the more robust mixture to errors in materials properties, mixing procedure and measurement.

3.2. VARATIONS IN WATER CONTENT

The induced variations of water in the cement paste, ±21 ml and ±42 ml, correspond to changes of ±5 l and ±10 l per cubic meter of concrete, respectively. The results of these variations are illustrated in Figs. 2 and 3 for mix designs 1, 2 and 3. The viscosity and yield stress values, at each different water content, are expressed relative to the reference values based on the repeatability results (Table 3), for each mixture separately. The solid horizontal lines represent the 90% confidence interval for mix design 1, while the dashed horizontal lines delimit the 90% confidence interval for mix design 3. As can be seen, the changes in water content have a significant impact on the plastic viscosity and yield stress of the mixtures. Mix design 1 and 2 are clearly less robust than mix design 3, especially for the plastic viscosity measurements, while for the yield stress, mix design 2 appears to be the most robust. The behavior found for mixtures 1 and 3 corresponds well with the literature [5, 7], as mixtures with lower w/p are more sensitive to a change in water content than mixtures with a higher w/p. The selected VMA-type mix design appears to show good robustness in terms of yield stress, but is less robust when considering viscosity. The exact reason for this behavior is unknown. It may potentially depend on the working principle of the VMA (forming bonds between cement particles vs. increasing viscosity of the water), and on how the effectiveness of the VMA was tested during the development process (workability vs. rheology).

3.3. VARATIONS IN SP DOSAGE

Figures 4 and 5 show the rheological behavior as a consequence of the variations in the amount of superplasticizer added for mixtures 1 and 3. These variations were ±5% and ±10% compared to the reference value. The yield stress shows a significant decrease with the increase of SP dosage, while viscosity is not much affected. These results are in agreement with the rheographs of Wallevik and Wallevik [45], stating that changing the amount of SP mainly influences the yield stress.

3.4. VARATION IN ADDITION TIME OF SP

The results in Figures 6 and 7, changing the addition time of the SP from 100% delayed to 100% with water significantly affect rheological properties, mainly for the VMA-type mix design. Changing the adding time of SP 1 (mix designs 1 and 3) affects viscosity more than the amount of SP 1 (compare Fig 6 to Fig 4). The change in plastic viscosity of mix design 2 is however extensive, more important than the change induced by the variations in water content. The effect could be attributed to a lower efficiency of the SP as it gets overgrown by hydration products [46]. This could keep more water trapped in between the coagulated cement(-itious) particles increasing viscosity. However, for the powder type mix designs, the yield stress results seem to contradict this, as the yield stress decreases slightly with the 100% addition with the mixing water, but the change is significant. For mix design 2, the change in yield stress due to the change in adding time is larger than the induced reduction in water content. For the selected VMA-type mix design, the addition time of the SP appears to be very important. The specific cause for this substantial difference is unknown at this point, as it could be attributed to the different manufacturers of the SP (although both are polycarboxylates), the presence of silica fume which is hard to disperse or the presence of VMA in mixture 2.

3.5. VARATIONS IN MIXING ENERGY: MIXING TIME AND MIXING SPEED

Viscosity and yield stress were evaluated to determine the influence of the mixing time and speed. Mix designs 1 and 3 were prepared and mixed at two different speeds (speed 1 = low (=ref) and speed 2 = medium). The variations on the mixing time were made on mix designs 1, 2 and 3 and the time of mixing was short, reference and long, as described in Table 2. The influence of these induced changes is illustrated in Figures 8 and 9 where the mixing energy is expressed as the amount of revolutions the paste underwent in the mixer. The data points from left to right reflect the short, reference and long procedure and the reference procedure with increased speed (speed 2). The figures show that an increase in mixing time caused a decrease in yield stress and plastic viscosity (except for the yield stress of mix design 1 with the short mixing time). Increasing mixing speed also appears to lower the rheological properties. These results are in agreement with the theories stated by Lowke et al. and Schiessl et al. [24-25], indicating that an increase in mixing time causes more dispersion of cement particles and more trapped water to be liberated. The cement paste mixtures do not appear to be over-mixed. From the results, it can also be noticed that mix design 1 appears to be the least sensitive to a variation in mixing energy, while mix design 2 is more sensitive to a reduction in mixing energy, which may most likely be attributed to the presence of silica fume, as more energy is required to disperse this constituent.

3.6. COMPARING MAGNITUDES OF VARATIONS

Table 4 lists the minimum and maximum values of the relative viscosity and relative yield stress for each mix design and modified parameter. Figure 10 displays the magnitude of relative viscosity (Fig. 10.a) and relative yield stress (Fig. 10.b), calculated as the average of "maximum – 1" and "1 – minimum" values for the amount of water, amount of SP and the mixing time, and the sole "maximum – 1" or "1 – minimum" value for the addition time of the SP and the mixing speed. For example, the value for the influence of the amount of water on the relative viscosity for mix design 1 is 0.44. This is the average of 0.52 (max – 1), and 0.36 (1 – min). As there is only one value for the influence of the adding time of SP, the value displayed in Figure 10a for the relative viscosity is 0.19 (max – 1). For this example, it can be concluded that the amount of water has a larger influence on the relative viscosity of mix design 1, compared to the adding time of SP.

Following the same strategy for all parameters and all mix designs, no uniform conclusions which are valid for all mixtures tested can be drawn. For mix design 1: a powder-type mix design with low w/p, the variations induced by an increase or decrease in water content are the most important on yield stress and viscosity. Changing the SP content also significantly affects the yield stress, but has a low effect on viscosity. Changing the addition time of the SP and increasing mixing time induce large variations in the rheological properties, but not as important as the change in water content. Decreasing mixing time and increasing mixing speed have a minor effect.

For mix design 3, which is also a powder-type mix design, but with higher w/p compared to mix design 1, the most important variations in the yield stress were induced by decreasing the water and changing the SP content. Increasing mixing time and mixing speed also had an important influence. For the viscosity, the mixing speed appeared to have the largest influence, while changing water content, the adding time of the SP and extending the mixing time had comparable influence. While for powder-type mixtures with low w/p, investigation of robustness by means of changing the water content can be justified. But it appears that with an increase in w/p (or, even more correctly, an increase in water content), the importance of changing the water content decreases compared to other variations. This can be justified by the Krieger-Dougherty model, as an increase in water content decreases the packing density, making the relative viscosity less sensitive to a change in water content (or packing density) [6]. Other parameters, such as the mixing speed or the adding time of the SP appear even to have a larger effect with increasing water content. Studying robustness of mix designs with higher w/p may need to include more parameters than solely changing the water content.

For mix design 2, a VMA-type mix design with relatively high w/p, the adding time of the SP appeared to be the dominating parameter influencing the rheological properties, even more importantly than a change in water content. Reducing mixing time also appeared to have a large influence on the rheological properties, as the changes were slightly lower compared to the changes induced by the water content.

3.7. WHAT IN CASE OF CONCRETE?

This entire investigation has been performed on cement paste with SCC consistency. Can the results be applied on concrete? Yes, to a certain extent. Changes in paste rheology induced by constituent elements and mix design, as well as the adding time of the SP, are expected to have similar consequences on SCC, as aggregates amplify the rheological behavior [31-36]. For the mixing energy and the mixing speed, in general, the obtained conclusions should be valid, but it should be kept in mind that the presence of aggregates increases the shear rate in the paste during mixing. The mixing energy in the paste is different in a cement paste mixer compared to concrete mixing, which could alter the magnitude of the results. However, as mixing time and mixing speed are deemed important parameters for a part of the investigated mixtures, it should be controlled, which can be a challenge in the ready-mix industry.

4. CONCLUSION

Typically, small variations in the water content, through inaccuracies of the balances in the concrete production plant or small mistakes in the determination of the aggregate moisture content, is the most investigated parameter in robustness studies.

In this study, the influence of the mixing procedure and addition time of the superplasticizer on the robustness of SCC was investigated on cement-pastes with SCC consistency, by means of rheology. The mixtures' rheological properties: yield stress and viscosity were determined using the Anton Paar MCR 302. Two reference SCC mix design strategies were employed: the powder-type mix design and the VMA-type mix design.

For the tested cement pastes, 90% confidence intervals were determined and it was concluded that variations in water, amount of SP, variations in the adding time of the SP (with the mixing water or delayed by 2 min), variations in mixing time and speed (mixing energy) all have significant influence on the measured viscosity and yield stress.

Also, for the variations imposed, the selected powder-type mix designs appear more robust than the selected VMA-type.

For the powder-type cement paste with w/p = 0.275, the parameters conventionally used to study robustness: changing water and SP content, result in the largest variations in yield stress and viscosity. However, increasing w/p to 0.315 (by increasing the water content and decreasing the relative amount of limestone filler) has revealed that the influence of a change in water content is similar or even inferior to some of the other parameters tested. In this case, the influence of mixing speed appeared more important, while the adding time of the SP and increasing mixing time had similar influence as changing the water content, especially for the viscosity. For the selected VMA-type cement paste, the adding time of the SP appeared to be significantly more important than a change in water content.

As a general conclusion, it can thus be stated that changing the water content to study robustness can be an effective tool, but, especially for mixtures with a higher w/p or higher water content, the influence of other variables, such as mixing speed or adding time of the SP can become more important. Especially in practice, when implementing SCC technology in the field, it will be important to consider the variations induced by mixing and addition sequence, and transportation time, in addition to variations in water content and admixture dosage, especially for SCC mixtures with relatively high water contents.

ACKNOWLDGEMENT

The authors would like to acknowledge the National University Transportation Center at the Missouri University of Science and Technology (project R333) and the Science Foundation in Flanders (FWO) for the financial support of this project, as well as the Center for Infrastructure Engineering Studies (CIES) at Missouri S&T for the technical and administrative assistance.

Table 1. Selected SCC mix designs from which the paste mix designs (Table 2) were derived. All units are in kg/m^3.

	Cement	Limestone Filler	Fly ash	Silica Fume	Water	Sand	Coarse Aggr.	Admixtures
Mix Design 1	300	300			165	850	700	SP 1 – no VMA
Mix Design 2	344		119	12	181	960	728	SP 2 – corresponding VMA
Mix Design 3	325	245			180	850	700	SP 1 – no VMA

Table 2. Reference mix designs 1, 2 and 3. All units are expressed in g for 1.5 liter of paste.

	Cement	Limestone Filler	Fly ash	Silica Fume	Water	SP1	SP2	VMA	W/P
Mix Design 1	1211	1211			666	5.20			0.275
Mix Design 2	1443		499	50	759		9.69	1.25	0.38
Mix Design 3	1309	982			720	3.80			0.31

Table 3. Mixing procedures (reference, short, long and at higher speed). The number in between brackets for the high-speed column indicates the speed setting on the mixer.

Step	Duration				Action
	Reference	Short	Long	High speed	
1	30 s	30 s	30 s	30 s (1)	Dry Materials
2 (=t_0)	1 min	30 s	2 min	1 min (1)	Adding Water
3	1 min	1 min	1 min	1 min	Scraping
4	30 s	30 s	30 s	30 s (1)	Mixing
5	2 min	1 min	4 min	2 min (2)	Add SP / VMA
6	30 s	30 s	30 s	30 s	Scraping
7	1 min	1 min	1 min	1 min (2)	Mixing
Duration since t_0	6 min	4.5 min	9 min	6 min	
Total rotations	613	409	1022	1047	

Table 4. Average values for viscosity and yield stress of reference mixtures 1, 2 and 3 and 90% confidence intervals, based on 4 measurements, for mixtures 1 and 3.

	Mix Design 1	Mix Design 2	Mix Design 3
Average Viscosity (Pa s)	0.435	0.132	0.333
+ 90% Confidence Limit	0.443		0.336
- 90% Confidence Limit	0.426		0.330
Average Yield Stress (Pa)	3.63	5.69	2.60
+ 90% Confidence Limit	4.10		2.72
- 90% Confidence Limit	3.15		2.48

Table 5. Maximum and minimum values of viscosity and yield stress, relative to the values of the reference mixtures, for each induced variation.

	Relative viscosity		Relative yield stress	
	Max	Min	Max	Min
Mix Design 1				
Amount Water	1.52	0.64	1.86	0.45
Amount SP	1.11	0.87	1.43	0.48
Adding time SP	1.19			0.79
Mixing time	1.02	0.79	-	0.73
Mixing Speed		0.87		1.00
Mix Design 3				
Amount Water	1.20	0.76	1.79	0.80
Amount SP	1.06	0.82	1.62	0.52
Adding time SP	1.27			0.88
Mixing time	1.12	0.79	1.09	0.73
Mixing Speed		0.66		0.68
Mix Design 2				
Amount Water	1.65	0.82	1.30	0.63
Adding time SP	2.55		1.55	
Mixing time	1.46	0.79	1.32	0.89

Figure 1. Anton Paar MCR 302, equipped with the sandblasted coaxial cylinders set.

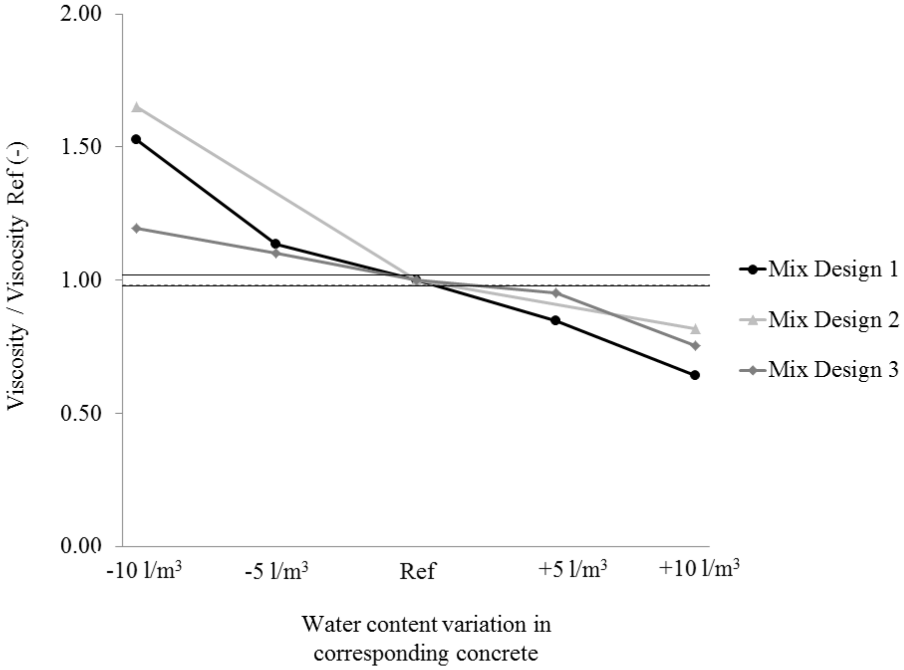


Figure 2: Variation of the viscosity, relative to the viscosity of the reference test, as a function of a change in water content. The water content changes correspond to ±5 and ±10 l/m^3 in the corresponding concrete.

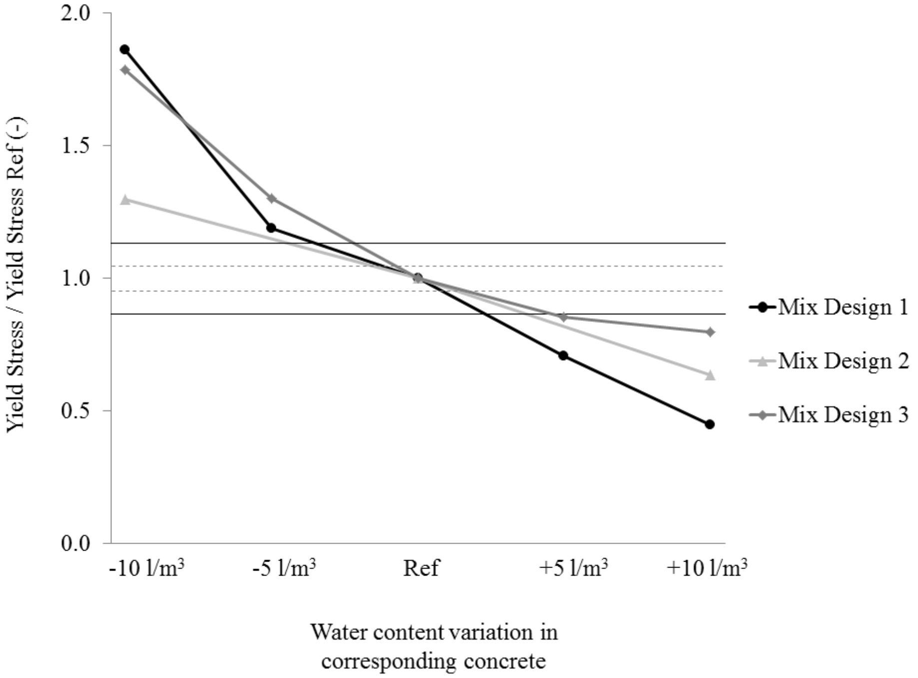


Figure 3: Variation of the yield stress, relative to the yield stress of the reference test, as a function of a change in water content. The water content changes correspond to ±5 and ±10 l/m^3 in the corresponding concrete.

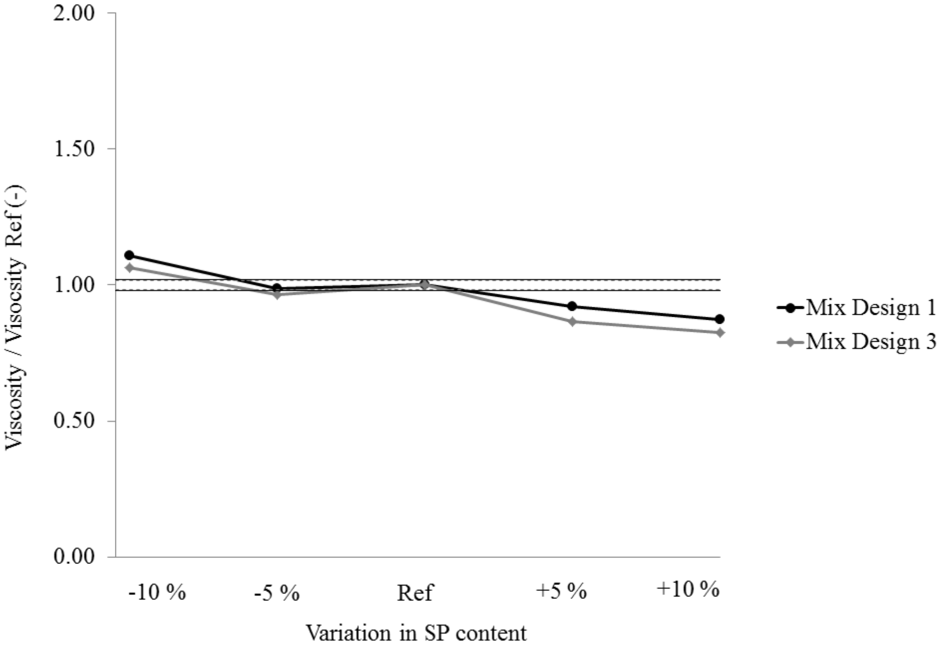


Figure 4: Variation of the viscosity, relative to the viscosity of the reference test, as a function of a change in superplasticizer content.

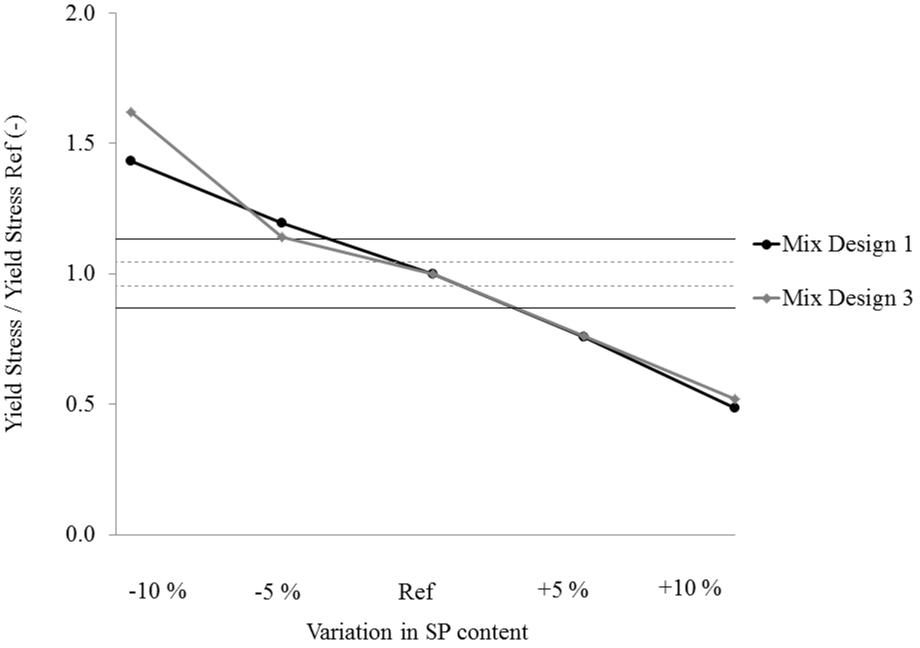


Figure 5: Variation of the yield stress, relative to the yield stress of the reference test, as a function of a change in superplasticizer content.

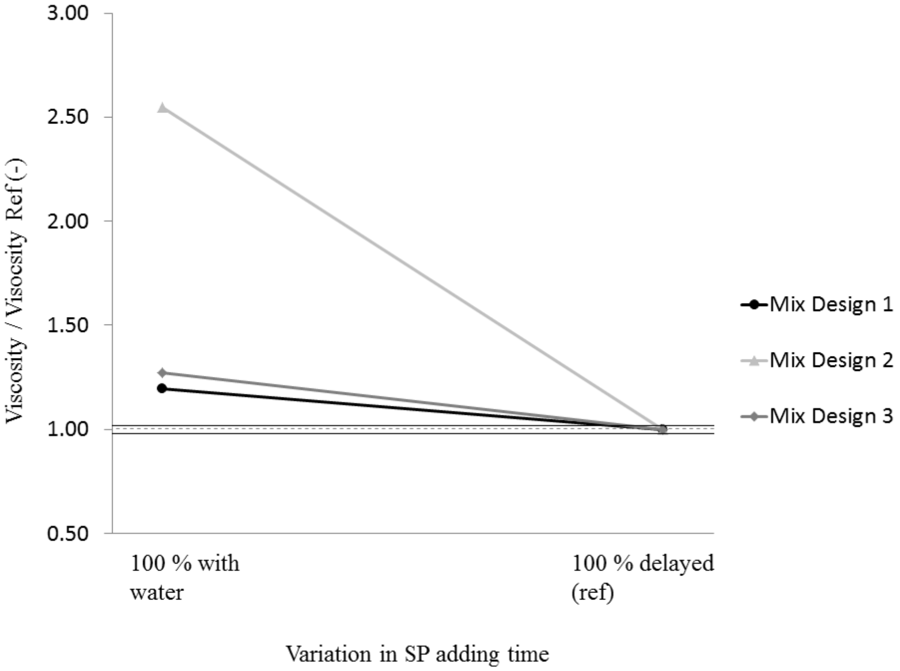


Figure 6: Variation of the viscosity, relative to the viscosity of the reference test, as a function of the addition time of the superplasticizer (100% with water, or delayed by 2 minutes).

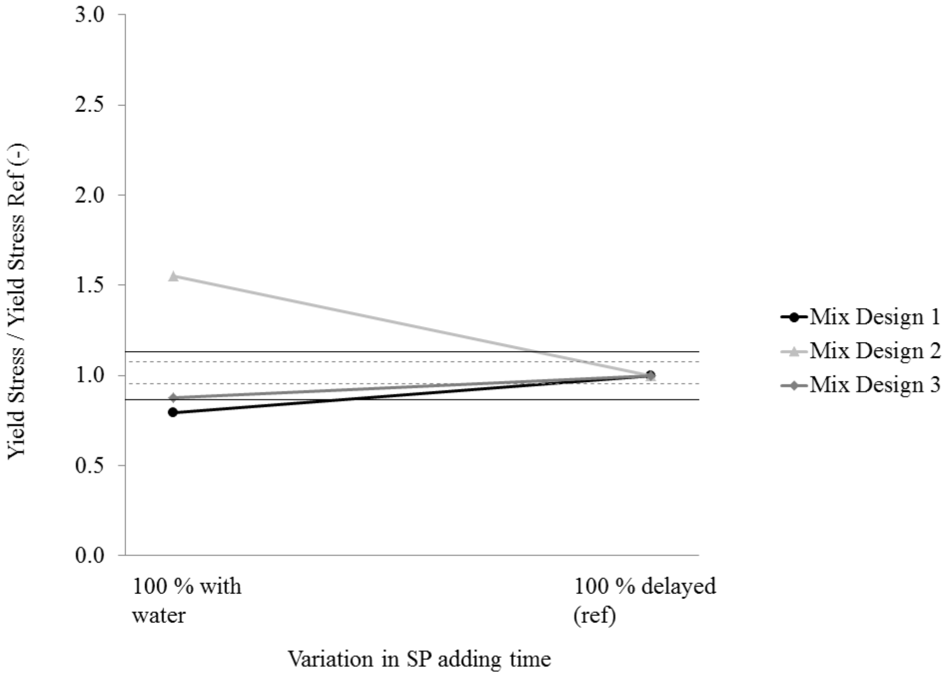


Figure 7: Variation of the yield stress, relative to the yield stress of the reference test, as a function of the addition time of the superplasticizer (100% with water, or delayed by 2 minutes).

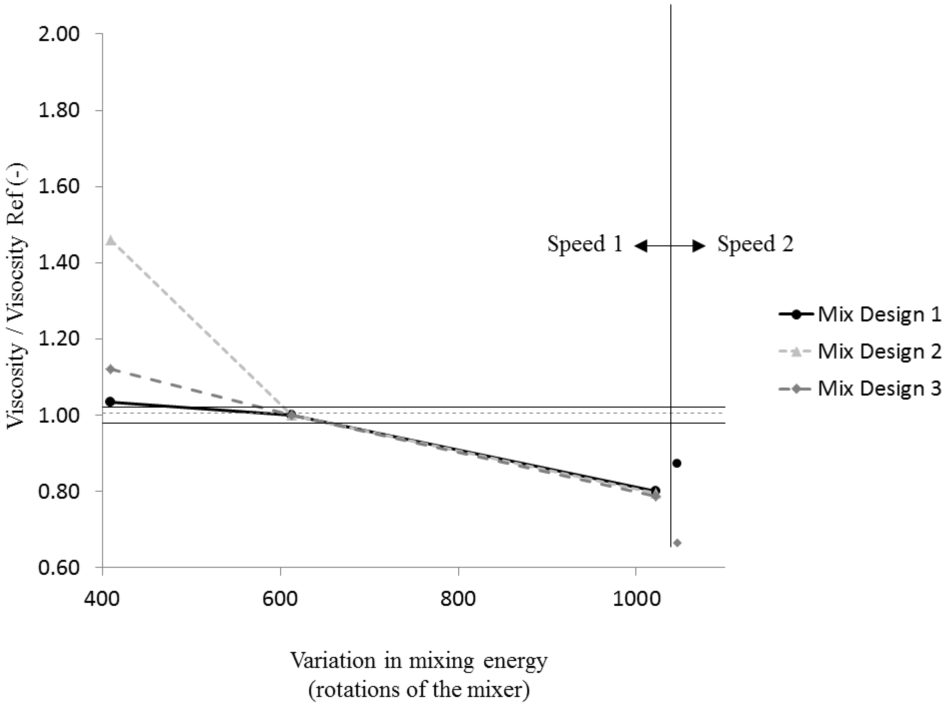


Figure 8: Variation of the viscosity, relative to the viscosity of the reference test, as a function of number of rotations in the mixer.

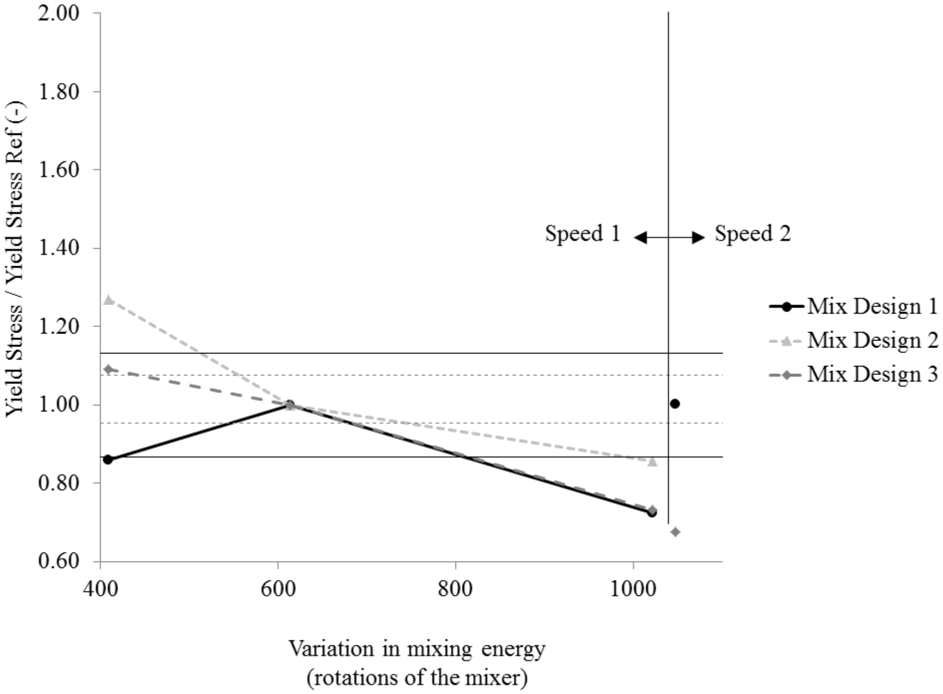


Figure 9: Variation of the yield stress, relative to the yield stress of the reference test, as a function of number of rotations in the mixer.

a)

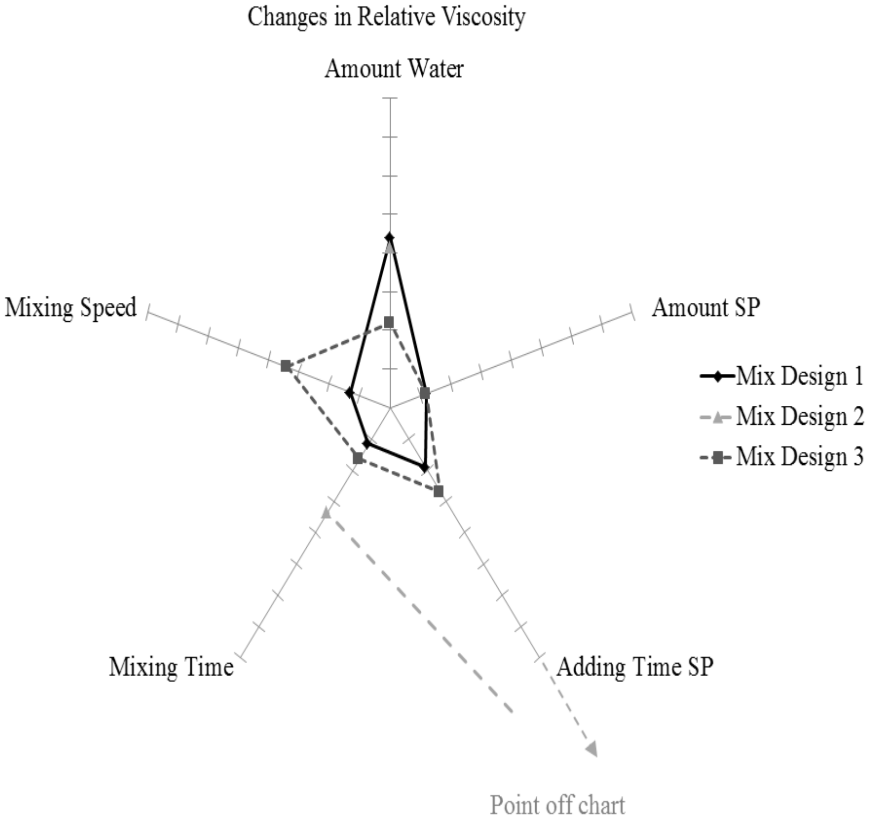


Figure 10. a) Changes in relative viscosity for each tested parameter, b) Changes in relative yield stress for each tested parameter.

b)

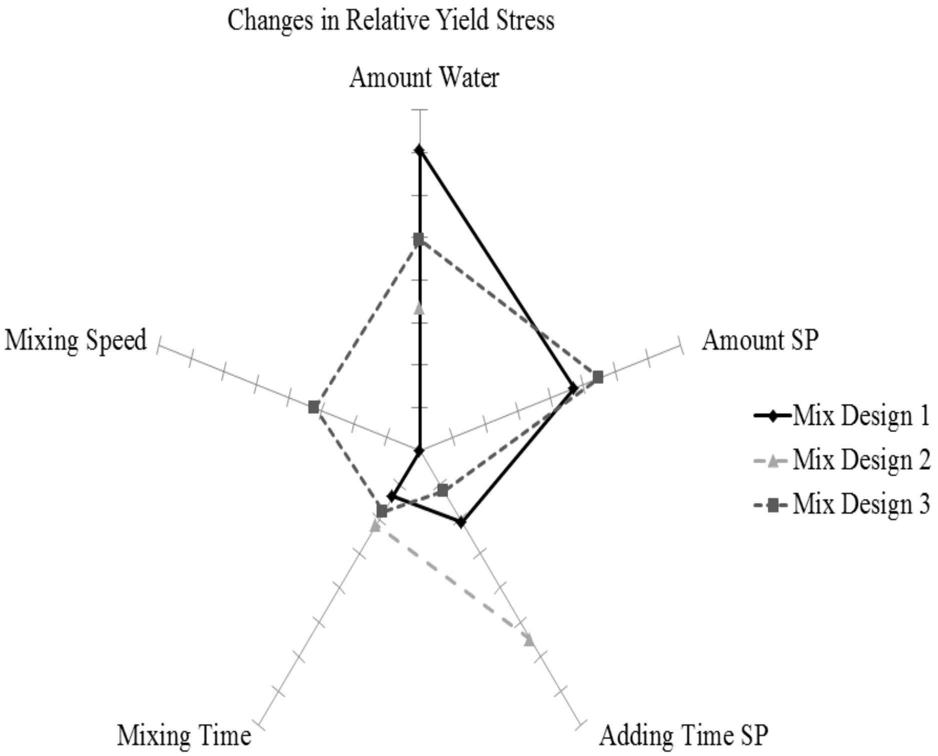


Figure 10. a) Changes in relative viscosity for each tested parameter, b) Changes in relative yield stress for each tested parameter (Cont.).

REFERENCES

[1] Okamura H, Ouchi M (2003), Self-compacting concrete, *J. of Advance Concrete Technology*, 1, 5-15.

[2] Khayat KH (1999), Workability, Testing, and Performance of Self-Consolidating Concrete, *ACI Mat. J.* 96-3, 346-353.

[3] De Schutter G, Bartos PJM, Domone P, Gibbs J (2008), Self-compacting concrete, Whittles Publishing, Caithness.

[4] Li LG, Kwan AKH (2013), Concrete mix design based on water film thickness and paste film thickness, *Cem. Conc. Comp.* 39-5, 33-42.

[5] Billberg P (2011), Influence of powder type and VMA combination on certain key fresh properties of SCC, in: Proc. of 9th Int. Symp. on High Performance Concrete, Rotorua, New Zealand.

[6] Krieger IM (1972), Rheology of monodisperse latices, *Adv Colloid Interface Science* 3-2, 111-136.

[7] Kwan AKH, Ng IYT (2009), Optimum superplasticiser dosage and aggregate proportions for SCC, *Mag. Conc. Res.* 61-4, 281-292.

[8] Billberg P, Westerholm M (2008), Robustness of fresh VMA-modified SCC to varying aggregate moisture, *NCR J.*, 38-7, 103-119.

[9] Bonen D, Deshpande Y, Olek J, Shen L, Struble L, Lange DA, Khayat K (2007), Robustness of selfconsolidating concrete, in: Proc. of the 5th Int. RILEM Symp. on Self-Compacting Concrete, Ghent, Belgium.

[10] Leemann A, Winnefeld F (2007), The effect of viscosity modifying agents on mortar and concrete, *Cem. Conc. Comp.* 29-5, 341-349.

[11] Sakata N, Yanai S, Yoshizaki M, Phyfferoen A, Monty H (2001), Evaluation of S-657 Biopolymer as a new viscosity-modifying admixture for self-compacting concrete, in: Proc. of the 2nd Int. Symp. on Self-Compacting Concrete, Tokyo, Japan.

[12] Phyfferoen A, Monty H, Skags B, Sakata N, Yanai S, Yoshizaki M (2002), Evaluation of the biopolymer, diutan gum, for use in self-compacting concrete, in: Proc. of the 1st North American Conference on the Design and Use of Self-Consolidating Concrete, Evanston, IL, USA.

[13] Gettu R, Shareef SN, Ernest KJD (2009), Evaluation of the robustness of SCC, *The Indian Concrete Journal* 83-6, 13-19.

[14] Naji S, Hwang S-D, Khayat KH (2011), Robustness of self-consolidating concrete incorperating different viscosity-enhancing admixtures, *ACI Mat. J.* 108-4, 432-438.

[15] Haldenwang R, Fester VG (2011), The influence of different super-plasticisers on the flowability and reproducibility of a SCC mix, in: Proc. of at the 9th Int. Symp. on High Performance Concrete, Rotorua, New Zealand.

[16] Bokan-Bosiljkov V, Gasperic N, Zevnik L (2013), New type of superplasticizer for SCC mixtures with increased robustness, in: Proc. of the 7th Int. RILEM Symp. on Self-Compacting Concrete, Paris, France.

[17] Kubens S (2010), Interaction of cement and admixtures and its effect on rheological properties, Ph-D dissertation, Bauhaus-Universität Weimar – Reykjavik University, Götingen - Reykjavik.

[18] Nunes S, Oliveira PM, Coutinho JS, Figueiras J (2011), Rheological characterization of SCC mortars and pastes with changes induced by cement delivery, *Cem. Conc. Comp.* 33-1, 103-115.

[19] Wallevik OH, Kubens S, Müller F (2007), Influence of cement-admixture interaction on the stability of production properties of SCC, in: Proc. of the 5th Int. RILEM Symp. on Self-Compacting Concrete, Ghent, Belgium.

[20] Yamada K, Ogawa S, Takahashi T (2001), Improvement of the compatibility between cement and superplasticizer by optimizing the chemical structure of the polycarboxylate-typ superplasticizer, in: Proc. of the 2nd Int. Symp. on Self-Compacting Concrete, Tokyo, Japan.

[21] Yamada K, Hanehara S (2001), Interaction mechanism of cement and superplasticizers - The roles of polymer adsorption and ionic conditions of aqueous phase, *Concrete Science and Engineering* 3-11, 135- 145.

[22] Yoshioka K, Sakai E, Daimon M, Kitahara A (1997), Role of steric hindrance in the performance of superplasticizers for concrete, *J. of the American Ceramic Society*, 80-10, 2667-2671.

[23] Sakai E, Yamada K, Ohta A (2003), Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan, *J. of Advanced Concrete Technology*, 1-1, 16-25.

[24] Lowke D, Schiessl P (2005), Effect of mixing energy on fresh properties of SCC, in Proc. of the combined 2nd North American Conf. and the 4th Int. RILEM Symp. on Self-Compacting Concrete, Chicago, IL, USA.

[25] Schiessl P, Mazanec O, Lowke D (2007), SCC and UHPC - Effect of mixing technology on fresh concrete properties, in: Advances in Construction Materials, Ed: Grosse CU, Heidelberg, Germany, 513-522.

[26] Cazacliu B, Roquet N (2009), Concrete mixing kinetics by means of power measurement, *Cem. Conc. Res.* 39-3, 182-194.

[27] Uchikawa H, Sawaki D, Hanehara S (1995), Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement pastes, *Cem. Conc. Res.* 25, 353–364.

[28] Aiad I, Abd El-Aleem S, El-Didamony H (2002), Effect of delaying addi- tion of some concrete admixtures on the rheological properties of cement pastes, *Cem. Conc. Res.* 32, 1839–1843.

[29] Aiad I (2003), Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes, *Cem. Conc. Res.* 33, 1229–1234.

[30] Fernandez-Altable V, Casanova I (2006), Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures, *Cem. Conc. Res.* 36, 1222–1230.

[31] Ferraris CF, Gaidis JM (1992), Connection between the rheology of concrete and rheology of cement paste, *ACI Mat. J.* 89-4, 388-393.

[32] Hidalgo J, Chen CT, Struble LJ (2008), Correlation between paste and concrete flow behavior, *ACI Mat. J.* 105-3, 281-288.

[33] Geiker MR, Brandl M, Thrane LN, Nielsen LF (2002), On the effect of coarse aggregate fraction and shape on the rheological properties of self-compacting concrete, *Cem. Concr. Aggr.* 24, 3–6.

[34] Erdogan TS (2005), Determination of aggregate shape properties using X-ray tomographic methods and the effect of shape on concrete rheology, PhD thesis, University of Texas at Austin.

[35] Toutou Z, Roussel R (2006), Multi scale experimental study of concrete rheology: from water scale to gravel scale, *Mat. Struct.* 37, 167–176.

[36] Mahaut F, Mokéddem S, Chateau X, Roussel R, Ovarlez G (2008), Effect of coarse particle volume fraction on the yield stress and thixotropy of cementitious materials, *Cem. Conc. Res.* 38-11, 1276–1285.

[37] Tattersall GH, Banfill PFG (1983), The rheology of fresh concrete, Pitman, London.

[38] Reiner M (1949), Deformation and flow. An elementary introduction to theoretical rheology. H.K. Lewis & Co, Limited, Great Britain.

[39] Wallevik JE (2003), Rheology of particle suspensions, Fresh concrete, mortar and cement paste with various types of lignosulfonates, Ph-D dissertation, the Norwegian University of Science and Technology, Trondheim.

[40] Yahia A, Khayat KH (2001), Analytical models for esti- mating yield stress of high-performance pseudoplastic grout, *Cem. Conc. Res.* 31, 731–738.

[41] Feys D, Verhoeven R, De Schutter G (2008), Fresh self compacting concrete: a shear thickening material. *Cem. Conc. Res.* 38, 920–929.

[42] Feys D, Wallevik JE, Yahia A, Khayat KH, Wallevik OH, (2013), Extension of the Reiner–Riwlin equation to determine modified Bingham parameters measured in coaxial cylinders rheometers, *Mat. Struct.* 46, 289-311.

[43] Kuroiwa S, Matsuoka Y, Hayakawa M, Shindoh T, (1993), Application of Super Workable Concrete to Construction of a 20-Story Building, In ACI SP-140: High Performance Concrete in Severe Environments, Zia P, Ed., Detroit, MI: American Concrete Institute, 147-161.

[44] Bartos PJM, Sonebi M, Tamimi AK (Eds.) (2002), Workability and Rheology of Fresh Concrete: Compendium of Tests, RILEM, Cachan, France.

[45] Wallevik OH, Wallevik, JE (2011), Rheology as a tool in concrete science: The use of rheographs and workability boxes, *Cem. Conc. Res.* 41, 1279-1288.

[46] Flatt R, Schober I (2012), Superplasticizers and the rheology of concrete: In: Understanding the rheology of concrete, Ed: Roussel N, Woodhead Publishing Ltd, Oxford.

II. MIX DESIGN FACTORS AFFECTING MAGNITUDE OF VARATIONS IN RHEOLOGICAL PROPERTIES OF SELF-CONSOLIDATING CEMENT PASTE INDUCED BY THE ADDITION TIME OF PCE-SUPERPLASTICIZER

Azadeh A. Asghari, Dimitri Feys, and Geert De Schutter

ABSTRACT

Robustness, which is defined as the capacity of a mixture to tolerate changes and variations in materials and procedures that are inevitable with production at any significant scale, is a key property to expand the use of self-consolidating concrete (SCC). Typically, small variations in the water content, through inaccuracies of the balances in the concrete production plant or small mistakes in the determination of the water content, is the most investigated parameter in robustness studies.

This paper evaluates the effect of the adding time of superplastizer (SP) on the rheological properties of cement pastes with SCC consistency. Two different SCC mix design concepts, the powder-type (mixture 1) and VMA-type (mixture 2), were selected for this research. The results show that the selected powder-type mix design is more robust than the VMA-type to a change in addition time of SP. In the next step, different mix design parameters have been evaluated by varying the binder combination, the type of PCE-SP and the addition of viscosity-modifying agent (VMA) to determine which particular parameters cause the largest difference in rheological behavior due to a change in adding time of SP. The results have revealed that the limestone filler appears to have the most beneficial effect on the robustness of the cement pastes.

Keywords: Rheology, Robustness, Addition time of SP, Self-consolidating cement paste, limestone filler.

1. INTRODUCTION

Self-consolidating concrete (SCC) exhibits typically high fluidity and deformability, enabling the concrete to flow through congested reinforcement or in formworks inducing difficult casting conditions [1]. The initial use of SCC in Japan in the late 1980s was intended to improve the construction speed, ease its placement, eliminate the need for vibration, resulting in an increase in durability of concrete structures [2-3]. SCC is though more sensitive to small changes in mix design and in the mixing procedure, compared to conventional vibrated concrete. Therefore, robustness is an important aspect when studying and optimizing rheological properties and workability of SCC. The robustness of concrete (or cement-based materials in general) is defined as the capacity of a mixture to retain its performance despite variations in the raw materials and mixing procedures that are inevitable when producing on any significant scale [4-8].

Variations in water content, type of superplasticizer (SP) or viscosity-modifying admixture (VMA), and different mixing procedures, such as adding time of the SP, mixing duration and intensity, have an effect on the rheological properties and workability of SCC. The water content appears to be a key factor influencing the robustness of SCC. Therefore, many researches [5-10] investigated robustness by varying the amount of water. SCC tolerating a change in water content of up to 5 to 10 l/m^3 and still meeting certain performance criteria has been defined as a robust SCC in the European Guidelines for SCC [11]. Some researchers have reported more robustness of SCC with higher water-to-cement ratio (w/cm) [8-9]. On the other hand, sometimes it is reported that the robustness of SCC decreases when increasing w/cm [10]. Usually, the presence of VMA increases the robustness of SCC [5, 9, 12-14]. SCC stability is improved by using VMA when moisture content variations occur in aggregate, especially in sand [15]. However, some results show that SCC robustness decreases when employing some types of VMA [16]. Presence of supplementary cementitious materials or mineral fillers, such as fly ash (FA), silica fume (SF) and limestone filler (LF) could improve the robustness of SCC [17-18].

Mixing time [19-21] and addition time of admixtures [22-27] play a significant role in changes in rheology and workability loss of SCC. Studies illustrated that the slump flow increases with increasing mixing energy, up to an optimum, after which the slump flow decreases due to overmixing [19-21]. For chemical admixtures, it has been shown that the adsorption of polynaphtalene sulfonate (PNS) on Portland clinker particles is mainly governed by the cement composition, fineness and C_3A content of the cement [25-28]. A Langmuir isothermal adsorption model, which elevates the negative ζ-potential of the solid particles, has demonstrated the adsorption behavior of PNS on cement particles. [29]. Polycarboxylate ethers (PCE) have rather different behavior. Because of the negative backbones of PCE, when PCEs are added, they are adsorbed on positively charged particles [30]. The nature of the repulsion force for PCE is electrostatic and steric [31]. Some researchers investigated the effect of addition time of SP (simultaneous and delayed addition to water) [22, 32-35]. By delaying the addition of the chemical admixtures to the concrete, the reactive cementitious particles adsorb water molecules quickly, and a hydrated cover on these elements is formed in advance. Sufficient SP molecules can be adsorbed by the C_3S and C_2S for their dispersion. Therefore, the yield stress and plastic viscosity of cement paste at the early ages (15 min) as well as at later early ages (120 min) are lower for the same quantity of admixture. The optimum delaying time of naphthalene and melamine-based SP that does not relate to the type of cement or superplasticizer addition, is found to be at the beginning of the dormant period (10-15min) [33, 36-37].

In this paper, the delayed addition of PCE SP is investigated. For a VMA-type mix design reported in a previous paper [38], it has been observed that delaying the addition of the SP in cement paste with SCC consistency has a larger effect on the yield stress and plastic viscosity than a change in water which corresponds to 10 l/m^3 in the corresponding concrete. This paper studies the sensitivity of cement paste mixtures to a delayed addition of SP, with varying types of supplementary cementitious materials or mineral fillers, w/cm, presence or absence of VMA and with two different types of SP.

2.EXPERIMENTAL PROGRAM

2.1. MATERIALS

2.1.1. Cement, Supplementary Cementitious Materials and Filler. ASTM C 150 type I/II Ordinary Portland cement (OPC, density (ρ) = 3150 kg/m^3) was used in this project. Silica fume (SF, ρ = 2200 kg/m^3) and class C fly ash (FA, ρ = 2400 kg/m^3) were utilized as supplementary cementitious materials (SCM) while limestone filler (LF, ρ = 2700 kg/m^3), consisting of more than 98% $CaCO_3$, was used as mineral filler. The cement, limestone filler, silica fume and class C fly ash are commercial products available on the local market.

2.1.2. Chemical Admixtures. Two different PCE-based SP were applied. SP 1, used in mix design 1, showed a larger decrease in slump flow with time but was more efficient compared to SP 2. The SP for mix design 2 (SP 2) had relatively long workability retention. Both SPs are commercial products from two different manufacturers. For mix design 2, a VMA was used to assure stability. The VMA was selected from the same manufacturer as the superplasticizer to prevent compatibility issues. No air-entraining agents were used in this research project.

2.2. RHEOLOGICAL MEASURMENTS

The Anton Paar MCR 302 Rheometer (Figure 1) is a rheometer based on the principle of concentric rotating cylinders. The inner cylinder rotates at different velocities, while the outer cylinder remains stationary. The resulting torque is registered at the inner cylinder. Sandblasted cylinders were used for cement paste to minimize slip and prevent the formation of a lubricating layer. The sandblasted configuration has the following dimensions: the inner cylinder radius (R_i) measures 13.33 mm, the outer cylinder radius (R_o), 14.56 mm and the height (h) is 40.00 mm.

The following testing procedure was employed to each sample to determine the rheological properties of cement pastes with SCC consistency. At the start of each test, the cement paste is pre-sheared for 60 s at the maximum shear rate employed during the test, which is 100 s^{-1}. This time period was sufficient in most cases to eliminate the effect of thixotropy from the results. After the pre-shearing period, the cement paste is subjected to a stepwise decrease in shear rate from 100 to 10 s^{-1} in 10 steps. The testing procedure is shown in Figure 2.

The large majority of cement-based materials can be considered as Bingham materials (Eq. 1) in their fresh state [39].

$$\tau = \tau_0 + \mu_p \dot{\gamma} \qquad (1)$$

Where τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μ_p is the plastic viscosity (Pa s), and $\dot{\gamma}$ is the shear rate (s^{-1}). For some of the mixtures, the modified Bingham model was used because non-linear, shear-thickening rheological behavior was observed [40-41]. Yahia and Khayat [42] have shown that the modified Bingham model [42] (Eq. 2) can deliver a better description of the non-linear behavior, as long as the material is not highly shear-thickening.

$$\tau = \tau_0 + \mu_p \dot{\gamma} + c\dot{\gamma}^2 \qquad (2)$$

For this equation, τ is the shear stress (Pa), τ_0 is the yield stress (Pa), μ is linear term of the modified Bingham model (Pa s), $\dot{\gamma}$ is the shear rate (s^{-1}) and c is the second order term (Pa s^2). For the Bingham model, the plastic viscosity (μ_p) is the slope of the line, but for the modified Bingham model, the inclination is $\mu + 2c\dot{\gamma}$. To solve the dependency of the viscosity on the shear rate, the reported viscosity values in this paper are the inclination of the rheological curve at a fixed shear rate, which is chosen at 50 s^{-1}.

2.3. MIX DESIGNS

Two different self-consolidating cement pastes; mix designs 1 and 2, were investigated in this research project. Mix designs 1 is based on the powder-type approach (popular in Europe), while mixtures 2 is based on the VMA-type approach (more common in North America). For both reference cement pastes, the amount of SP was determined to obtain a mini-slump flow value of 330 ± 10 mm at 20 °C and 7 min after mixing. Table 1 displays the reference mix designs 1 and 2, and all variations produced. The highlighted values indicate the varied parameter compared to the reference. All replacements are based on a volumetric basis to keep the amount of water constant for each mixture. Except for mix designs 1-1, 1-2, 2-1 and 2-2, the SP dosage for each of the other mixtures was adapted to achieve the targeted mini-slump flow.

2.4. MIXING PROCEDURE

The preparation of the cement pastes was performed in a small Hobart mixer. All mixing occurred at the lowest speed available and the contact time between cement and water is taken as reference time (t_0). The reference mixing procedure consisted of homogenizing the dry materials (cement, SCM and/or fillers) for 30 s, mixing with water for 1 min, scraping the bowl of the mixer for 1 min and mixing for an additional 30 s. The SP and VMA are added (if applicable) and the paste is mixed for 2 additional minutes, followed by some minor scraping (30 s) and everything is homogenized during the final minute (see Table 2). The total mixing duration is 6.5 minutes. Each mixture was produced twice. The delayed addition serves as base-point for each mixture, and the SP content, to obtain the target mini slump-flow, was adjusted based on the mixture with delayed addition. The mixture was then repeated while physically mixing the same amount of SP with the mixing water. The adding time of the VMA was not altered.

3. TEST RESULTS AND DISCUSSIONS

3.1. COMBINATION OF VARATION IN WATER WITH ADDITION TIME OF SP

A single parameter analysis was performed on mix designs 1 and 2 to investigate the influence of the amount of water, the amount of SP, the adding time of the SP and the mixing energy in [38]. One of the most remarkable results from that analysis was that the adding time of the SP had a more significant influence on the rheological properties of mix design 2, compared to changing the water content, especially for the viscosity. In this paper, the combined influence of the amount of water and addition time of SP, influencing the robustness of powder-type (mix design 1) and VMA-type mix design (mix design 2) is investigated. The addition time of SP is either 100% with water or 100% delayed, the latter taken as reference.

The viscosity and yield stress values of both mixtures subjected to variations in the addition time of SP and in the amount of water are illustrated at Figs. 3 and 4, respectively. For the powder-type SCC cement paste (Mix design 1 displayed on the left side of both figures), the sensitivity to a change in water content is significantly larger than the sensitivity to a change in addition time of the SP. It also appears that changing the addition time of SP does not largely affect the robustness of the investigated powder-type cement paste to variations in water content. For the VMA-type SCC cement paste (displayed on the right), the conclusions are opposite. It appears that plastic viscosity and dynamic yield stress undergo more significant variations due to a change in addition time of SP than due to a variation in water content corresponding to 10 l/m^3 in concrete. With increasing water content, the robustness to the addition time of SP appears to increase, but still remains significant. By delaying the SP addition relative to the water addition, the robustness of the mixtures to a variation in water content appears to increase. Comparing both mixtures, it can be concluded that mixture 1 is more sensitive to a change in water content compared to mixture 2, but mixture 2 is significantly more sensitive to a change in addition time of the SP, compared to mixture 1.

Based on the results in Figs. 3-4, it can be concluded that the most significant factor affecting robustness in mix design 2 is the addition time of the SP. In the next section, it is investigated which particular mix design parameters cause the largest difference in behavior between mixtures 1 and 2. The parameters investigated are the presence of VMA, the different SP types used, the presence of silica fume and fly ash and the influence of the limestone filler. For all following mixtures, the dosage of the SP is adapted to reach the target mini-slump flow (330 ± 10 mm). The SP dosages can be found in Table 1. The rheological properties of all mixtures can be found in Table 3.

3.2. CHANGE IN CEMENT DELIVERY

During the research work, the original cement was replaced by cement of the same type (and same producer), but it led to significantly different results. Mix designs 1, 1-1, 1-2, 1-3, 2, 2-1, 2-2 and 2-3 were produced with the original cement. Mix designs 2b, 2b-4, 2b-5, 2b-6 and 2b-7 were produced with the new cement. Figure 5 shows the percent increase of viscosity and yield stress, taken as follows (similar for the yield stress):

$$\Delta\mu(\%) = 100\frac{\mu_{with\ water} - \mu_{delayed}}{\mu_{delayed}} \qquad (3)$$

As can be seen in Figure 5, the change in yield stress remains approximately constant, but the viscosity is significantly more affected. The reason for the increase in yield stress and viscosity can be attributed to “overgrowing” of the SP by the initial hydration products. The rheological properties of the pastes with both cements, when the SP was delayed, are of the same order of magnitude. Mix design 2b required also a little more SP, but rather insignificant to explain the major difference. The similar increases in yield stress due to not delaying the addition of the SP could be indicative of a similar interaction between the SP and the cement, but the change in viscosity is remarkable.

3.3. PRESENCE OF VMA

Starting for mix design 2, the influence of different constituent elements is analyzed step by step to discover the most critical parameter(s) influencing the response due to the delayed addition. The first parameter investigated is the presence of the viscosity-modifying agent (VMA). The increase in viscosity and yield stress due to the non-delayed addition are shown in Fig. 6. The left part of the figures show the response to a change in adding time of the SP of the mixtures with the VMA, while the right side is exactly the same mix design, but without VMA and a modified dosage of SP to obtain the same mini-slump flow for the mixtures (with 100% delayed addition). It should also be noted that the VMA was added 2.5 min after mixing, after the SP in all cases, regardless of the adding time of the SP.

When focusing on Table 3, comparing mix design 2b and 2b-4, it can be observed that the presence of VMA does not significantly affect viscosity (0.120 vs. 0.126 Pa s), but more the yield stress (5.01 vs. 4.18 Pa). The consequence of adding the SP with the water instead of delayed on the viscosity is not majorly affected. However, the presence of VMA does significantly alter the yield stress behavior when the cement paste is subjected to a variation in adding time of SP. As the adding time of the VMA is not altered, it can be assumed that the VMA has more potential to form hydrogen-bridges in case the SP is added with the water, as more uncoated surfaces of hydration products may be available. The VMA is always added after the SP. However, seeing no change in yield stress due to the change in adding time of the SP in absence of the VMA is remarkable, but this is in line with the results obtained on mix design 1 (not containing VMA).

Figure 7 shows a similar graph, in which mix design 2b without VMA was reproduced, but with SP 1 instead of SP 2, while mix design 2b-6 was also made with SP 1 and with a different VMA from the same manufacturer as SP 1. Similarly, a lower increase in viscosity can be observed when omitting the VMA, but an opposite results than in Figure 6 can be found for the yield stress.

3.4. INFLUENCE SP MANUFACTURER

Reference mixtures 1 (powder-type) and 2 (VMA-type) were produced with SP from different manufacturers. SP 1, used for mixture 1 is a PCE with relatively short workability retention, while SP 2 used in mixture 2 is a PCE with long workability retention. Although no details on the molecular structures are known, it is most probable that the chemical molecules are significantly different. To investigate the influence of the SP type, mixture 2 was reproduced with SP 1, adjusting the dosage to obtain the target mini-slump flow after mixing for the mixtures with the delayed addition of SP. The VMA was omitted to avoid any potential compatibility problems between SP 1 and the VMA (which is from the same manufacturer of SP 2). Similarly, mix design 1 was produced with SP 2.

Figure 8 shows the percent increase in yield stress and viscosity for mixture 2b (with SP 2 and VMA), mixture 2b-4 (SP 2 without VMA), and mixture 2b-5 (SP 1 without VMA). In absolute values, the rheological of the cement pastes with SP 1, when the SP addition is delayed, are slightly higher in mix design 2. The increase in viscosity for mix design 2 with SP 1 is in the same order of magnitude as the increase in viscosity of mix design 1-1, but larger than for mix design 1 and 1-2. However, only a small decrease is remarked for the viscosity comparing mix designs 2b-4 and 2b-5. Concerning the yield stress, a small increase is noted for SP 1, compared to no increase for SP 2 (without VMA) in mix design 2. However, for mix design 1-1, a slight increase in yield stress (although it seems large in relative values), is also observed. Figure 9 shows a similar trend. The rheological properties of mix design 1, made with SP 1 seem less sensitive than the rheological properties of mix design 1-3, produced with SP 2. It can thus be concluded that using the SP with longer workability retention leads to a larger difference in rheological properties when adding the SP at different times.

3.5. BINDER COMBINATIONS

The changes in viscosity and yield stress due to a change in adding time of SP are shown in Fig. 10 for mix design 2 with and without fly ash and silica fume. The results on the right are thus obtained on mixtures with 100% cement as powder material and the replacement of fly ash and silica fume was done by volume to keep the water content in the mixtures constant. The dosage of SP is adjusted for the mixtures with the delayed addition to obtain the target mini-slump flow. Both mixtures contained an equal dosage of VMA. In absolute values, the viscosity of the mix design without FA and SF is substantially larger in case of delayed addition (factor 2), but when the SP is added with the mixing water, the viscosity values are similar. As a consequence, the increase caused by adding the SP with the mixing water is significantly smaller when the FA and SF are not added. However, for the yield stress, the opposite is observed, the difference in yield stress is significantly larger in case no FA and SF are present. These results are in accordance with the literature, where initially adsorbed SP can be overgrown by hydration products. The fact a lower increase in yield stress is observed for the mixture with FA and SF may be attributed to the large affinity of SP to adsorb to the SF surfaces. As a consequence, the large change in viscosity could maybe be attributed to a significantly worse packing of the particles, but no physical explanation has been found at this point.

To enable comparison with mix design 1, all FA and SF in mix design 2b was replaced, by volume, with limestone filler. The percent change in viscosity is the lowest observed for all mix designs 2, and in absolute values, it shows the lowest change of all mix designs tested in this paper. Compared to mix design 2-3 (pure cement, but with VMA), the percent change in viscosity is 5% lower, but the change in viscosity is about half in absolute values. As a result, the limestone filler has a beneficial effect on reducing the change in viscosity due to the adding time of the SP. Also for the yield stress, mix design 2b-7 shows the second lowest change, after mix design 2b-4. Also here, it can be concluded that limestone filler has a beneficial effect. Comparing mix designs 2, 2b, 2-3 and 2b-4 with 2b-7, the mixture with limestone filler requires the lowest amount of SP to maintain the mini-slump flow, proving that limestone filler acts an inert, filler material, showing less interaction with the admixtures.

3.6. SUMMARY OF ALL PARAMETERS

Table 4 shows the average increase in yield stress and viscosity due to not delaying the addition of the SP in mix design 2. The last column in Table 4 shows the maximum % increase in either yield stress or viscosity. For all tested modifications, the largest increase was noted in the viscosity, except for the mixture without FA and SF (2-3). When considering the average values, it can be concluded that omitting the VMA (2b-4) or incorporating limestone (2b-7) provoke the lowest average increase in yield stress and viscosity. However, the beneficial effect of the VMA is only noticeable on the yield stress for mix design 2b-4, while the viscosity still undergoes a major increase. However, this increase is lower than in the reference mix design (2b). Replacing a part of the cement with limestone filler reduces the percent increase in yield stress and viscosity due to not delaying the adding time of the SP.

4. CONCLUSIONS

Robustness is the sensitivity of concrete mixtures to a small variation in constituent elements or mixing procedure. It is an important reason slowing down the practical implementation of self-consolidating concrete (SCC). Especially the sensitivity of fresh SCC properties to a small variation in water content can be found in literature.

The influence of the addition time of SP on the robustness of SCC mixtures is not extensively reported.

In this study, the influence of the addition time of SP was investigated on the rheological properties of cement-pastes with SCC consistency. The VMA-type mix design showed a significant sensitivity to the adding time of the SP and the resulting change in rheological properties was larger than the changes induced by varying the water content. For the powder-type cement paste, the change in water content was more important than the adding time of the SP. Especially the viscosity is largely affected by the adding time.

The source of the PCE-SP appears to play a minor but important role, as mixtures with a long workability-retaining admixture (SP 2) appeared more sensitive to the adding time of the SP.

Omitting VMA reduces the sensitivity of viscosity of the cement paste, regardless of the VMA manufacturer. For the yield stress, different results were obtained.

The presence of silica fume and fly ash renders the viscosity of the tested VMA-type mixture very sensitive to a change in adding time, while for cement paste without SCMs, the yield stress is more affected. Replacing a part of the binder with limestone filler reduces the variations in rheological properties due to the adding time of the SP.

In most cases, the viscosity of the mixture was more affected than the yield stress due to a delayed addition of SP.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the National University Transportation Center at Missouri S&T and the Science Foundation in Flanders (FWO) for the financial support of this project.

Table 1. Mix designs for 1.5 liter of cement paste

	Cement type I/II (g)	Filler or SCM (g)	Water (g)	SP1 (g)	SP2 (g)	VMA (g)	W/C	W/P	C/P
Mix Design 1	1210.8	LF: 1210.8	665.9	5.2	-	-	0.55	0.275	0.5
Mix Design 1-1	1210.8	LF: 1210.8	707.9	5.203	-	-	0.58	0.29	0.5
Mix Design 1-2	1210.8	LF: 1210.8	623.9	5.197	-	-	0.52	0.26	0.5
Mix Design 1-3	1210.8	LF: 1210.8	665.9	-	7.247	-	0.55	0.275	0.5
Mix Design 2	1443.3	SF: 50.4 FA: 499.3	759.4	-	9.690	1.250	0.53	0.38	0.724
Mix Design 2b	1443.3	SF: 50.4 FA: 499.3	759.4	-	10.018	1.250	0.53	0.38	0.724
Mix Design 2-1	1443.3	SF: 50.4 FA: 499.3	801.4	-	9.686	1.250	0.55	0.40	0.724
Mix Design 2-2	1443.3	SF: 50.4 FA: 499.3	717.4	-	9.690	1.250	0.50	0.36	0.724
Mix Design 2-3	2168.5	FA: 0 SF: 0	759.4	-	12.806	1.250	0.35	0.35	1
Mix Design 2b-4	1443.3	SF: 50.4 FA: 499.3	759.4	-	9.690	0	0.53	0.38	0.724
Mix Design 2b-5	1443.3	SF: 50.4 FA: 499.3	759.4	6.113	-	0	0.53	0.38	0.724
Mix Design 2b-6	1443.3	SF: 50.4 FA: 499.3	759.4	12.21	-	26.99 *	0.53	0.38	0.724
Mix Design 2b-7	1443.3	LF: 623.5	759.4	-	7.09	0	0.53	0.37	0.7

*VMA for mix design 2b-6 compatible with SP 1 (different from VMA used in all other mix designs)

Table 2. Mixing Procedure

Step	Duration	Action
1	30 s	Dry Materials
2 (=t_0)	1 min	Adding Water
3	1 min	Scraping
4	30 s	Mixing
5	2 min	Add SP / VMA
6	30 s	Scraping
7	1 min	Mixing
Duration since t_0	6 min	

Table 3. Rheological properties of tested mixtures

	Plastic Viscosity (Pa s)		Yield Stress (Pa)	
Mixture	SP with water	SP delayed	SP with water	SP delayed
Mix design 1	0.313	0.253	2.24	2.83
Mix design 1-1	0.224	0.142	1.96	0.87
Mix design 1-2	0.544	0.449	6.63	7.92
Mix design 1-3	0.459	0.329	3.24	2.38
Mix design 2	0.356	0.125	10.02	5.69
Mix design 2b	0.210	0.120	8.40	5.01
Mix design 2-1	0.234	0.108	6.34	3.61
Mix design 2-2	0.356	0.125	10.02	5.69
Mix design 2-3	0.354	0.269	5.16	2.03
Mix design 2b-4	0.200	0.126	4.11	4.18
Mix design 2b-5	0.222	0.146	6.81	5.25
Mix design 2b-6	0.348	0.189	8.65	7.04
Mix design 2b-7	0.212	0.167	3.69	2.80

Table 4. Average and maximum % increase in viscosity and/or yield stress due to not delaying the addition time of the SP.

	Modification	Average % increase	Maximum % increase
Mix design 2		130	184 (μ)
Mix design 2b	New cement delivery	71	75 (μ)
Mix design 2-1	+ Water	96	117 (μ)
Mix design 2-2	- Water	108	117 (μ)
Mix design 2-3	100% cement	93	154 (τ_0)
Mix design 2b-4	No VMA	29	59 (μ)
Mix design 2b-5	SP 1	41	52 (μ)
Mix design 2b-6	SP 1 + VMA	53	84 (μ)
Mix design 2b-7	Limestone filler	29	32 (μ)

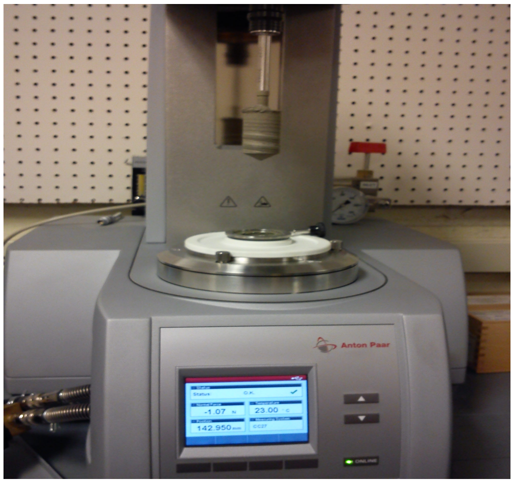


Figure 1. Anton Paar MCR 302 Rheometer

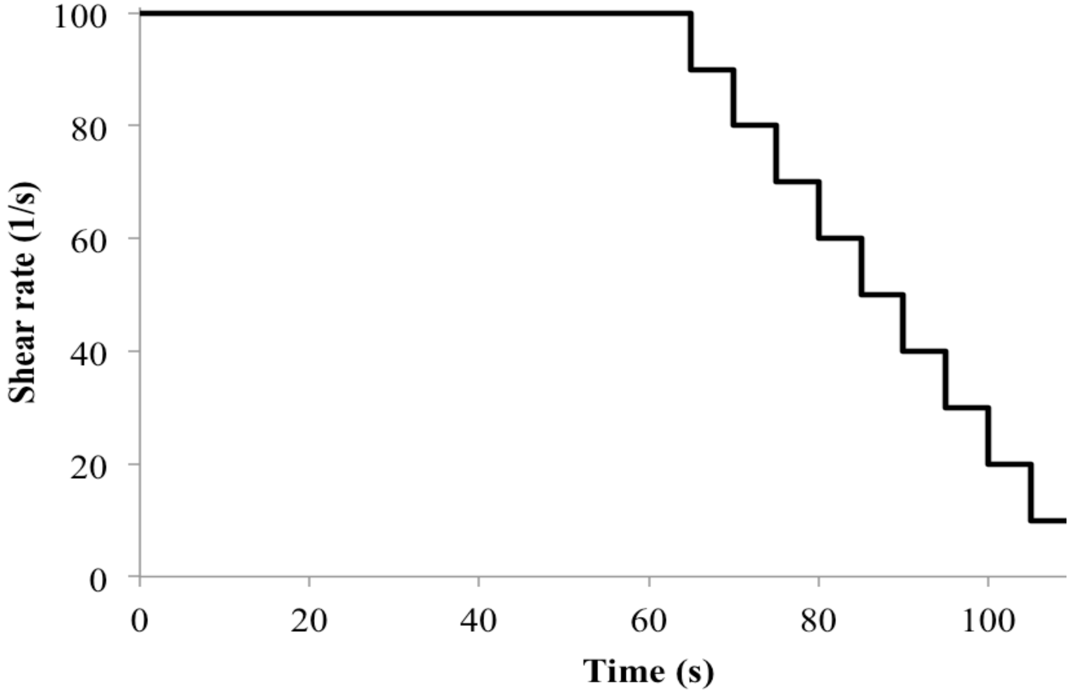


Figure 2. Testing procedure for cement pastes in the Anton Paar MCR 302 rheometer.

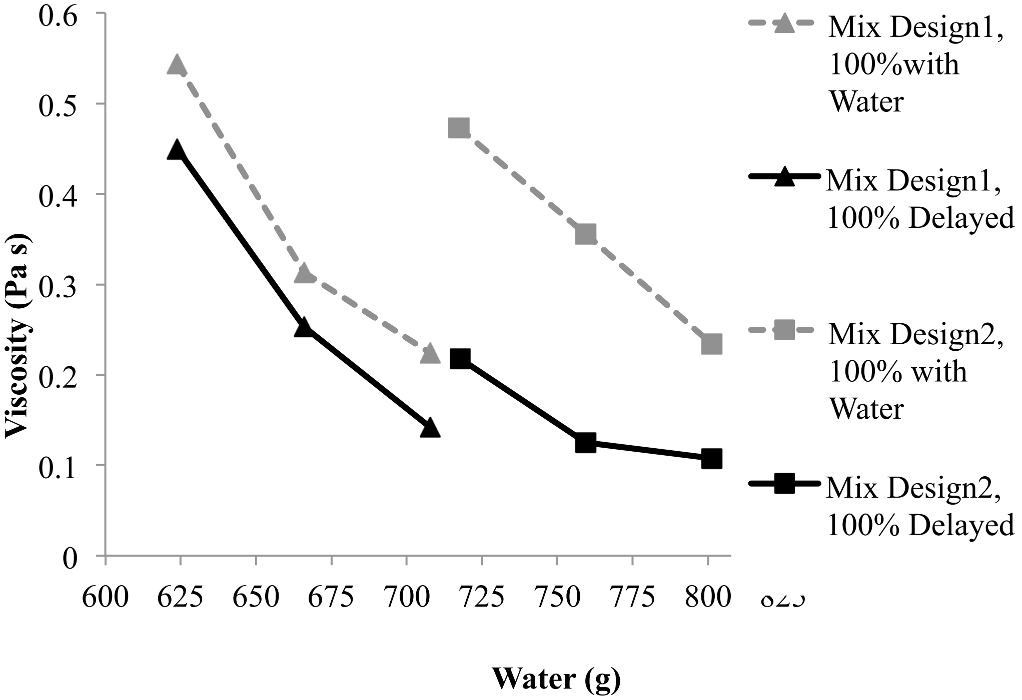


Figure 3. Viscosity of Mix Design 1 and 2 at different addition time of SP as a function of water content.

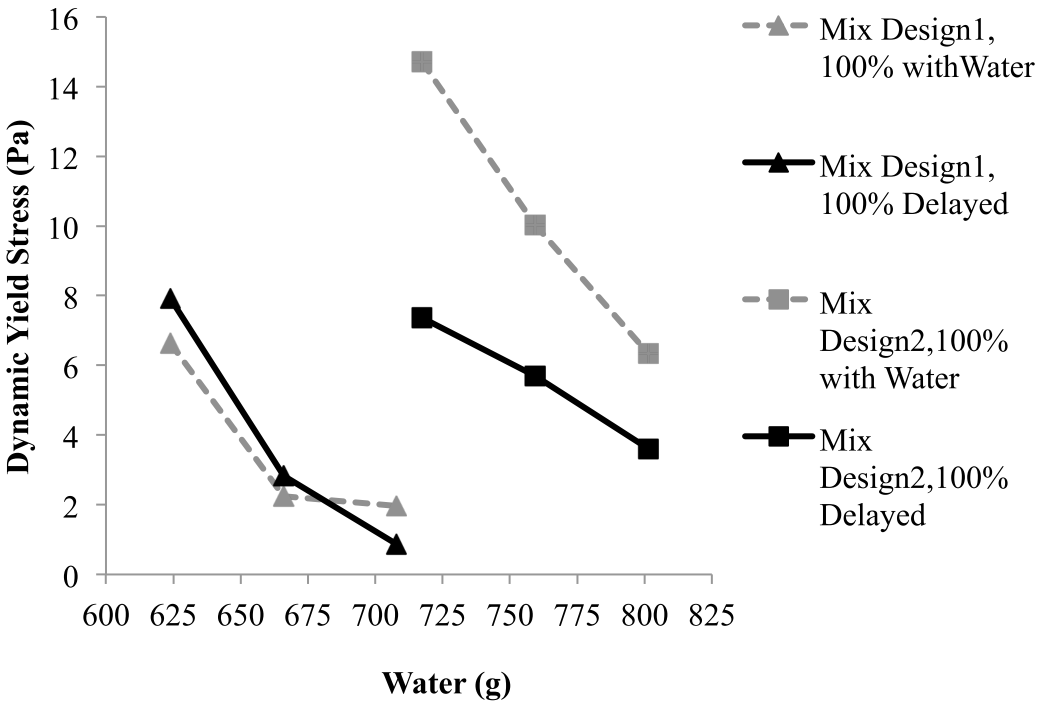


Figure 4. Yield stress of Mix Design 1 and 2 at different addition time of SP as a function of the water content.

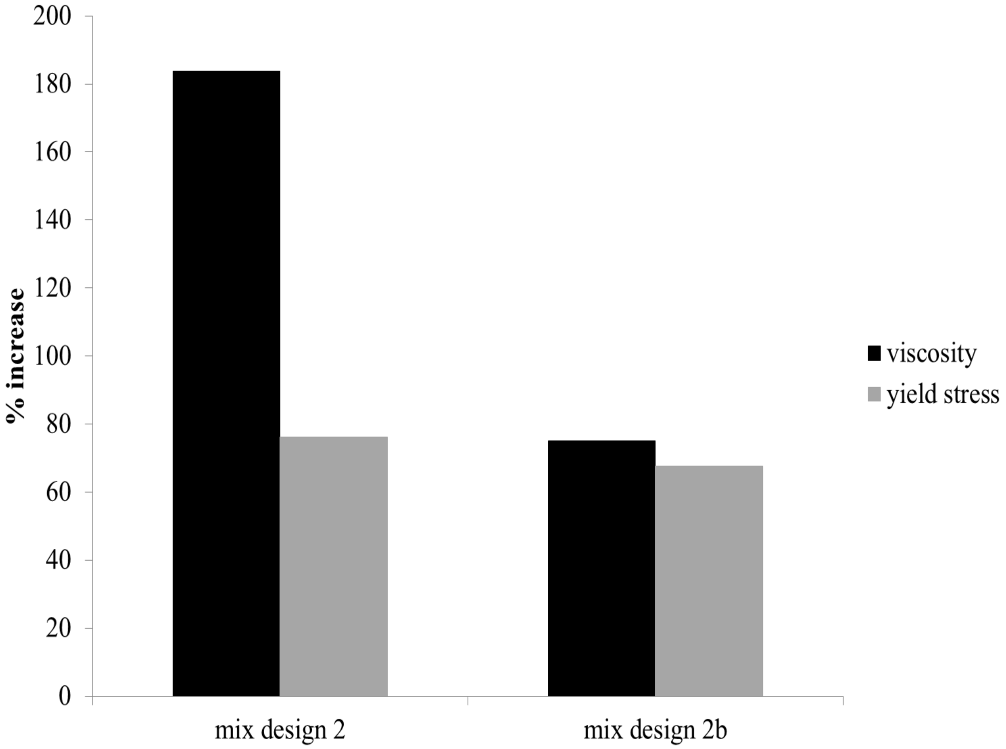


Figure 5. Influence of a change in delivery of cement from the same manufacturer on the increase in viscosity and yield stress due to not delaying the addition of the SP.

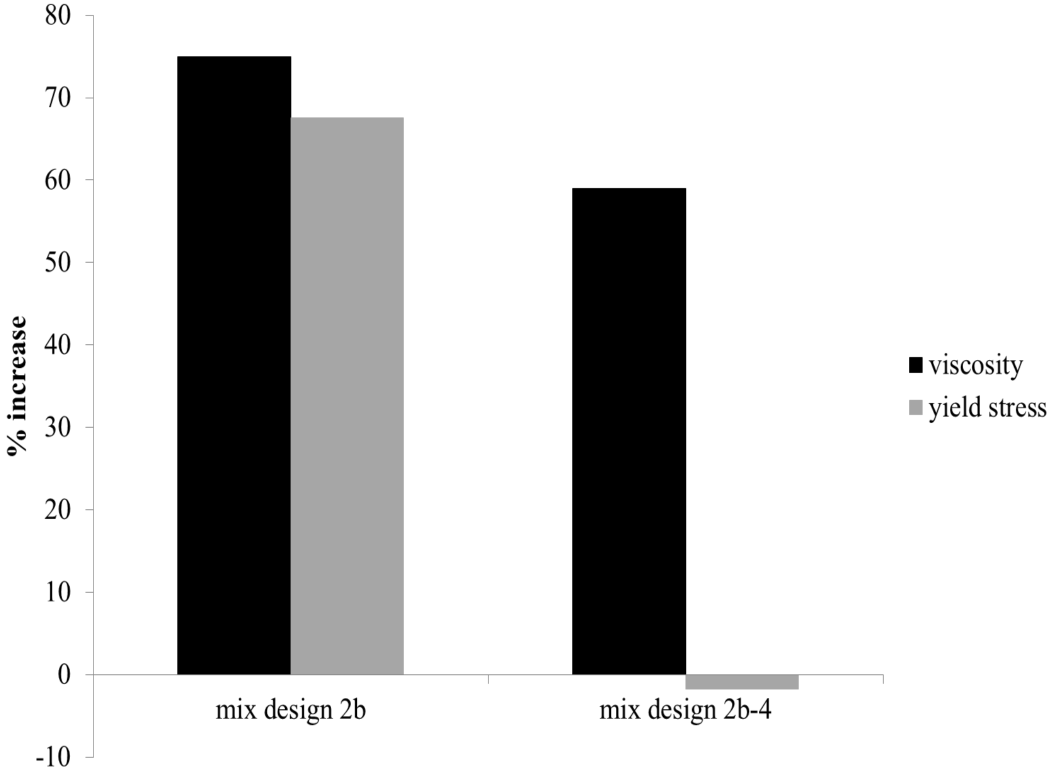


Figure 6. Influence of the presence of VMA on increase in viscosity and yield stress in mixtures with SP 2 due to omitting VMA (left part is with VMA, right part without).

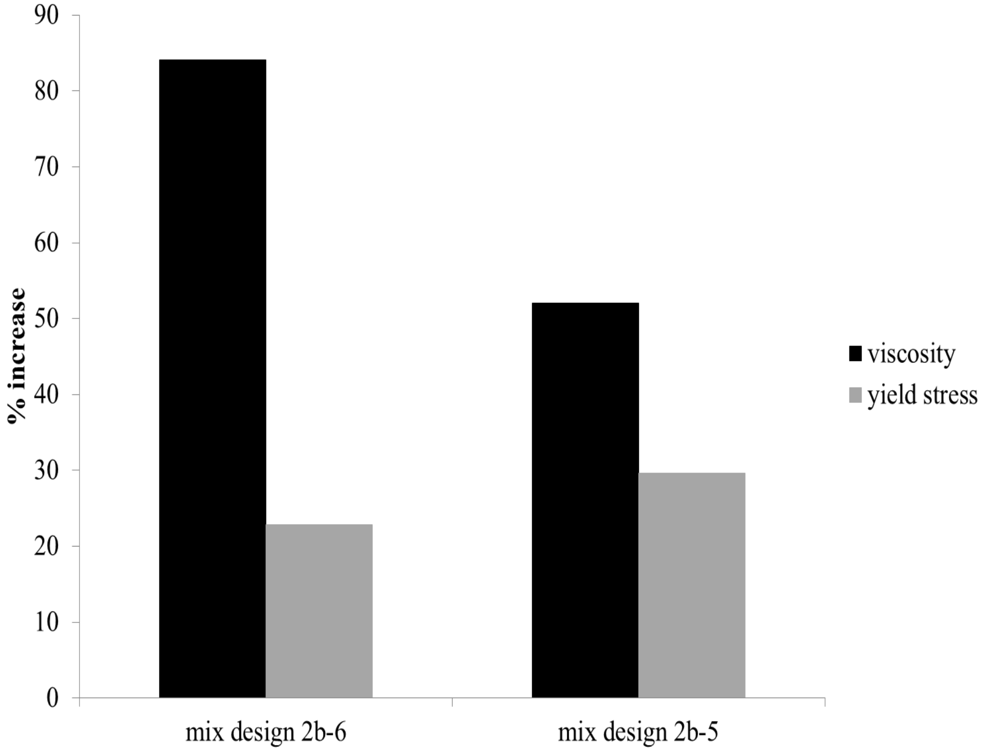


Figure 7. Influence of the presence of VMA on increase in viscosity and yield stress, in mixtures with SP 1 due to omitting VMA (left part is with VMA, right part without).

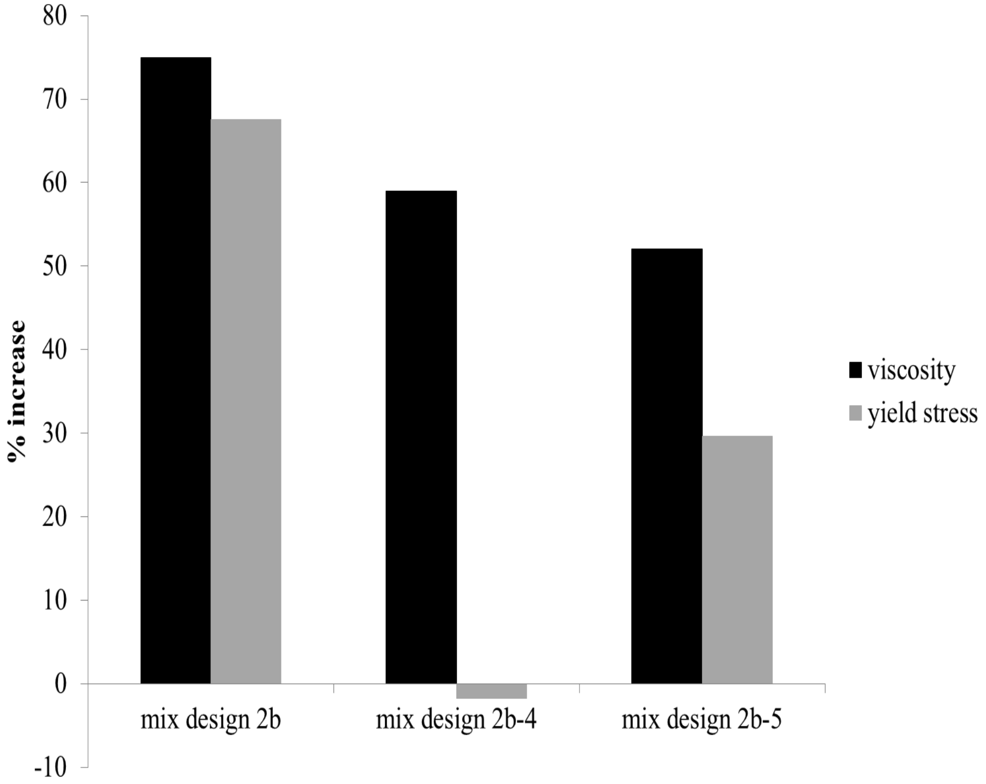


Figure 8. Influence of the type of SP on the increase in viscosity and yield stress. Mix design 2b is made with SP 2 and VMA, mix design 2b-4 is produced with SP 2 without VMA and mix design 2b-5 is made with SP 1.

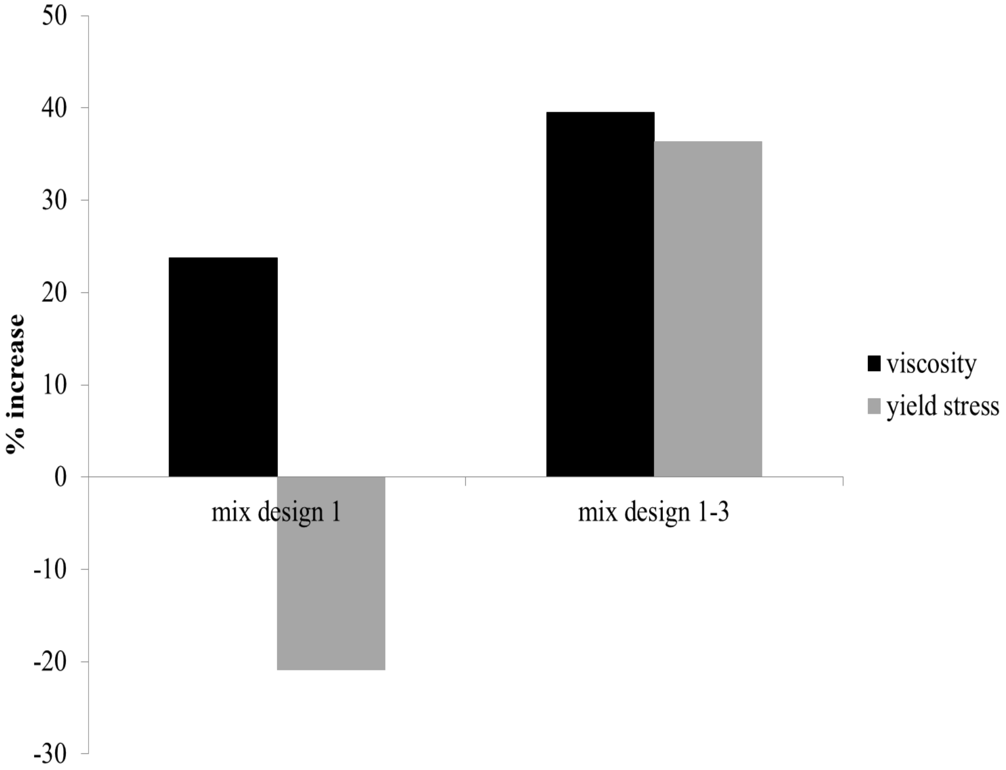


Figure 9. Influence of the type of SP on the change in viscosity and yield stress. Mix design 1 is made with SP 1 while mix design 1-3 is made with SP 2.

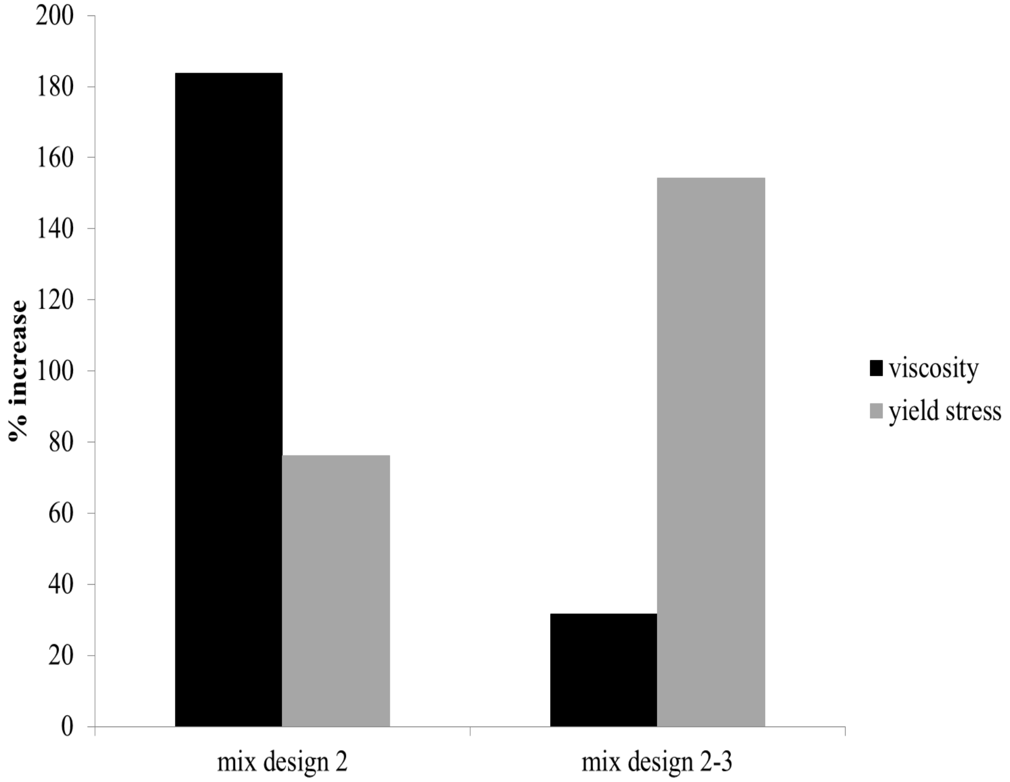


Figure 10. Increase in viscosity and yield stress for mixtures with fly ash and silica fume (left), and with 100% cement (right)

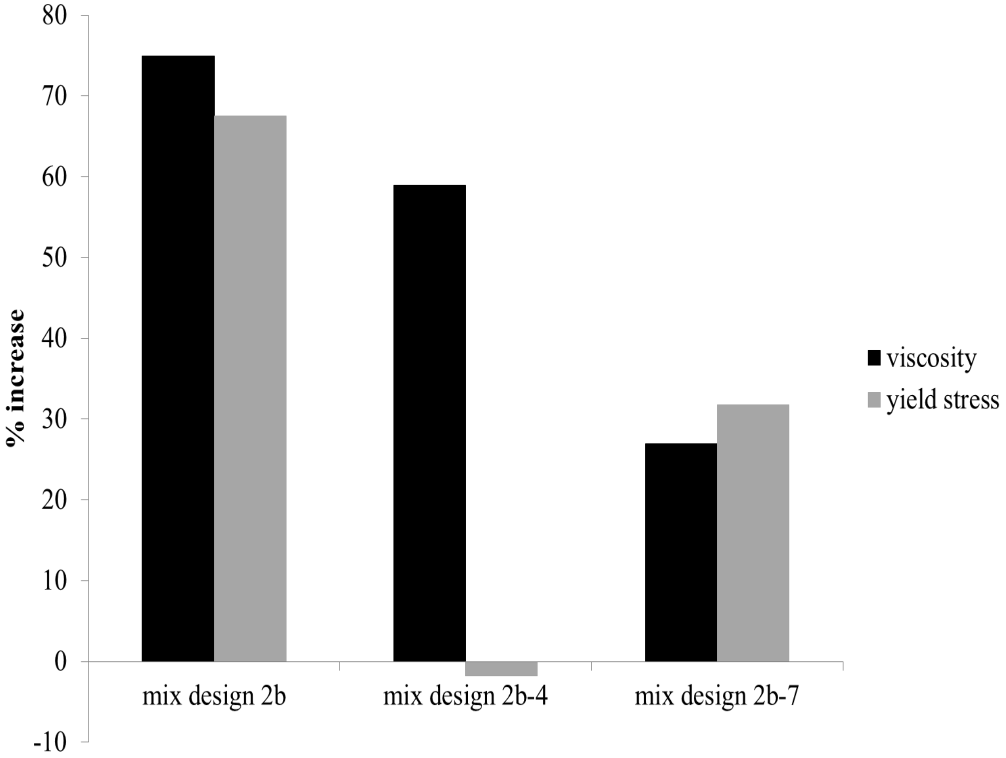


Figure 11. Increase in viscosity and yield stress for mix design 2b (reference: with FA and SF), 2b-4 (reference, without VMA) and 2b-7 (with limestone filler).

REFERENCES

[1] Khayat KH (1999), Workability, Testing, and Performance of Self-Consolidating Concrete, *ACI Mat. J.* 96-3, 346-353.

[2] Okamura H, Ouchi M (2003), Self-compacting concrete, *J. of Advance Concrete Technology* 1, 5-15.

[3] Khayat KH, Manai K, Trudel A (1997), In Situ Mechanical Properties of Wall Elements Cast Using Self-Consolidating Concrete, *ACI Mat. J.* 94-6, 491-500.

[4] De Schutter G, Bartos PJM, Domone P, Gibbs J (2008), Self-compacting concrete, Whittles Publishing, Caithness.

[5] Gettu R, Nawaz Shareef S (2009), Evaluation of the Robustness of SCC, *Indian Concrete Journal* 83-6, 13-19.

[6] Rigueira JW, García-Taengua E, Serna-Ros P (2009), Self- Consolidating Concrete in Continuous Production Regarding Fresh and Hardened State Properties, *ACI Mat. J.*, 106-3 301-307.

[7] Nunes S, Figueiras H, Oliveira PM, Coutinho JS, Figueiras J (2006), A Methodology to Assess Robustness of SCC Mixtures, *Cem. Concr. Res.* 36, 2115-2122.

[8] Billberg P (2009), Increase of SCC Robustness to Varying Aggregate Moisture Content Using VMA, *Proceedings of the Second International Symposium on Design, Performance, and Use of Self-Consolidating Concrete (SCC)*, China, 473-493.

[9] Billberg P (2011) Influence of powder type and VMA combination on certain key fresh properties of SCC, *9th International Symposium on High Performance Concrete*, Rotorua, New Zealand.

[10] Li LG, Kwan AKH (2013), Concrete mix design based on water film thickness and paste film thickness, *Cem. Conc. Comp.* 39-5, 33-42.

[11] BIBM, CEMBUREAU, ERMCO, EFCA, and EFNARC (2005), European Guidelines for Self Consolidating Concrete: Specification, Production and Use, 63 pp. http://www.efnarc.org/pdf/SCCGuidelinesMay2005.pdf.

[12] Yurugi M, Sakai G, Sakata, N (1995), Viscosity Agent and Mineral Admixtures for Highly Fluidized Concrete, *Proceedings, Concrete under Severe Conditions, Environmental and Loading*, 995-1004.

[13] Sakata N, Yanai S, Yoshizaki M, Phyfferoen A, Monty H (2001), Evaluation of S-657 Biopolymer as a new viscosity-modifying admixture for self-compacting concrete, *presented at the Second International Symposium on Self-Compacting Concrete*, Tokyo, Japan.

[14] Naji S, Hwang S-D, Khayat KH (2011), Robustness of self-consolidating concrete incorporating different viscosity-enhancing admixtures, *ACI Mat. J.* 108-4, 432-438.

[15] Billberg P, Khayat KH (2008), Use of Viscosity-Modifying Admixtures to Enhance Robustness, *Proceedings of the Third North American Conference on the Design and Use of Self-Consolidating Concrete*, Chicago, IL.

[16] Billberg P, Westerholm M (2008), Robustness of fresh VMA-modified SCC to varying aggregate moisture, *NCR J.* 38-7, 103-119.

[17] Bonen D, Deshpande Y, Olek J, Shen L, Struble L, Lange DA, Khayat K (2007), Robustness of selfconsolidating concrete, *Proc. of the 5th Int. RILEM Symp. on Self-Compacting Concrete*, Ghent, Belgium.

[18] Kwan AKH, Ng IYT (2010), Improving performance and robustness of SCC by adding supplementary cementitious materials, *Constr. Build. Mat.* 24, 2260–2266.

[19] Lowke D, Schiessl P (2005), Effect of mixing energy on fresh properties of SCC, *2th North American Conference on the Design and Use of Self-consolidating Concrete / 4th International RILEM Symposium on Self-Compacting Concrete*, Chicago, IL, USA.

[20] Schiessl P, Mazanec O, Lowke D (2007), SCC and UHPC - Effect of mixing technology on fresh concrete properties, *Advances in Construction Materials*, Ed: Grosse CU, Heidelberg, Germany, 513-522.

[21] Cazacliu B, Roquet N (2009), Concrete mixing kinetics by means of power measurement, *Cem. Conc. Res.* 39-3, 182-194.

[22] Uchikawa H, Sawaki D, Hanehara S (1995), Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement pastes, *Cem. Conc. Res.* 25, 353–364.

[23] Kim BG, Jiang S, Jolicoeur C, Aitcin PC (2000), The adsorption behavior of pns superplasticizer and its relation to fluidity of cement paste, *Cem. Concr. Res.* 30, 887–893.

[24] Jolicoeur C, Sharman J, Otis N, Lebel A, Simard MA, Page M (1997), The influence of temperature on the rheological properties of super- plasticized cement pastes, *5th International Conference on Super- plasticizer and other Chemical Admixtures in Concrete*, Rome, 379–406.

[25] Simard MA, Nkinamubanzi PC, Jolicoeur C (1993), Calorimetry, rheology, and compressive strength of superplasticized cement pastes, *Cem. Concr. Res.* 23, 939–950.

[26] E. Hanna, K. Lake, D. Perraton, P.-C. Aitcin (1989), Rheological behavior of Portland cement paste in the presence of a superplasticizer, *ACI SP-119:* V.M. Malhotra (Ed.), *3rd International Conference on Superplasticizers and other Chemicals Admixtures in Concrete*, ACI, Ottawa, 171 – 188.

[27] Bonen D, Sarkar SL (1995), The superplasticizer adsorption capacity of cement pastes pore solution composition and parameters affecting flow loss, *Cem. Concr. Res*. 25, 1423–1434.

[28] Yamada K, Hanehara S, Honma K (1998), The effect of naphthalene sulfonate type and polycarboxylate type superplasticizers on the fluidity of belite-rich cement, *Proceeding of Self-Compacting Concrete Workshop*, Kochi, 201 – 210.

[29] Hsu KC, Chiu JJ, Chen SD, Tseng YC (1999), Effect of Addition Time of a Superplasticizer on Cement Adsorption and on Concrete Workability, *Cem. Concr. Comp.* 21-(5-6), 425-430.

[30] Ferrari L, Kaufmann J, Winnefeld F, Plank J (2010), Interaction of Cement Model Systems with Superplasticizers Investigated by Atomic Force Microscopy, Zeta Potential, and Adsorption Measurements, *J. Colloid Interface Sc.* 347-1, 15-24.

[31] Collepardi M (1998), Admixtures Used to Enhance Placing Characteristics of Concrete, *Cem Concr. Comp.* 20-(2-3), 103-112

[32] Aiad I, Abd El-Aleem S, El-Didamony H (2002), Effect of delaying addition of some concrete admixtures on the rheological properties of cement pastes, *Cem. Conc. Res.* 32, 1839–1843.

[33] Aiad I (2003), Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes, *Cem. Conc. Res.* 33, 1229–1234.

[34] Kwan AKH, Ng IYT (2009), Optimum superplasticiser dosage and aggregate proportions for SCC, *Mag. Conc. Res.* 61-4, 281-292.

[35] Fernandez-Altable V, Casanova I (2006), Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures, *Cem. Conc. Res.* 36, 1222–1230.

[36] Houst YF, Flatt RJ, Bowen P, Hofmann H, Mäder U, Widmer J, Sulser U, Bürge TA, Sika AG (1999), Influence of Superplasticizer Adsorption on the Rheology of Cement Paste, *Proceedings of the International Conference, The Role of Chemical Admixtures in high Performance Concrete,* Monterrey, Mexico, 387-402.

[37] Plank J, Hirsch C (2007), Impact of ζ-potential of Early Cement Hydration Phases on Superplasticizer Adsorption, *Cem. Concr. Res.* 37-4, 537-542.

[38] Asghari AA, Hernandez AM, Feys D, De Schutter G (2016) Which parameters, other than the water content, influence the robustness of cement paste with SCC consistency? *Constr. Build. Mat.* 124, 95-103.

[39] Tattersall GH, Banfill PFG (1983), The rheology of fresh concrete, Pitman, London.

[40] Feys D, Verhoeven R, De Schutter G (2007), Evaluation of time independent rheological models applicable to fresh Self-Compacting Concrete, *Appl. Rheol.* 17–5, 56244.

[41] Feys D, Heirman G, De Schutter G, Verhoeven R, Vandewalle L, Van Gemert D (2007), Comparison of two concrete rheometers for shear thickening behaviour of SCC, *Proc 5th Int RILEM Symp SCC*, Ghent, 365–370.

[42] Yahia A, Khayat KH (2001), Analytical models for estimating yield stress of high-performance pseudoplastic grout, *Cem. Concr. Res.* 31, 731–738.

III. TIME EVALUTION OF RHEOLOGY OF CEMENT PASTES AFFECTED BY MIX DESIGN AND MIXING PROCEDURE

Azadeh A. Asghari, Dimitri Feys and Geert De Schutter

ABSTRACT

Robustness is defined as the capacity of cement-based materials to retain fresh properties when subjected to either small variations in the constituent elements or small changes in the mixing procedure. Compared to normal concrete, self-consolidating concrete (SCC) may show less tolerance to those changes. Most robustness studies focus on initial rheological properties or workability, but concentrate less on the evolution of these properties within the first hour(s). This paper presents the results of an investigation aimed at evaluating the change of yield stress and viscosity with time of cement pastes with SCC consistency, which is mainly affected by variations in the water content and the adding time of the superplasticizer. A change in water content also influences the initial rheological properties, and these differences are amplified over time. The difference due to the different adding time of the superplasticizer is however reduced or even reversed over time.

Keywords: Cement Paste; Constituent Elements; Mixing Procedure; Rheology; Robustness; Workability Loss

1. INTRODUCTION

Self-consolidating concrete (SCC) has less tolerance to small changes in the quantities and properties of constituent materials and mixing procedure, compared to conventional vibrated concrete. Those slight changes induce small alterations in the rheological properties of SCC [1-2], which can lead to segregation in case of a decrease in yield stress or viscosity, or a loss of filling capacity in case of an increase in yield stress or viscosity. Controlling the variations in the rheological properties is essential to ensure proper characteristics of SCC during mixing, transport and placement [3-7]. If the initial rheological properties, and their change as a function of time are inadequate, mechanical properties and durability of the cast structure can be negatively affected [8]. Most robustness studies have focused on the influence of mix design, constituent material properties and mixing procedure on the rheological properties of concrete. The paste component of the concrete plays hereby a crucial role, as the rheological properties are strongly related to the water-to-cement (w/cm) ratio, the presence of supplementary cementitious materials, chemical admixtures, and temperature [9-12]. An incorrect assessment of the sand moisture content is considered to significantly influence the cement paste composition and properties (larger relative change in water content), in a more prominent way than any change in rheological properties induced by the sand content.

On paste level, the initial rheological properties, mostly measured between 10 and 30 min after mixing started, are significantly affected by w/cm, sometimes showing an exponential relationship with the change in water content [13-15]. Furthermore, in cement pastes (or concrete mixtures) with different w/cm, different parameters are dominant in controlling the robustness, resulting in some apparent disparity in research conclusions [3-6, 16-17]. Employing superplasticizers (SP) causes dispersion of flocculated cement grains and the release of entrapped water [18-21]. Bonen and Shah [22] reported the effects of the SP content on the flow properties of concrete, revealing that the robustness of the flow is proportional to the mass ratio of SP to binder. Mixture composition and mixing procedures can affect the efficiency of the SP in decreasing the water demand in cement paste [23-24]: increasing mixing intensity decreases both plastic viscosity and yield stress dramatically [14, 25-26], unless the mixture is overmixed. SP adsorption on cement is also affected by the concentration of sulfate ions in the interstitial solution [27-28]. In addition, the time of adding the SP can change the initial rheological properties of SCC dramatically [29-34]. The effect of limestone filler on the initial rheological properties has been studied by Carlsward et al. [35], showing that limestone filler has small influence on the plastic viscosity and the yield stress. Bonen [2] reported that incorporation of high specific gravity fine materials such as limestone, slag and dolomite increases the SCC robustness.

Most of these studies solely focus on the robustness of the initial rheological properties. However, their change with time should also be considered, especially when focusing on ready-mix applications as transport times can be extensive. The change in rheological properties with time is generally induced by two factors: physical factors (such as flocculation, destruction and restructuring of the microstructure) and chemical factors (cement hydration and decrease in free water content) [36]. Typically, the physical factors (which are reversible) are considered as thixotropy, while the chemical factors are associated to the non-reversible workability loss, although recent work has shown that the distinction is not so straightforward [37]. Cement hydration, mixture composition, and the interaction between the binder particles and chemical admixtures are dominant factors which influence the workability loss over time [38]. In addition, differences in the quantity and composition of superplasticizer influence the cement hydration process and thus affect the workability loss once more [39-42]. Correlations between mixture compositions, the initial rheological properties of the cementitious system and the development of rheological properties over time have been investigated by several researchers [43-46]. It is reported that the change of rheological properties as a function of time in cement-based materials is strongly influenced by superplasticizer type and dosage, w/cm, and cement type [45, 47]. Golaszewski and Szwabowski [45] concluded that the type and dosage of superplasticizers affect the rheological behavior of cement mortars. PCE superplasticizer makes mortars with lower workability loss compare to SNF superplasticizers. Zhang et al. [42] investigated the effect of polycarboxylate superplasticizer to cement ratio (Sp/C), water to cement ratio (w/c) and time on the rheological behavior of fresh cement pastes. For Sp/C from 0 to 2.0% and w/c ratio of 0.25 to 0.50, it has been indicated that with an increase in SP dosage, the initial flowability and flowability retention over time increase because of plasticizing and retardation induced by the superplasticizer. At low Sp/C, similar trends have been observed for yield stress and plastic viscosity, while in the case of high Sp/C, the yield stress and viscosity deceased over the elapsed time [42].

Petit et al. have investigated the influence temperature on the evolution of rheological properties with time. When expressing the elapsed time as a function of the final setting time, nearly linear increases were found for the yield stress and viscosity. However, especially for PCE-based SP, the evolution of the rheological properties with time could follow a more complex pattern when temperature was below a certain threshold, dependent on the mix design [36, 47-48].

2. RESEARCH SIGNIFICANCE

In this paper, the robustness of the "loss of workability" of flowable cement pastes is discussed. Similar to performing a robustness study on the initial rheological properties, the change in their time evolution is described. The influence of the change in water content, SP dosage, varying mixing time, mixing speed and different addition time of SP is demonstrated. The results are compared to the influence of these parameters on the initial rheological properties [49], and a more accurate vision on robustness of cement paste, and also concrete, can be developed by taking into account the time-dependency of the rheological properties.

3. EXPERIMENTAL PROGRAM

3.1. MATERIALS

Three different cement pastes with SCC consistency were prepared based on SCC mixtures commonly used in Europe and North-America [49]. Mix designs 1 and 3 are based on the powder-type approach. Mix design 1 was prepared with a water-to-powder ratio (w/p) of 0.275. The powder is composed of 50% Type I/II cement (according to ASTM C150), and 50% finely ground limestone (by mass). Mix design 3 is based on the same principle, but the powder consists of 57% cement and 43% limestone filler, while w/p = 0.31. Both mix designs are produced with an efficient polycarboxylate ether-based superplasticizer (PCE). As will be discussed further, this SP, named SP 1, has a relatively short workability retention.

Mix design 2 is based on a VMA-type mix design using silica fume (SF) and class C fly ash (FA) as supplementary cementitious materials (SCM), with a more elevated w/p (= 0.38) compared to the other mix designs. A different PCE (SP 2), from a different manufacturer, was used. This SP had relatively long workability retention. A viscosity-modifying agent (VMA) has been added to mix design 2 to assure stability. The VMA is from the same manufacturer as SP 2 to prevent compatibility problems. The mix proportions of the cement pastes are listed in Table 1. For all reference cement pastes, the amount of each SP was determined to reach a mini-slump flow value of 330 ± 10 mm *(11.8 ± 0.4 in.)* at 7 min after mixing, ensuring SCC consistency. It should be noted that halfway the experiments on mix design 2, a new delivery of cement causes some modifications in the HRWRA demand, and the rheological properties.

3.2. MIXING PROCEDURE

The preparation of the cement pastes occurred at the lowest speed available in a small Hobart mixer. The contact time between cement and water is taken as reference time (t_0), while the reference mixing procedure is presented in table 2. The total mixing duration is 6 minutes, after contact between cement and water. The repeatability of the mixture and the mixing procedure, the influence of water and the influence of SP variations were investigated by employing the reference mixing procedure.

To investigate the influence of a modification in the mixing procedure, the addition time of the SP has been altered: instead of delaying the SP addition, the same amount of SP was mixed with the mixing water and added to the mixer. A second modification in mixing procedure was performed by altering the mixing time. The details of these mixing procedure are presented in Table 2. In addition, the influence of a different mixing speed was investigated by mixing the cement paste at intermediate speed (4.68 rps) in the Hobart mixer, for mixing steps 5 and 7 in Table 2. The mixing speed was only increased for the reference mixing time. The influence of mixing time and mixing speed will be reflected by the mixing energy further in this paper. The number of rotations of the paddle (Table 2), considering the speed of 2.27 rps for the lowest setting, and 4.68 rps for the intermediate setting is ought to be representative for the mixing energy.

3.3. RHEOMETRY

The Anton Paar MCR 302 Rheometer (Figure 1) was employed to measure the rheological properties of the cement pastes. A coaxial cylinders geometry was selected for these tests. Both inner and outer cylinders were sandblasted to limit slippage. The inner cylinder radius (R_i) measures 13.33 mm (0.5248 in.), the outer cylinder radius (R_o) is 14.56 mm (0.5732 in.), and the height (h) is 40.00 mm (1.575 in.). Prior to each measurement of the rheological properties, the sample was pre-sheared for 60 s at a shear rate of 100 s^{-1}, to ensure the same reference state of the sample for each measurement. The rheological properties were determined by measuring the torque response to a stepwise decreasing function of the shear rate: the shear rate was decreased in 10 intervals, with a duration of 5 s each, from 100 to 10 s^{-1}. From the raw torque and rotational velocity data, the yield stress and plastic viscosity (eq. 1) were determined based on the Reiner-Riwlin principle.

$$\tau = \tau_0 + \mu_p \dot{\gamma} \qquad (1)$$

For this equation, τ is the shear stress (Pa), τ_0 is the Bingham yield stress (Pa), μ_p is the Bingham plastic viscosity (Pa s), and $\dot{\gamma}$ is the shear rate (s^{-1}). While the yield stress is defined as the stress needed to start the flow, the plastic viscosity is the resistance of the material to enhance in flow rate once the yield stress is exceeded [13].

The time evolution of the rheological properties is taken as the (linear) slope of four consecutive measurements, performed at 15 (initial), 30, 45 and 60 min after initial contact between cement and water. The temperature in the rheometer is kept constant at 23°C (73.5 F) to eliminate the influence of temperature on the time evolution of the rheological properties [e.g. 36, 47].

4. RESULTS AND DISCUSSION

4.1. REPEATABILITY

A 90% confidence interval for all three mixtures is calculated for the increase in yield stress (in mPa/min) and viscosity (in mPas/min) with time based on four repetitive productions of the cement pastes. Figure 2 shows the evolution of plastic viscosity and yield stress with time for all mixtures, and all results are summarized in Table 3. Table 3 contains the average increase in viscosity and yield stress for both reference mixtures, as well as the corresponding confidence intervals. In Table 3, two sets of results are shown for mix design 2, as these correspond to the different cement deliveries. The influence of water and SP content is relative to the first reference for mix design 2, while the adding time and mixing energy will be compared to the second reference.

Evaluating the numbers in Table 3, the difference between the two SP employed is clearly visible. Mixtures prepared with SP 1 (mix design 1 and 3) show a steady increase of yield stress and viscosity with time. Mix design 2, in which SP 2 with long workability retention is incorporated, shows a nearly steady or slightly increasing viscosity with time, and a significantly smaller increase in yield stress (for the 2nd reference) and even a decrease in yield stress with time (1st reference), rendering the cement paste more fluid over time.

From the confidence intervals in Table 3, it can also be seen that the repeatability of the measurements is good. The standard deviation of the slopes of yield stress and viscosity with time (see Table 3) is similar for mix designs 2 and 3, resulting in confidence intervals of similar size. Mix design 1 shows a larger confidence interval, but the absolute values of increase in yield stress and viscosity are also substantially higher.

4.2. VARATIONS IN WATER CONTENT

The quantity of water is the most utilized parameter in robustness studies, as most practical issues can be related to an incorrect or inadequate assessment of the moisture content of the fine aggregates. In this project, the amount of water varied in the mix designs was ± 21 ml (0.71 fl oz.) and ± 42 ml (1.42 fl. Oz.), corresponding to a ± 5 l and ± 10 l difference for 1 m^3 of the corresponding concrete mixtures (or ± 1.01 gal and ± 2.02 gal for 1 yd^3 of corresponding concrete). Figures 3 and 4 show respectively the increase in yield stress and increase in viscosity with elapsed time. The thick black and grey lines with markers represent the results of a water content variation. The corresponding thin black and grey lines represent the 90% confidence intervals established in Table 3, and are an indication on the significance of a change in water content. Focusing on mix designs 1 and 3, both based on the powder-type principle, but with different ratios of water-to-powder and cement-to-powder, similar conclusions can be drawn. More water reduces the slope of yield stress and viscosity with time, which is significant for both parameters for mix design 3. For mix design 1, the larger increase in yield stress with time is manifested at decreasing water contents, while the slower increase in viscosity is visible at increasing water contents. Also, the differences are more substantial for mix design 1 than for mix design 3. The change of yield stress and viscosity with time is typically attributed to slowly continuing hydration, creating C-S-H bridges between cement particles. In mixtures with lower water contents, the inter-particle spacing is smaller, leading to a higher chance of C-S-H bridging and potentially a stronger connection between the particles. As a result, for the applied shear rate (approx. 100 s^{-1}) and with a decreasing water content, an increasing number of particles can no longer be separated, leading to an increase in yield stress and viscosity.

For mix design 2, however, no significant changes in the change of rheological properties with time are observed, as all points fall in between the 90% confidence limits. For the reference mixture, the viscosity did barely vary with time, and changing the water content does not seem to affect this evolution. The yield stress decreases with time, which can be attributed to different polymers in SP 2, which become active at different times. This time-release of dispersing molecules can inhibit or slow down the formation of C-S-H bridges, leading to the constant or decreasing rheological properties. Furthermore, the w/p in mix design 2 is higher compared to mix design 1 and 3, which could also reduce the influence of the water content.

4.3. VARATIONS IN SP DOSAGE

The sensitivity of the time-evolution of the rheological properties to a change in SP content is measured by changing the SP content with ± 5% and ± 10%, relative to the reference value. From previous work [49], it was concluded that a change in SP content mainly affected the yield stress at 15 min. Figure 5 shows that the yield stress increases faster with time with increasing SP content (not considering the -10% SP for mix design 1). It can be argued here that with increasing SP content, a larger portion of the cement surface is covered, which also means that more SP can be overgrown with hydration products over time, leading to a larger loss of efficiency for the yield stress. For the viscosity change as a function of time (Figure 6), however, the opposite trend is observed: increasing the SP content leads to a slower increase of viscosity with time (again not considering the -10% SP for mix design 1). A potential reasoning for this is that the addition of SP slows down the dissolution of ions and thus the formation of hydration products, leading to less C-S-H bridges between particles. In fact, it can be assumed that the nucleation of hydration products remains relatively unaffected (hence the larger increase in yield stress), but that the growth of hydration products is slowed down, relating to less C-S-H bridges. The observed effect on viscosity could also be due to a decrease in water available to flow, as more and larger particle clusters will be present with lower SP contents, entrapping more water. Furthermore, the changes induced by the modification of the SP content appear smaller than those induced by the water amount.

4.4. VARATION IN ADDING TIME OF SP

The adding time of the SP can have a significant influence on the rheological properties of the mixture. It has been shown that in most cases, the SP is more effective in reducing yield stress when it is added in a delayed fashion. It has been postulated that in case of immediate addition (with the mixing water), parts of the SP get intercalated between the initial hydration products formed. A small delay allows for these hydration products to form prior to the SP attaching to a surface. In previous work by the authors [49], it has been shown that the viscosity is largely affected by delaying the addition of the SP. Figures 7 and 8 compare the increase in yield stress and viscosity with time respectively between a 2.5 min delayed addition of the SP, and an equal amount of SP physically mixed in the mixing water prior to contact with the solid particles of the cement paste. A smaller increase in yield stress and in viscosity with time for mix design 1 and 3 can be observed, in case of an immediate addition of the SP. It seems that when less of the SP is intercalated within the hydration products formed in the first 2.5 min, more of its efficiency is lost over a more extended time.

In addition to the above results, mix designs 1 and 2 were repeated, but the SP type was reversed. In other words, the influence of the adding time of the SP was also investigated on mix design 1 with SP 2, and mix design 2 with SP 1. No VMA was employed, and the SP dosages were adjusted to ensure a mini-slump flow of 330 mm (11.8 in.) for the delayed SP addition. Similar as in Figure 7, Table 4 shows a slower increase in yield stress (or a decrease) when the SP is added with the water, compared to the delayed addition, regardless of the SP type, regardless of the mix design. However, for the viscosity, a slower increase in viscosity with time is noted for mix design 1 in case of intermixing the SP with the water (Figure 8), while for mix design 2, a slightly larger increase in viscosity is noted when adding the SP with all mixing water. Table 4 shows that the behavior of the viscosity increase with time is more related to the mix design, as regardless of which SP used, the qualitative behavior is similar for each mix design.

4.5. VARATIONS IN MIXING ENERGY: MIXING TIME AND MIXING SPEED

Modifications in the mixing procedure were also investigated by either changing the mixing time, or mixing speed (only for mixtures 1 and 3). The mixing procedures are described in Table 2. For mix designs 1 and 3, the modifications in mixing energy appear not to have a major effect on the change in rheological properties with time (Figures 9 and 10). For mix design 2, a slightly slower increase in yield stress and a slightly faster increase in viscosity with time are observed for the shorter mixing time. For the longer mixing time, especially a reduction in the rate of change of the viscosity is noticed. A potential hypothesis for this behavior is as follows: Decreasing mixing time results in less dispersing of the particles and more water which is entrapped in the particle clusters. This may lead to a faster increase in viscosity with time, and vice-versa for the longer mixing time. For the yield stress however, more particles remain flocculated when the mixing time is shorter, potentially reducing the amount of adsorbed SP, keeping more SP available in the suspension which can reduce the increase in yield stress with time (or lead to a decrease in yield stress with time as observed).

5. CONSEQUENCES

As shown in the previous sections, the distinction between SP 1 and SP 2 is very clear, and some of the conclusions need to be drawn separately for each of the SP. For mix design 1 and 3 (SP 1), the amount of water and the adding time of the SP appear to have the most significant influence on the evolution of yield stress and viscosity with time. In this section, the time-evolution results are compared to the sensitivity of the initial rheological properties to the studied parameters, as described in [49]. Increasing the water content results in a lower yield stress and plastic viscosity, and slows down the increase of these rheological properties with time. As a result, the rheological properties at later age are even more influenced by a modification of the water content, as both the initial rheological properties and their time evolution are influenced in the same way. For mix design 2 though, the change in water content only appears to affect the initial rheological properties, while the evolution with time remains unaffected.

For the second most significant factor, the adding time of the SP, the time-evolution of the viscosity compensates for the difference in initial viscosity for the mixtures with SP 1. As shown in [49], a substantially higher viscosity is obtained when SP 1 is added with the mixing water, but from the results above, the viscosity increases at a slower rate with time. For mix design 1, at 45 min, the viscosity with the delayed addition is higher than for the mixture with initial addition, and for mix design 3, the viscosity values are similar at 60 min of age. The effects on the yield stress are of minor importance, with a slightly more important increase in yield stress with time when the addition is delayed. For mix design 2 though, mainly the yield stress is affected by modifying the adding time of the SP, but the difference in yield stress increase with time is minor compared to the differences in initial rheological properties.

The amount of SP has a large influence on the yield stress. Overshooting the SP content leads to a lower initial yield stress, but time appears to compensate for this by a slightly larger increase of yield stress with time. However, the difference in slope of yield stress with time is insufficient to overcome the large differences in initial yield stress. For the viscosity, the changes are rather minor compared to the influence of water and SP adding time. The mixing time has no significant influence on the change in yield stress and viscosity with time for mixtures with SP 1, maintaining the difference in initial rheological properties over time. For mix design 2, the differences are deemed significant, but the difference in the time evolution of the rheological properties is not substantial compared to the difference in the initial rheological properties. As a result, any difference in initial rheological properties induced by the mixing time appears to be maintained over time.

6. CONCLUSIONS

By means of three mix designs based on the powder-type and VMA-type approaches, the sensitivity of the change of yield stress and viscosity with time of cement pastes with SCC consistency was investigated. From this research, the following conclusions can be drawn:

- A significant difference has been noted for the two different superplasticizers employed. Not only is the time-dependent behavior different, the response of the mixtures made with the different SP to changes in other parameters is also different.

As example, for the VMA-type mixtures made with the long workability-retention SP, the change in yield stress and viscosity with time appears not significantly affected by either a change in water or SP content.

- For the mixtures with the short workability retention SP: A change in water content significantly affects the increase (or decrease) of both yield stress and viscosity with time: a reduction in water content results in a faster increase in rheology, while an increase in water results in a slower increase in rheology. As a result, any influence of water on the initial rheological properties either remains constant (SP 2), or gets amplified (SP 1). This can be attributed to the increased inter-particle spacing when more water is added, resulting in less connections growing between cement particles.
- The adding time of the SP is the second most important factor influencing the change of yield stress and viscosity with time: in case of a delayed addition, these properties increase faster with time. As a result, the beneficial effect of delaying the SP addition on the initial rheological properties is reduced or even removed over time. Immediate addition of SP results in more intercalation of the SP in between hydration products immediately after mixing. This renders a delayed addition more efficient. However, with time, more hydration products are formed and as more of the SP is "active" in case of a delayed addition, it is speculated that more SP gets overgrown with time.
- For mix designs 1 and 3 (SP 1), increasing the amount of SP results in a faster increase in yield stress with time, however, the change of yield stress increase with time is too small to compensate for the significant change in initial yield stress due to an increase in SP addition. The hypothesis for this behavior is similar to the differences between immediate and delayed addition: if more SP is added, more SP

can be overgrown, resulting in a faster decline in efficiency. The changes in the increase of viscosity with time are of minor importance.

- Changing the mixing energy appeared to have a minor, less significant importance on the change in rheological properties with time. A reduction in mixing energy could lead to more entrapped water as less flocs of cement particles are broken, and a faster increase in viscosity with time was noted for mix design 2 (the changes for mix designs 1 and 3 were insignificant). However, less deflocculated particles results in less exposed surface, and thus a reduction in the adsorbed SP in the system. Although it was not explicitly noticed for SP 2, a reduction in (total) SP 1 content leads to a slower increase in yield stress with time. Applying this principle on the influence of a shorter mixing duration can explain why the yield stress increases slower with time. However, the changes induced in the time evolution in rheological properties are insufficient to either reduce or amplify the difference in initial rheological properties.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the National University Transportation Center at Missouri S&T and the Science Foundation in Flanders (FWO) for the financial support of this project.

Table 1: Reference mix designs 1, 2 and 3. All units are expressed in kg/m^3 (lbs/yd^3) of paste.

	Cement	Limestone Filler	Fly ash	Silica Fume	Water	SP1	SP2	VMA	W/P
Mix Design 1	808 (1362)	808 (1362)			444 (748)	3.47 (5.85)			0.275
Mix Design 2	1013 (1707)		351 (592)	35 (59)	533 (898)		6.80 (11.46)	0.88 (1.48)	0.38
Mix Design 3	872 (1470)	654 (1102)			479 (807)	2.53 (4.26)			0.31

Table 2: Mixing procedures (reference, short and long). Values in italic indicate the times when the speed was increased to study the influence of mixing speed.

Step	Duration			Action
	Reference	Short	Long	
1	30 s	30 s	30 s	Dry Materials
2 (=t_0)	1 min	30 s	2 min	Adding Water
3	1 min	1 min	1 min	Scraping
4	30 s	30 s	30 s	Mixing
5	2 min	1 min	4 min	Add SP / VMA
6	30 s	30 s	30 s	Scraping
7	1 min	1 min	1 min	Mixing
Duration since t_0	6 min	4.5 min	9 min	
Total rotations	613 / 1047	409	1022	

Table 3: Average values for viscosity and yield stress of reference mixtures 1, 2 and 3 and 90% confidence intervals, based on 4 measurements, for mixtures 1, 2 and 3.

	Mix Design 1	Mix Design 2		Mix Design 3
		CEM delivery 1	CEM delivery 2	
Average increase in Viscosity (mPa s/min)	10.3	-0.1	1.2	3.7
+ 90% Confidence Limit	12.2	0.5	1.4	4.3
- 90% Confidence Limit	8.6	-0.7	1.0	3.1
Average increase in Yield Stress (mPa/min)	91	-49	9	62
+ 90% Confidence Limit	112	-26	16	69
- 90% Confidence Limit	70	-72	2	55

Table 4: Effect of adding time on the increase in yield stress and viscosity with time, for both mix designs 1 and 2, with both SP types.

	SP 1		SP 2	
	With water	Delayed	With water	Delayed
Increase in yield stress Mix design 1 (mPa/min)	78	101	-33	144
Increase in yield stress Mix design 2 (mPa/min)	-18	196	-20	9
Increase in viscosity Mix design 1 (mPas/min)	5.8	11.0	0.7	1.2
Increase in viscosity Mix design 2 (mPas/min)	2.5	2.2	1.3	1.2

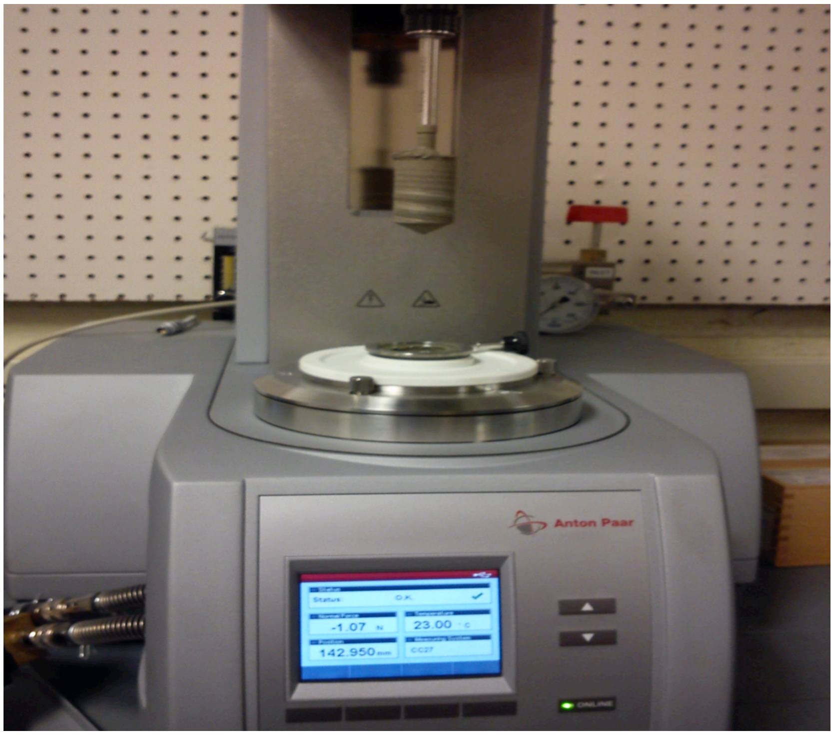


Figure 1. Anton Paar MCR 302, equipped with the sandblasted coaxial cylinders.

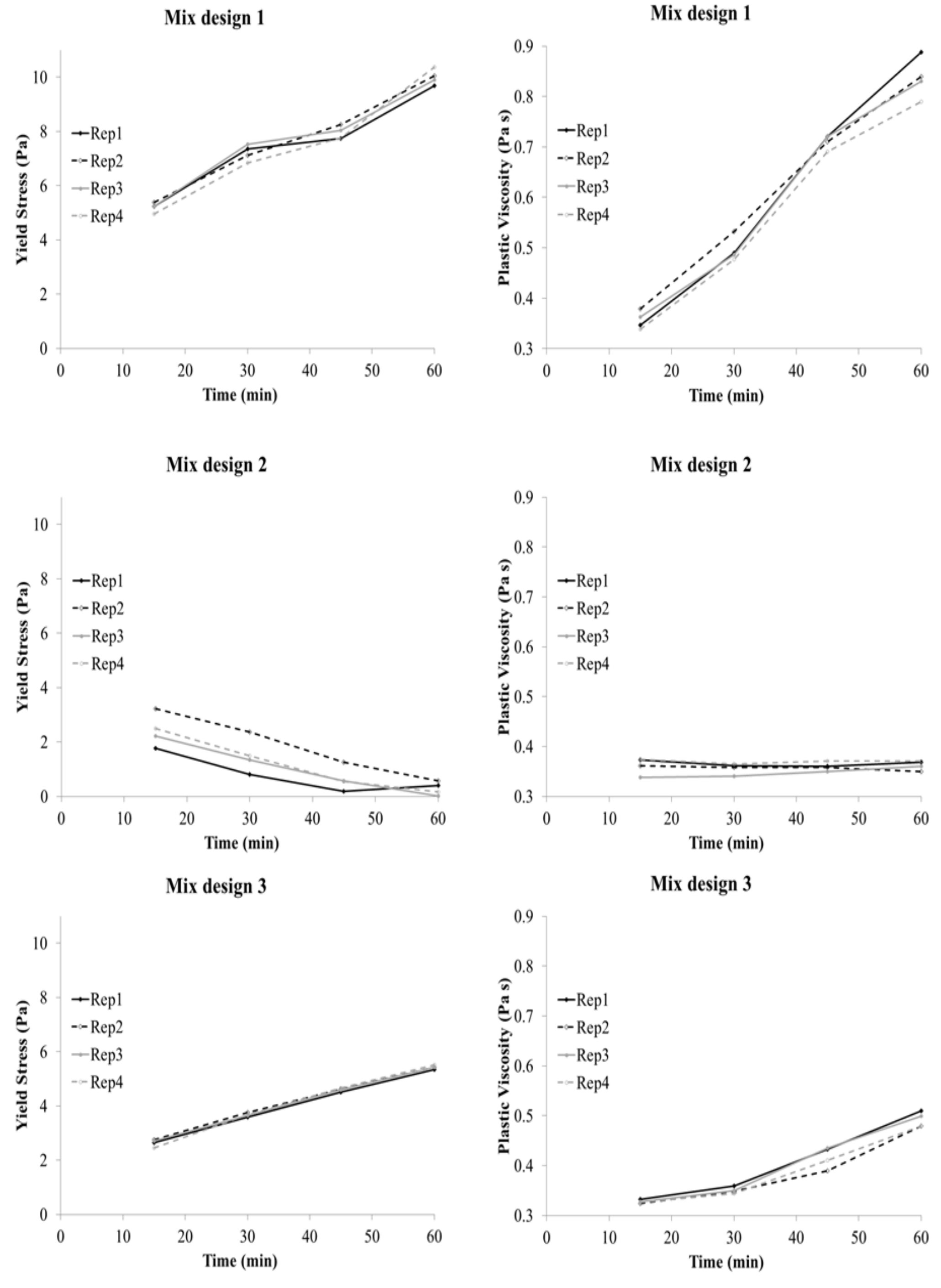


Figure 2. Evolution of plastic viscosity and yield stress over time, repeated four times.

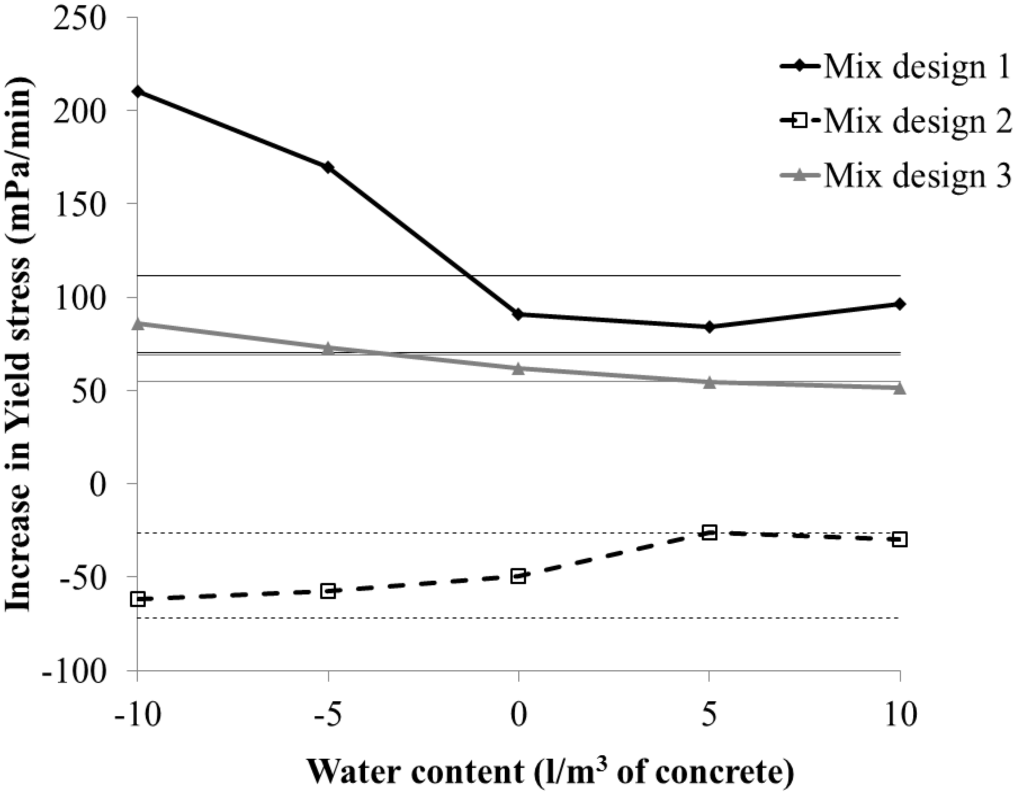


Figure 3. Variation of the increase of yield stress with time, as a function of a change in water content. A change of ± 5 l or 10 l per m^3 of corresponding concrete is equivalent to a change of ± 1.01 and ±2.02 gal/yd^3 of concrete.

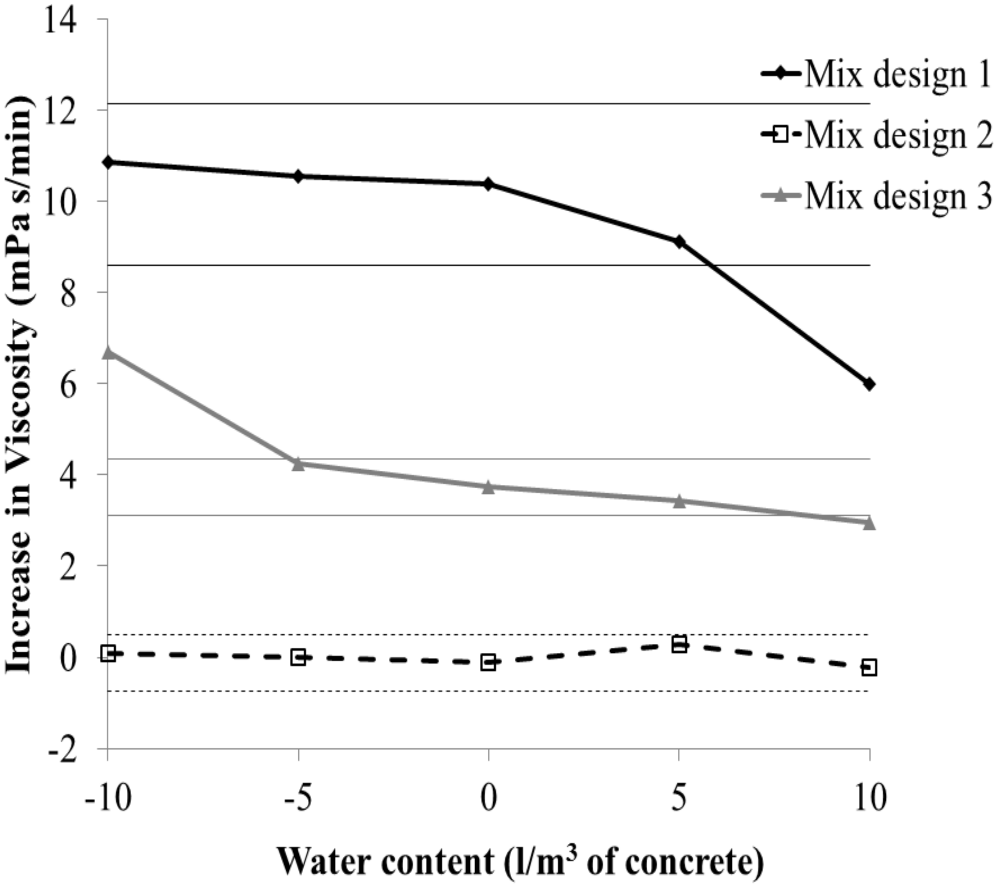


Figure 4. Variation of the increase of viscosity with time, as a function of a change in water content.

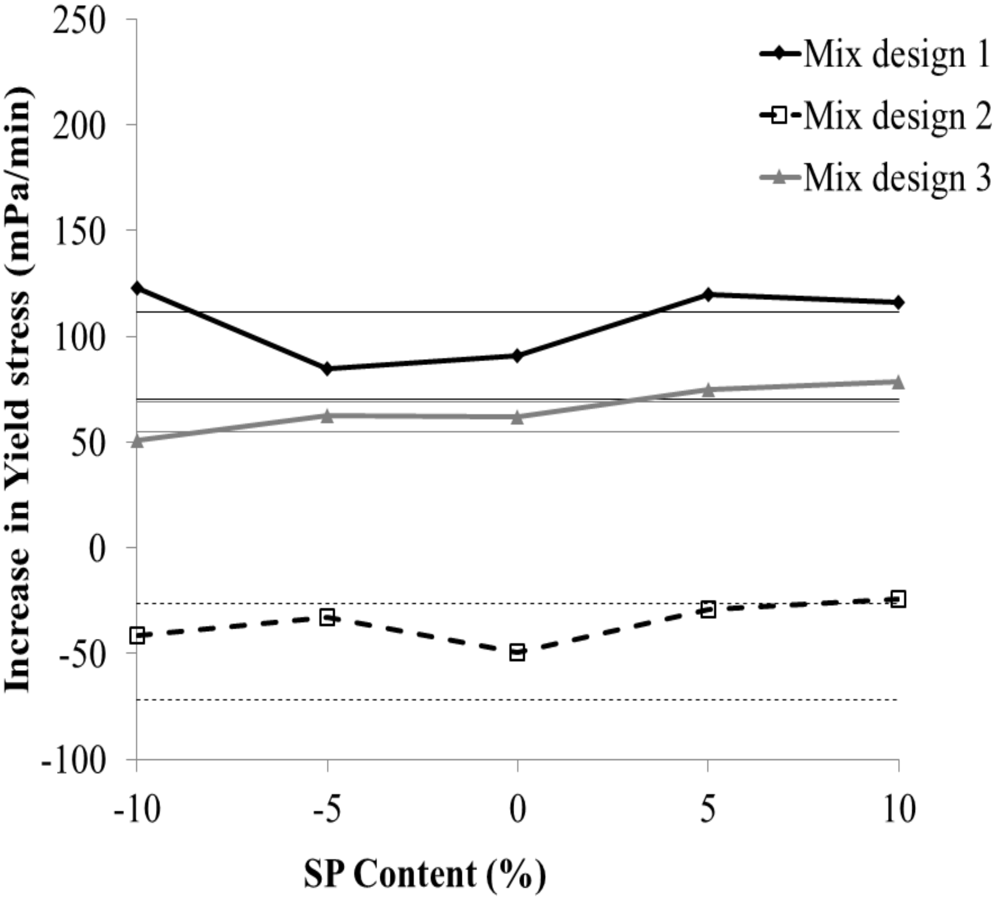


Figure 5. Variation of the increase of yield stress with time as a function of a change in SP content.

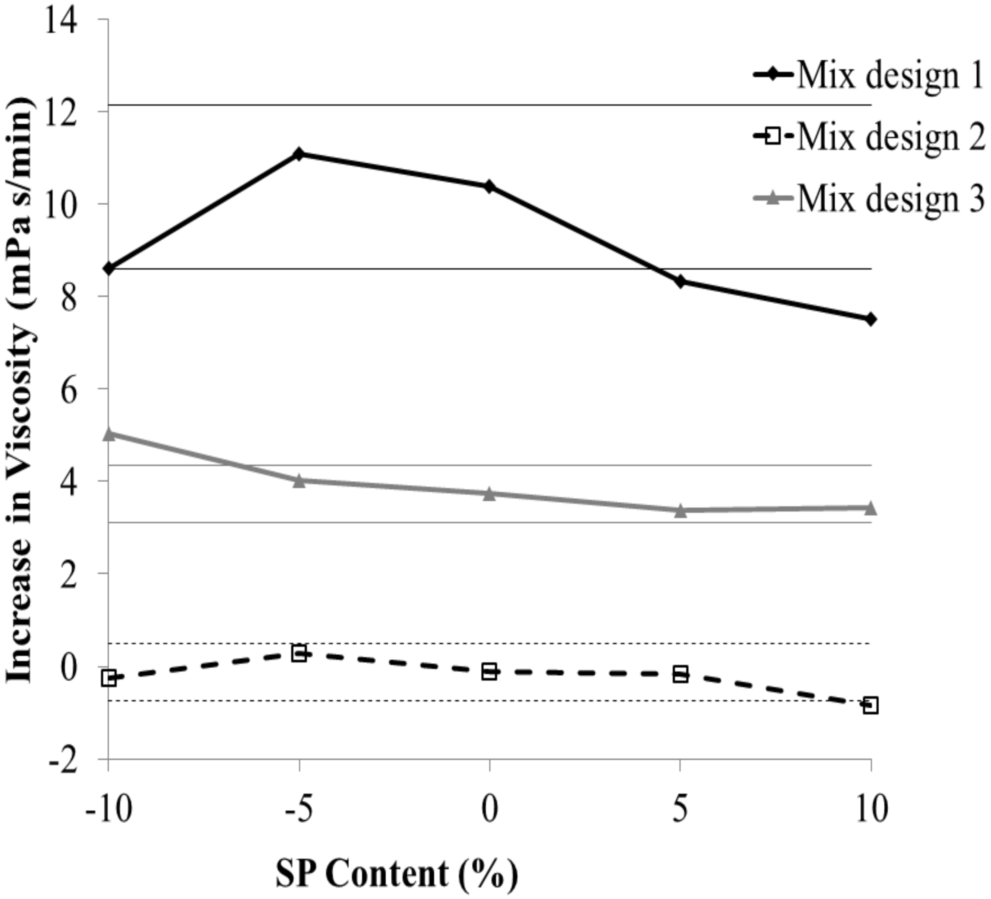


Figure 6. Variation of the increase of viscosity with time, as a function of a change in SP content.

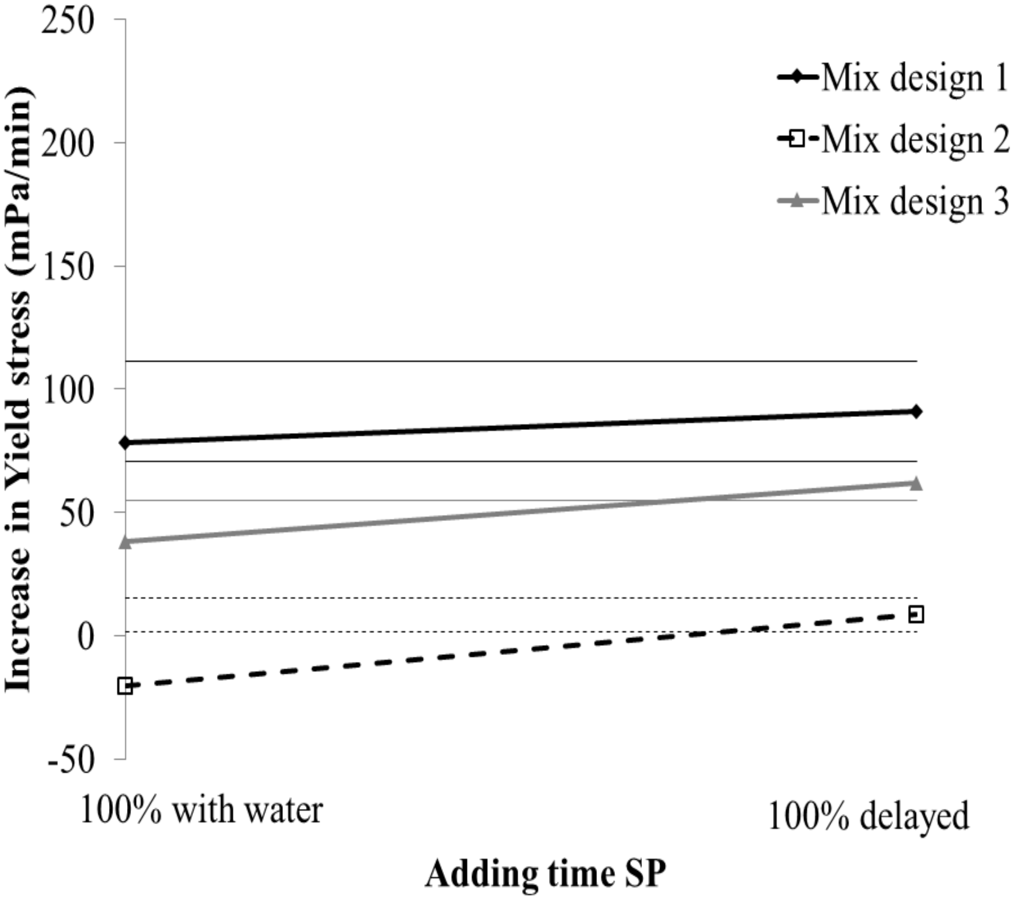


Figure 7. Variation of the yield stress with time, as a function of the addition time of the superplasticizer (100% with water, or delayed by 2.5 minutes).

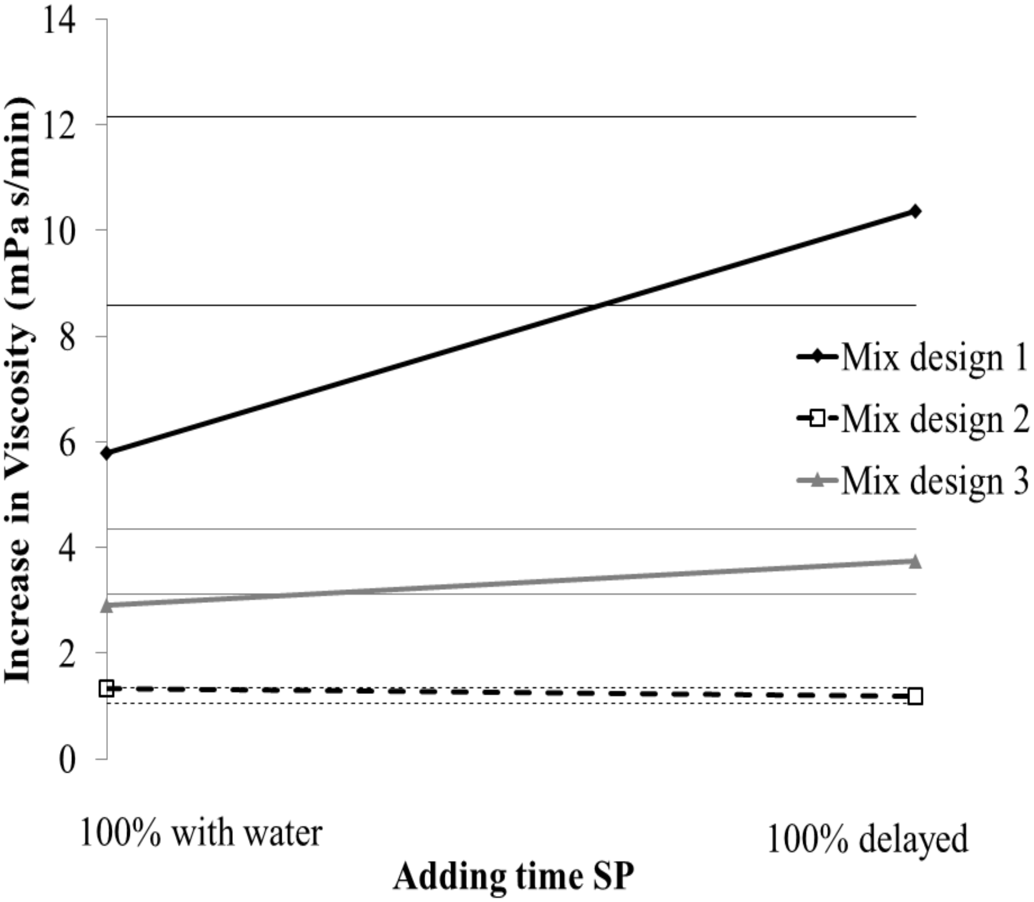


Figure 8. Variation of the viscosity with time, as a function of the addition time of the superplasticizer (100% with water, or delayed by 2.5 minutes).

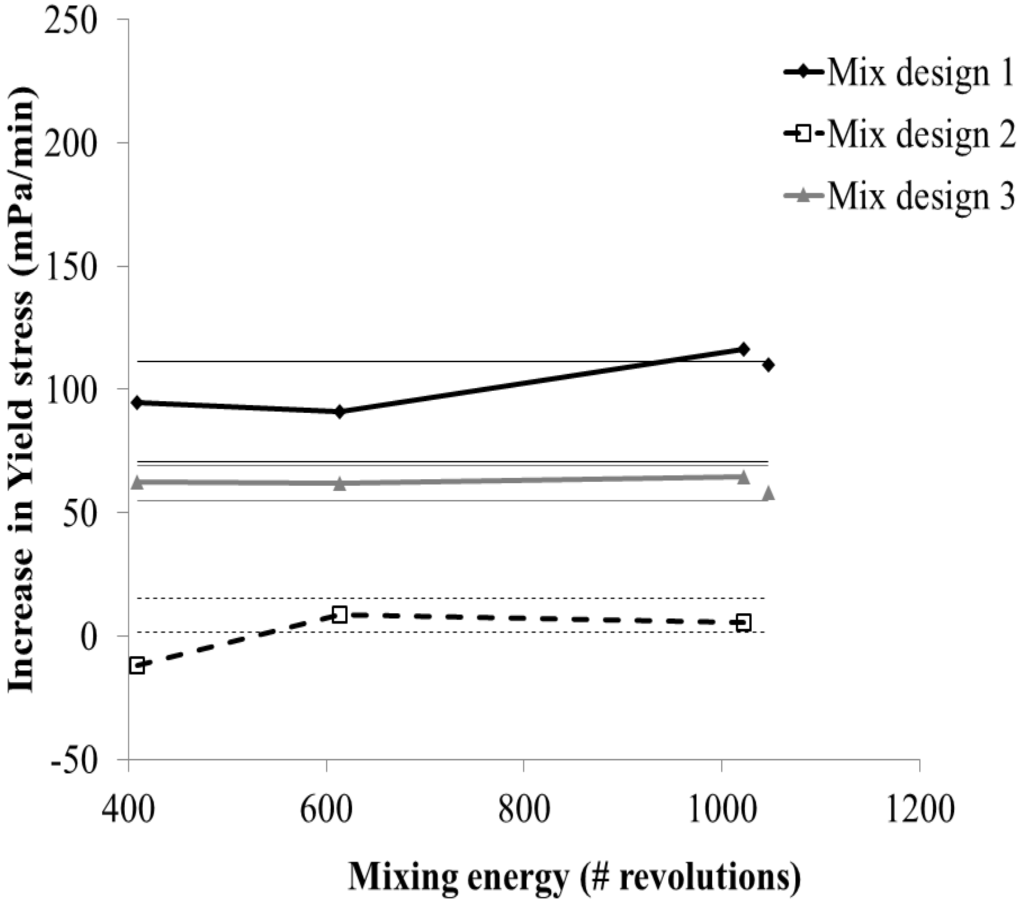


Figure 9. Variation of the yield stress with time, as a function of number of revolutions in the Hobart mixer.

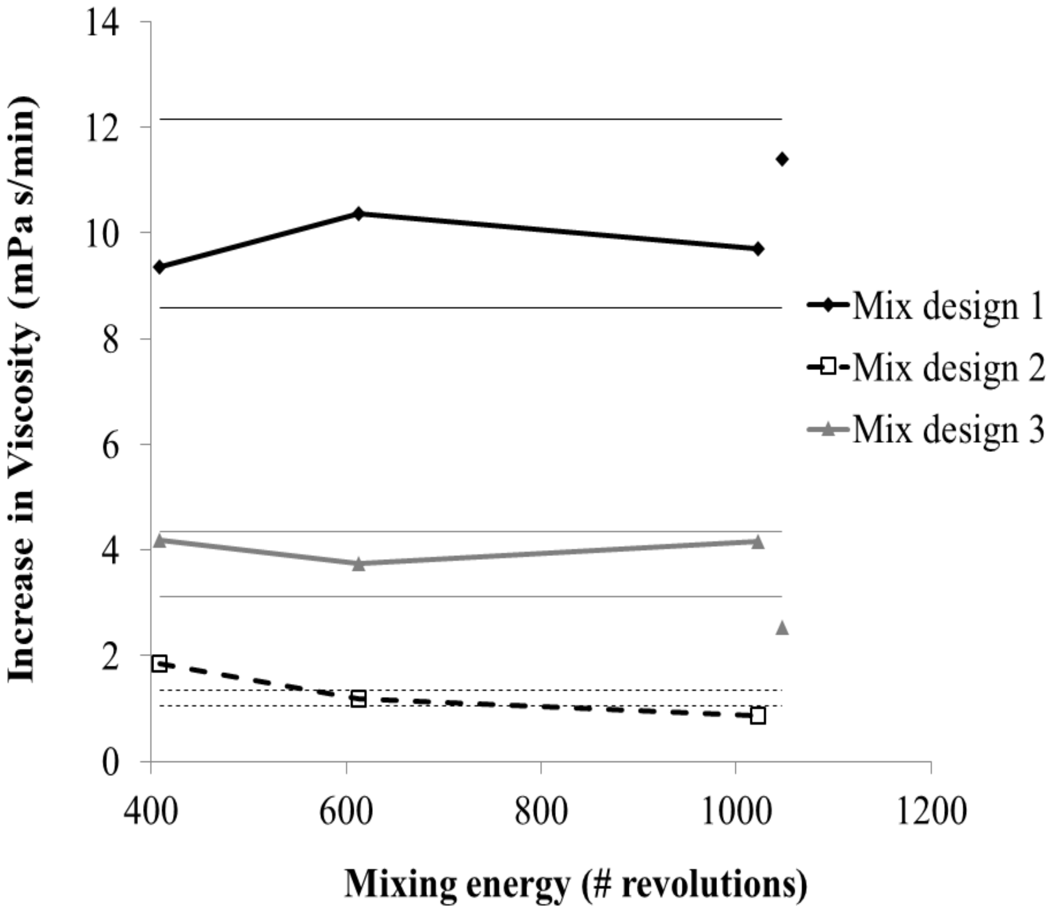


Figure 10. Variation of viscosity with time, as a function of number of revolutions in the Hobart mixer.

REFERENCES

[1] Emborg M, Simonsson P, Carlswärd J, Nilsson M (2007), Industrial Production Methods and Materials, like a Robust SCC, Utilizing Lean Construction Principles, Proc. of the 5th Int. RILEM Symposium on SCC, Ghent, Belgium, pp. 485-491.

[2] Bonen D, Deshpande Y, Olek J, Shen L, Struble L, Lange D, Khayat K (2007), Robustness of Self-Consolidating Concrete, Proc. of the 5th Int. RILEM Symposium on SCC, Ghent, Belgium, pp. 33-42.

[3] Gettu R, Nawaz Shareef S, Ernest KJD (2009), Evaluation of the Robustness of SCC, *Indian Concrete Journal*, **83-6**, pp. 13-19.

[4] Rigueira JW, García-Taengua E, Serna-Ros P (2009), Self-Consolidating Concrete in Continuous Production Regarding Fresh and Hardened State Properties, *ACI Materials Journal*, **106-3**, pp. 301-307.

[5] Nunes S, Figueiras H, Oliveira PM, Coutinho JS, Figueiras J (2006), A Methodology to Assess Robustness of SCC Mixtures, *Cement and Concrete Research*, **36**, pp. 2115-2122.

[6] Billberg P (2009), Increase of SCC Robustness to Varying Aggregate Moisture Content Using VMA, Proc. of the 2nd Int. Symp. on SCC, Beijing, China, pp. 473-493.

[7] Naji S, Hwang S-D, Khayat KH (2011), Robustness of self-consolidating concrete incorporating different viscosity-enhancing admixtures, *ACI Materials Journal*, **108-4**, pp. 432-438.

[8] Sahmaran M, Yurtseven A, Yaman IO (2005), Workability of hybrid fiber reinforced self-compacting concrete, *Building and Environment*, **40-12**, pp. 1672–1677.

[9] Ferraris CF, Obla, KH, and Hill R (2001), The influence of mineral admixtures on the rheology of cement paste and concrete, *Cement and Concrete Research*, **31-2**, pp. 245–255.

[10] Han S, Yan PY, and Kong XM (2011), Study on the compatibility of cement-superplasticizer system based on the amount of free solution, *Science China Technological Sciences*, **54-1**, pp. 183–189.

[11] Rubio-Hernández FJ, Velázquez-Navarro JF, Ordonez-Belloc LM (2013), Rheology of concrete: A study case based upon the use of the concrete equivalent mortar, *Materials and Structures*, **46-4**, pp. 587–605.

[12] Sheinn AM, Ho DW, Tam CT (2002), Rheological model for self-compacting concrete-paste rheology, Proc. 27th Conf. on Our World in Concrete and Structures, CI-Premier, Singapore.

[13] Tattersall GH, Banfill PFG (1983), The rheology of fresh concrete, Pitman, London.

[14] Banfill PFG (1981), A Viscometric Study of Cement Pastes Containing Superplasticizers with a Note on Experimental Techniques, *Magazine of Concrete Research*, **33-114**, pp. 37-47.

[15] Douglas R, Gregori A, Sun Z, Bonen D, Shah SP (2005), The Effect of ingredients and shear history on the thixotropic rate of rebuilding of SCC, Proc. Of 2^{nd} North American Confer. & 4th Intern. RILEM Confer. On Self-Consolidating Concrete, Chicago, IL, pp. 591-596.

[16] Billberg P (2011), Influence of powder type and VMA combination on certain key fresh properties of SCC, Proc. of 9th Int. Symp. on High Performance Concrete, Rotorua, New Zealand.

[17] Li LG, Kwan AKH (2013), Concrete mix design based on water film thickness and paste film thickness, *Cement and Concrete Composites*, **39-5**, pp. 33-42.

[18] Banfill PFG (1979), A discussion of the paper 'Rheological properties of cements mixes', *Cement and Concrete Research*, **9-6**, pp. 795–796.

[19] Flatt RJ (2004), Towards a prediction of superplasticized concrete rheology, *Materials and Structures*, **37-5**, pp. 289–300.

[20] Lei L, Plank J (2011), Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete, *Cement and Concrete Research*, **42-1**, pp. 118–123.

[21] Zingg A, Winnefeld F, Holzer L, Pakusch J, Becker S, Gauckler L (2008), Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases, *Journal of Colloid Interface Science*, **323-2**, pp. 301–312.

[22] Bonen D, Shah SP (2005), Fresh and hardened properties of self-consolidating concrete, *Progress in Structural Engineering Materials Journal*, **7-1**, pp. 14-26.

[23] Hanehara S, Yamada K (1999), Interaction between cement and chemical admixtures from the points of cement hydration, admixture adsorption and paste rheology, *Cement and Concrete Research*, **29-8**, pp. 1158-1165.

[24] Aitcin PCA, Jolicoeur C, McGregor JG (1994), Superplasticizers: How they work and why they occasionally don't, *Concrete International*, **16-5**, pp. 45-52.

[25] Roy DM, Asaga K (1979), Rheological properties of cement mixes: III The effects of mixing procedures on viscometric properties of mixes containing superplasticizers, *Cement and Concrete Research*, **9**, pp. 731-739.

[26] Jones TER, Taylor SA (1977), Mathematical model for the flow curve of cement paste, *Magazine of Concrete Research*, **29-101**, pp. 207-212.

[27] Yamada K, Ogawa S, Hanehara S (2001), Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase, *Cement and Concrete Research*, **31-3**, pp. 375-383.

[28] Yamada K, Ogawa S, Hanehara S (2000), Influence of Silica Fume/Fly Ash/Superplasticizer Combinations in Powder-Like Complex Modifiers on Cement Paste Porosity and Concrete Properties, Proc. 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete, ACI SP 195, Nice, p. 367.

[29] Uchikawa H, Sawaki D, Hanehara S (1995), Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement pastes, *Cement and Concrete Research*, **25**, pp. 353–364.

[30] Kim BG, Jiang S, Jolicoeur C, Aitcin PC (2000), The adsorption behavior of pns superplasticizer and its relation to fluidity of cement paste, *Cement and Concrete Research*, **30**, pp. 887–893.

[31] Jolicoeur C, Sharman J, Otis N, Lebel A, Simard MA, Page M (1997), The influence of temperature on the rheological properties of superplasticized cement pastes, Proc. 5th International Conference on Super- plasticizer and other Chemical Admixtures in Concrete, Rome, pp. 379–406.

[32] Simard MA, Nkinamubanzi PC, Jolicoeur C (1993), Calorimetry, rheology, and compressive strength of superplasticized cement pastes, *Cement and Concrete Research*, **23**, pp. 939–950.

[33] Hanna E, Lake K, Perraton D, Aitcin PC (1989), Rheological behavior of Portland cement paste in the presence of a superplasticizer, Proc. 3rd International Conference on Superplasticizers and other Chemicals Admixtures in Concrete, ACI SP 119, Ottawa, pp. 171–188.

[34] Bonen D, Sarkar SL (1995), The superplasticizer adsorption capacity of cement pastes pore solution composition and parameters affecting flow loss, *Cement and Concrete Research*, **25**, pp. 1423–1434.

[35]Carlsward J, Emborg M, Utsi S, Oberg P (2003), Effects of constituents on the workability and rheology of self-compacting concrete, pp. 143-153, Proc. 3rd Intern. RILEM Symp. on self-compacting concrete, Eds. Wallevik O, Nielsson I, RILEM Publications S.A.R.L.

[36] Petit J-Y, Khayat KH, Wirquin E (2006), Coupled effect of time and temperature on variations of yield value of highly flowable mortar, *Cement and Concrete Research*, **36**, pp. 832–841.

[37] Roussel N, Ovarlez G, Garrault S, Brumaud C (2012), The origins of thixotropy of fresh cement pastes, *Cement and Concrete Research*, **42-1**, pp. 148-57.

[38] Kong X, Zhang, Y, Hou S (2013), Study on the rheological properties of Portland cement pastes with polycarboxylate superplasticizers, *Rheologica Acta*, **52-7**, pp. 707–718.

[39] Heikal M, Morsy MS, Aiad I (2005), Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes, *Cement and Concrete Research*, **35-4**, pp. 680–687.

[40] Jolicoeur C, Simard MA (1998), Chemical admixture-cement interactions: Phenomenology and physico-chemical concepts, *Cement and Concrete Composites*, **20-2**, pp. 87–101.

[41] Kreppelt F, Weibel M, Zampini D, Romer M (2002), Influence of solution chemistry on the hydration of polished clinker surfaces—A study of different types of polycarboxylic acid-based admixtures, *Cement and Concrete Research*, **32-2**, pp. 187–198.

[42] Zhang Y, Kong X, Lu Z, Lu Z, Hou S (2015), Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes, *Cement and Concrete Research*, **67**, pp. 184–196.

[43] Flatt RJ, Bowen P (2006), Yodel: A yield stress model for suspensions, *Journal of the American Ceramic Society*, **89-4**, pp. 1244–1256.

[44] Flatt RJ, Bowen P (2007), Yield stress of multimodal powder suspensions: An extension of the YODEL (yield stress model), *Journal of the American Ceramic Society*, **90-4**, pp. 1038–1044.

[45] Golaszewski J, Szwabowski J (2004), Influence of superplasticizers on rheological behavior of fresh cement mortars, *Cement and Concrete Research*, **34-2**, pp. 235–248.

[46] Struble L, Sun GK (1995), Viscosity of Portland cement paste as a function of concentration, *Advances in Cement Based Materials*, **2-2**, pp. 62–69.

[47] Petit J-Y, Wirquin E, Duthoit B (2005), Influence of temperature on yield value of highly flowable micromortars made with sulfonate-based superplasticizers, *Cement and Concrete Research*, **35-2**, pp. 256-266.

[48] Petit J-Y, Khayat KH, Wirquin E (2009), Coupled effect of time and temperature on variations of plastic viscosity of highly flowable mortar, *Cement and Concrete Research*, **39**, pp. 165-170.

[49] Asghari A, Ley Hernandez AM, Feys D, De Schutter G (2016),Which parameters, other than the water content, influence the robustness of cement paste with SCC consistency?, *Construction and Building Materials*, **124**, pp. 95-103.

IV. INFLUENCE OF MAXIMUM APPLIED SHEAR RATE ON THE RHEOLOGYCAL PROPERTIES OF FLOWABLE CEMENT PASTES

Dimitri Feys, Azadehalsadat Asghari

ABSTRACT

Rheological properties of cement-based materials have been widely studied over the last decades. These materials show a yield stress and viscosity, which change over time due to thixotropic behavior and the hydration reaction. The consequence of thixotropy is that the rheological properties are dependent on the applied shear rate. This paper describes the change in rheological properties of well-dispersed cement pastes subjected to different shear rates. It is shown that a majority of the structural breakdown occurs when transitioning from rest to a low shear rate, but a number of connections can only be broken at more elevated shear rates. As a result, especially the viscosity decreases with increasing applied shear rate. The influence of temperature, binder composition and choice of chemical admixtures on the change in rheological properties with applied shear rate is evaluated in this paper.

Keywords: Cement paste, Rheology, Shear rate, Viscosity, Temperature

1. INTRODUCTION

Measuring the rheological properties of cement-based materials is a fundamental, scientific way to characterize the fresh properties [1-2]. This technique is commonly employed in the research field, and has assisted in the development, production, and placement of advanced cement paste or concrete types. However, the assessment of the rheological properties of cement paste, mortar or concrete is not straightforward due to a number of complexities. Mortar and concrete are concentrated suspensions containing a large number of particles with a variety of different sizes. If the amount of aggregates is too elevated, standard rotational rheology is no longer applicable as the material transitions from a suspension to frictional behavior [3]. If the aggregate concentration is sufficiently low, coarse particles can migrate to zones with lower shear rates [4-7]. This particle migration is beneficial for pumping operations [5-9], but is challenging for the correct assessment of rheological properties [4, 10-11].

Even when downscaling to cement paste, a good number of complexities still remain. The size of the particles in cement paste are on the boundary between colloidal and non-colloidal, and as such, their mobility can be affected by electrostatic attraction and repulsion forces [12-14]. Chemical admixtures, specifically dispersing agents, are developed to modify the interaction patterns between the cement(-itious) particles, typically reducing the total amount of clustered particles [15-19]. Other chemical admixtures modify the interaction between the particles in a different way, or alter the properties of the suspending medium: i.e. the mixing water [20]. Furthermore, cement displays a continuous chemical reaction in presence of water, causing the rheological properties to constantly change with time [21-24]. As a result, cement pastes are yield stress materials, with thixotropic characteristics and a chemical reaction binding all constituents together over time.

The consequence of thixotropy is that the rheological properties measured depend on the applied shear rate [25-27]. Considering a generalized thixotropy model for colloidal suspensions, a scalar variable λ is introduced to reflect the internal structure of the suspension, as represented in eqs. 1 and 2 [26].

$$\tau(\dot{\gamma}, \lambda) = \lambda \cdot \tau_0 + \lambda \cdot K_{st} \cdot \dot{\gamma}^n + K_\infty \cdot \dot{\gamma}^n \tag{1}$$

$$\frac{d\lambda}{dt} = -k_1 \cdot \dot{\gamma} \cdot \lambda + k_2 \cdot \dot{\gamma}^m \cdot (1 - \lambda) + k_3 \cdot (1 - \lambda) \tag{ 2}$$

When the suspension is completely dispersed, λ = 0, when it is completely flocculated, λ = 1. The general model shows the dependency of the yield stress on λ, as theoretically, if there is no flocculation, there is no yield stress (first term in RHS of eq. 1). The shear rate term is split in two parts, reflecting a "viscosity" at infinite shear rate (λ = 0) (last term in RHS of eq. 1), and an increase in the viscosity term as a function of λ (middle term in RHS of eq. 1). λ itself is described to increase with time at rest (flocculation induced by Brownian motion) (last term in RHS of eq. 2), and to decrease with time with increasing shear rate (first term in RHS eq. 2). An intermediate term, typically only significant at low shear rates enhances the build-up of the material (middle term in RHS of eq. 2). As a consequence, for each shear rate above the critical shear rate, which corresponds to the lowest shear rate for which dλ/dt can be zero [28], there is an equilibrium value of λ, and thus a set of constant rheological properties with time. However, changing the shear rate will change the equilibrium value of λ, and will create a new unique set of observed rheological properties. As such, to determine the rheological properties of a thixotropic suspension, one can await the equilibrium λ at each imposed shear rate and construct the equilibrium rheological curve (dashed line in Fig. 1) [29]. However, this can be a time-consuming process, as dλ/dt needs to be equal to zero at each imposed shear rate. It has been generally accepted to bring the material first in its reference state, which corresponds to the highest applied shear rate, and thus the lowest λ value [27, 30-31]. Once the reference state is reached, the measurement is executed quickly to minimize any effect of a non-zero dλ/dt. As a consequence, the higher the imposed shear rate, the lower λ, the lower the measured rheological properties (solid lines in Fig. 1).

For cement-based materials, the above-described thixotropic model is qualitatively valid, but hydration is another major factor influencing the time-dependent behavior, making the implementation of the general thixotropy model rather difficult. In addition to physical, reversible flocculation, chemical connections caused by the growth of hydration products also occur in cement-based materials [32]. Initially, this was considered to cause the loss of workability, but it has been shown that these connections can also be broken down under shear [14, 32-34]. In fact, the reversibility of the rheological behavior of cement-based materials cannot solely be attributed to flocculation [32]. Wallevik has modeled the time-dependent behavior of measurements on cement-based materials, based on similar principles as described above [12-14]. However, he has considered the chemical connections (called linkages) to break only once, and never rebuild within the timeframe considered [14]. He has also stated that a number of connections between cement particles, regardless of the origin, cannot be broken for the amount of work applied on the system. These connections are called irreversible and their number increases with time, implicitly taking rebuild due to hydration into consideration. However, increasing the amount of work can make some of these connections reversible.

As demonstrated, the rheological properties of cement pastes, and thus also mortars and concretes, are dependent on the applied shear rate. This paper evaluates the rheological properties of well-dispersed cement pastes subjected to different maximum shear rates to confirm the above theory. As will be shown, the choice of maximum shear rate during rheological measurements is critical for the values of the rheological properties.

2. CEMENT PASTES

2.1. MATERIALS

Cement pastes were produced with Type I/II ordinary Portland cement (OPC), a class C fly ash and a densified silica fume. The densities of these materials were 3160, 2700 and 2300 kg/m^3, respectively. A polycarboxylate-based dispersing admixture was selected and employed in most mixtures (SP 1). This PCE-SP had a density of 1.032 kg/l and a solid content of 26%. A different polycarboxylate (SP 2 – ρ = 1.07 kg/l, solid content 38%), from a different supplier was also employed in two mixtures. Except for two mixtures, in which a viscosity-modifying agent compatible with each SP was investigated ($\rho_{\text{VMA 1}}$ = 1.002 kg/l, $\rho_{\text{VMA 2}}$ = 1.207 kg/l), all other mixtures did not contain any VMA.

2.2. MIXING PROCEDURE

All mixtures were prepared in 1.5-liter batches in a small Hobart mixer at the lowest speed position. After insertion of the dry materials and homogenizing them during 30 s, the water was added and mixing continued for 1 min. The mixture was manually homogenized the following minute by scraping materials stuck on the side and bottom of the mixer. Mixing resumed and the dispersing admixture was added after 30 s, resulting in a total delay time of 2.5 min relative to water-cement contact. Mixing continued for 2 additional minutes, during which the VMA was added, if applicable. After a short second scraping period of 30 s, the paste was mixed for one additional minute. The mini-slump flow of the mixture was measured within 2 min after the end of mixing. Rheological testing was performed at 15 min after water-cement contact.

2.3. MIX DESIGNS

The binder combination of the reference mix design was 25% class C fly ash, 2.5% silica fume and 72.5% OPC by mass. The w/cm was 0.38, and the dispersant content was adjusted to reach the target mini-slump flow of 325 ± 15 mm. The reference mixture was repeated five times to establish an average, standard deviation and a 95% confidence interval for each of the measured parameters. The reference mixture was then reproduced, but evaluated at high (37°C) and low (7°C) temperature in the rheometer. Afterwards, the reference mixture was modified by omitting the fly ash or the silica fume, and by making a mixture with 100% OPC. However, it should be noted that the fly ash and/or silica fume were replaced by cement by volume (not by mass), to keep the solid content in the mixtures approximately constant. Hence, the w/cm is not equal for the mixtures with modified binder compositions. A VMA compatible with SP 1 was employed, and the reference mixture was repeated with SP 2, with and without a second VMA. Table 1 shows all mix designs evaluated in this paper, as well as the initial mini-slump flows of each mixture.

3. RHEOLOGICAL MEASUREMENTS

3.1. RHEOMETER

All rheological measurements were executed on an Anton Paar MCR 302 rheometer, equipped with sandblasted coaxial cylinders to minimize slip as much as possible. An inner radius of 13.33 mm, outer radius of 14.56 mm and height of 40.00 mm were the characteristics of the chosen geometry. Cement pastes were kept in the rheometer for 90 min at 23°C, unless specified otherwise, and evaluated according to the following measurement protocol.

3.2. MEASUREMENT PROTOCOL

As mixing of the cement paste occurred in a standard small Hobart mixer at the lowest speed setting, a reference state has been imposed for each paste. To achieve a reference state, a pre-shear period of 90 s at a shear rate of 100 s^{-1} was executed at 15 min after contact between cement and water. The preshear was followed by a linearly decreasing shear rate ramp, from 100 s^{-1} to 5 s^{-1}, over a period of 30 s, permitting a first characterization of the rheological properties at a shear rate of 100 s^{-1}. The sample was then left undisturbed for 12 min, followed by the application of a shear rate of 0.001 s^{-1} during 60 s to determine the static yield stress. Immediately after the static yield stress, at 30 min after water-cement contact, the shear rate was kept constant at 12.5 s^{-1} for 90 s, followed by a decreasing shear rate ramp from 12.5 to 5 s^{-1} over a 30 s period. This step was immediately followed by a second combination of pre-shear and flow curve, but now with 25 s^{-1} as maximum shear rate, and followed by two additional steps with 50 and 100 s^{-1} as maximum shear rate, respectively. The sample was then rested for 21 min, and the entire procedure: static yield stress, preshear + flow curve at four different shear rates, was repeated. After an additional 21 min of rest, a static yield stress was measured, followed by a preshear + flow curve at 100 s^{-1}. Figure 2 shows the shear rate profile for the entire procedure.

Employing this procedure delivers a number of variables to evaluate:

- Initial rheological properties at 15 min
- Workability loss by comparing the measurements at 100 s^{-1} at 15, 30, 60 and 90 min
- Structural build-up at 30, 60 and 90 min
- Breakdown of structure by comparing the four flow curves at different shear rates at either 30 or 60 min.
- Breakdown of structure by analyzing the evolution of the shear stress during each preshear period.

In this paper, the results of the breakdown at 60 min are investigated. The structural build-up at 60 min, and the workability loss from 15 to 90 min were also determined to facilitate interpretation. The authors have deliberately chosen to develop the paper with the 60 min results, as a longer resting time is imposed, compared to the 30 min test, and because the initial hydration reactions due to the aluminate phase in cement has relatively low importance after 30 min.

3.3. ANALYSIS

3.3.1. Preshear. The shear stress evolution during the preshear period was fitted with an exponentially decreasing function, according to eq. 3 [34]:

$$\tau(t) = Ae^{-Bt} + C \qquad (3)$$

$$\Delta\eta = Ae^{-B}/\dot{\gamma} \qquad (4)$$

A and B are fitting parameters, and the constant C is taken as the average shear stress during the last 5 s of the preshear period. Consequently, C is not a fitted parameter. Based on this equation, the shear stress after 1 s of preshear is calculated and the value of C is subtracted. This value is divided by the applied shear rate to obtain a change in apparent viscosity (Δη in eq. 4). Δη represents thus the change in apparent viscosity caused by the breakdown between 1 s and 85-90 s during each preshear period. The authors have opted to take the value of the fitted function at 1 s, instead of the measured value, as the former is less sensitive to errors. In the discussion section of this paper, the evolution of Δη with applied shear rate will be demonstrated.

3.3.2. Flow Curves. Figure 3 shows an example of the flow curves obtained at 60 min after water-cement contact, for one of the repetitions of the reference mixture. The flow curves were initially approached with the Bingham model, but some shear-thinning was observed, and significant issues were encountered when analyzing the yield stress and viscosity values. The modified Bingham model was consequently applied on the flow curves, providing a better fit [35]. However, the yield stress values extrapolated from the curves are not considered reliable. For the shown curves in Fig. 3, the fitted yield stress values were 4.41, 4.57, 4.83, and 5.27 Pa, for the flow curves at 12.5, 25, 50 and 100 s^{-1}, respectively. These obtained values are in opposite order than the curves at low shear rate in Fig. 3, indicating the extrapolation is not fully reliable. Detailed analysis has revealed some deviation from the modified Bingham model as most curves seem linear at shear rates higher than 20 s^{-1}. The extrapolated yield stress values are dependent on the shear rate range and the number of data points in the curve, and are not sufficiently accurate to provide a good analysis.

For the viscosity, the differential viscosity at the median shear rate can be calculated for each flow curve, but seen the non-linearity of the curves, this substantially twists the analysis and the conclusions. Instead, the differential viscosity at 10 s^{-1} was calculated for each flow curve, based on the fitted modified Bingham parameters. For the curves at maximum shear rates of 50 and 100 s^{-1}, however, the differential viscosity at 10 s^{-1} did not always correctly reflect the local slope of the curve, due to the large range of data on which the modified Bingham model was fitted. Instead, a different approach was chosen: The shear stress – shear rate curve was approximated with a 6th order polynomial, and differentiated to the shear rate, delivering a 5th order polynomial describing the slope (differential viscosity) of the flow curve. This differential viscosity function was evaluated for all data points measured between 8 and 12.5 s^{-1} for each flow curve, and the average is used as a measure of viscosity. In a similar fashion, the shear stress at 5 s^{-1} was determined based on the 6th order curve as a value which could resemble the yield stress. Table 2 shows the rheological properties obtained at 60 min for the mixtures evaluated at the four different shear rates.

The authors are aware that this style of analysis goes against all best practices of rheometry on cement-based materials, and that no physical meaning can be given to the constants in the polynomial. However, it was deemed to be the method which delivers the most useful results for analysis. It should also be noted that the authors took the values of shear stress and shear rate directly from the rheometer, but seen the complexity of the curves and the uncertainty on the determined yield stress, no other strategy, such as integration approaches, was deemed suitable.

3.3.3. Structural Build-up and Workability Loss. The workability loss is calculated based on the four flow curves obtained at 15, 30, 60 and 90 min, with 100 s^{-1} as maximum shear rate. Seen the concerns about the yield stress, two parameters are calculated: the slope of the shear stress at 5 s^{-1} with time (expressed in mPa/min), and the slope of the differential viscosity at 52.5 s^{-1} (expressed in mPas/min), which is the median shear rate of the measured interval. These two parameters are indicative of the number of connections between particles formed per unit of time, which cannot be broken at a shear rate of 100 s^{-1}.

Structural build-up is characterized by the increase in static yield stress with time, described as A_{thix} in literature [27, 36-37]. It is calculated as the difference between the measured static yield stress at 60 min and the modified Bingham yield stress at 30 min, divided by the resting time, which is 21 min. Although the modified Bingham yield stress is not deemed reliable, the static yield stress is typically around 1 order of magnitude larger than the dynamic yield stress, limiting the error induced by extrapolating the yield stress value. A_{thix} is an indicator of the total amount of connections formed between particles per unit of time, including reversible and irreversible connections, regardless whether they are the consequence of flocculation or hydration.

One can qualitatively compare the A_{thix} values to the workability loss data to get an indication of the reversibility of the connections. As an example, the mixture with 100% OPC shows relatively low A_{thix}, while the workability loss is similar to that of the reference mixture. The reference mixture at elevated temperature shows more workability loss and a higher A_{thix} compared to the mixture at room temperature.

.

4. INFLUENCE OF SHEARING ON RHEOLOGICAL PROPERTIES

4.1. AVERAGE DIFFERENTIAL VISCOSITY BETWEEN 8 AND 12.5 S^{-1}

Figure 4 shows the change in average differential viscosity, determined between 8 and 12.5 s^{-1} (see section 3.3.2) for the evaluated mixtures: $\Delta\mu_{average}$, which is calculated according to eq. 5, where $\dot{\gamma}$ stands for the applied shear rate:

$$\Delta\mu_{average} = \mu_{average,\dot{\gamma}} - \mu_{average,100} \tag{5}$$

$\Delta\mu_{average}$ is the difference in viscosity measured at each applied shear rate (12.5, 25, or 50 s^{-1}) and the measured viscosity at 100 s^{-1}. In each graph, the average of the reference mixture and calculated 95% confidence interval are shown, and other mixtures are compared to this reference mixture. Figure 4a shows the effect of temperature, clearly showing more dependency on the applied shear rate with increasing temperature. It is well know that an increase in temperature will increase the structural build-up and accelerate the hydration reaction. As such, more connections between the particles are expected, which can be clearly seen in Table 3. With increasing temperature, superior increases of rheological properties with time are observed. As more connections are built during the resting time, more can be broken during shear.

Figure 4b shows the influence of different binder compositions, from which it can be seen that for the mixture with pure OPC, the average viscosity shows less sensitivity to the applied shear rate. Although the mixture with pure OPC shows similar workability loss values as the reference mixture, the reversibility is substantially lower seen the lower A_{thix} value. This is reflected in the viscosity values. Also the mixture with only fly ash and cement shows slightly less sensitivity to the applied shear rate, although it is less significant. Table 3 shows that the fly ash mixture develops a lower number of permanent and total connections. To explain the effect of the binder composition, one needs to evaluate its effect on thixotropy and hydration. Silica fume particles are small in size and have a large tendency to flocculate, increasing the number of connections formed [38-39]. Also, these particles have large surface area, providing many nucleation sites for the reaction products [40]. Fly ash has similar size as cement particles, resulting in limited flocculation, and it is not a major player in the hydration reactions in the first hour. Hence, it acts more as a filler, slowing down the formation of connections between particles. Furthermore, due to the large replacement rate (25%), less cement particles are present to form hydration products.

Figure 4c shows the influence of the admixtures, clearly indicating that VMAs have a pronounced effect on the average viscosity as a function of the applied shear rate. It should be borne in mind that VMAs provide an additional dependency on the applied shear rate, as they generally induce shear thinning behavior due to the formation of hydrogen bridges between particles or the stretching of molecules in the water of the paste [20]. As such, the dependency of the viscosity on the applied shear rate is not only caused by breaking a number of connections between the particles, but also by the behavior of the VMAs under different shear rates. A different dispersing admixture also affects the relationship between the viscosity and the applied shear rate. Changes in dispersant not only change the inter-particle dynamics, they may also affect the dissolution of ions from cement particles and alter the rate of hydration [41-42]. .

4.2. DIFFERENTIAL VISCOSITY AT 10 S^{-1} AND SHEAR STRESS 5 s^{-1}

Figure 5 shows the results for the differential viscosity, calculated from the modified Bingham model at 10 s^{-1}. $\Delta\mu_{\text{diff}}$ is calculated in an analogical was as $\Delta\mu_{\text{average}}$ in eq. 5. One can generally see the same trends as for the average viscosity, except for the mixture with OPC and silica fume, and for the mixture with the different dispersant. Also the mixtures with VMA show a stronger dependency for the modified Bingham differential viscosity on the applied shear rate than the average viscosity. All observations can be related to the more pronounced shear thinning behavior at low shear rates of these mixtures, compared to the reference mixture (Figure 3). As such, this discrepancy is more due to a fitting error than material behavior.

Figure 6 shows the results for the shear stress at 5 s^{-1} ($\Delta\tau_{5/s}$), expressed in a similar fashion as $\Delta\mu_{\text{average}}$ and $\Delta\mu_{\text{diff}}$. At first, the large size of the confidence interval is due to one repeatability test significantly deviating from the others. The influence of temperature is similar to the results for viscosity (Fig. 6a). For the binder though, the mixture OPC + FA shows lower values at any shear rate compared to the values at 100 s^{-1}. The flow curves are more or less coinciding at 5 s^{-1}. Similarly, the OPC + SiF mixtures shows low dependency on the applied shear rate. However, the mixture with 100% OPC, and the mixture with the different dispersant display a larger dependency of the shear stress at 5 s^{-1}. For the latter mixture, the dependency is very strong at low applied shear rate. It is at these shear rates that the viscosity values for the REF + Diff SP showed deviating behavior compared to all other mixtures. Due to this large decrease in shear stress at 5 s^{-1} when changing from 12.5 to 25 and 50 s^{-1}, the flow curves at higher applied shear rates are below those at lower shear rates. As such, in general, a decrease in rheological properties with increasing shear rate is observed.

4.3. BREAKDOWN DURING PRESHEAR

Figure 7 shows the changes in apparent viscosity as a function of the applied shear rate: $\Delta\eta$, calculated according to Eq. 4. All graphs show a high $\Delta\eta$ at 12.5 s^{-1}, and substantially lower $\Delta\eta$ values at higher shear rates. This indicates that an important part of the built structure is destroyed at the lowest shear rate: when transitioning from rest to 12.5 s^{-1} shear rate. At the higher shear rates, most $\Delta\eta$ curves show either a minimum at 25 or 50 s^{-1}, but this can be attributed to the unequal increase in shear rate in between the curves. Dividing the change in apparent viscosity by the number of increments of 12.5 s^{-1} between each shear rate step delivers continuously decreasing curves.

However, more importantly, for the different mixtures, the curves are different. For example, the mixture at elevated temperature shows a more significant breakdown from 25 to 50 s^{-1}, indicating that there are still a significant number of connections which were not broken down at 12.5 s^{-1}. In this way, one can define the strength of connections between particles: each connection will need a specific shear rate to be broken down, and this required shear rate is increasing with time due to continuing structural build-up. In the performed experiments though, one can only determine the interval in which a number of connections are broken down.

Considering the results described in sections 4.1 and 4.2, the data in Figure 7 appear to correspond largely with the rheological properties: higher $\Delta\eta$ values correspond to larger slopes in Figures 4 to 6. The only exception seems to be the 100% OPC mixture, for which no explanation can be formulated at this point. It should be noted though that a large $\Delta\eta$ at 100 s^{-1} corresponds to a large difference between the rheological properties at 50 and 100 s^{-1}. As such, the $\Delta\eta$ values at 12.5 s^{-1} indicate the change between rest and the first preshear. From the results, it appears that in the 21 min rest time before the tests at 60 min, the mixture at elevated temperature and both mixtures without fly ash form stronger connections between the particles.

5. LIMITATIONS

The attentive reader will have noticed that two important variables were not included in this paper. The water-to-binder ratio and the dispersing admixture content were controlled in this series of experiments. The research team is in possession of such results, but the observations are different than for the data described in this paper. At higher w/b and at lower mini-slump flow, reflecting not well-dispersed cementitious systems, the data show deviating behavior. At some of the applied shear rates of 25, 50 or 100 s^{-1}, no breakdown is observed and $\Delta\eta$ is negative, indicating some kind of shear-induced build-up. The rheological properties show increasing and decreasing values with applied shear rate. The researchers are still investigating these observations and are attempting to formulate physical explanations for them. As such, these results are not included in this manuscript.

6. CONSEQUENCES

Although most of the structure is broken down at low shear rate in the paste, the dependency of the rheological properties on the applied shear rate can have substantial consequences on any application of fresh concrete. The influence of mixing or re-mixing energy on the rheological properties of cement-based materials can be related to the observations made in this paper [43-45]. Also the changes in rheology induced by pumping can be explained based on this paper [46], although the shear rates applied on the paste in the rheometer are still expected to be substantially smaller than for mixing or pumping concrete.

Imposing a reference state on cement paste, mortar or concrete is a relative principle, as with increased resting time, the number and the strength of the connections increases. When performing rheological measurements in time, the duration in between the measurements can influence the strength of the connections, and thus also the number of permanent connections. As such, the workability loss is definitely dependent on the applied shear rate, but also seems to be dependent on the time interval in between measurements.

On concrete scale, the paste volume and aggregate maximum packing density are important parameters as for an equal shear rate in the concrete of different design, a different shear rate in the paste occurs. As such, for example when determining the influence of paste volume on the rheological properties of concrete, the difference in shear rate in the paste can become a disturbing factor, distorting the data and potentially leading to erroneous conclusions. And as demonstrated, temperature, time, binder composition and admixture types all influence the relationship between paste rheology and applied shear rate, complicating any investigation on concrete scale significantly.

7. CONCLUSIONS

A series of experiments were executed on well-dispersed cement pastes, demonstrating the dependency of rheological properties on the applied shear rate. The following conclusions can be drawn from the executed research work:

- In a shear stress – shear rate diagram, the flow curves are not coinciding: the higher the applied shear rate, the lower the flow curve on the diagram. Increasing the applied shear rate breaks down more connections, regardless whether they are physical or chemical in nature, resulting in a decrease in rheological properties.
- A large influence of the applied maximum shear rate on the viscosity of the mixtures has been observed, showing sometimes more than a factor 2 difference between the viscosity at 12.5 and at 100 s^{-1}. Similarly, the difference between the initial stress and the equilibrium stress during the pre-shear period demonstrates the breakdown of internal structure.
- This dependency of the viscosity on the applied shear rate seems largely dependent on the temperature, as both flocculation and hydration are accelerated with increasing temperature. The workability loss and the structural build up prove the accelerated formation of connections between particles, resulting in more connections being broken when shearing at higher

temperature. Furthermore, a larger relative proportion of connections needs broken at more elevated shear rates at higher temperature, indicating that not only the number of connections increases with time, but also their strength.

- The binder composition appears to affect the dependency of the rheological properties on time and the applied shear rate according to their influence on thixotropy and the hydration reaction. Silica fume promotes flocculation due to its small size and facilitates hydration due to the abundance of nucleation sites for the hydration products. Mixtures with silica fume appear to show more sensitivity of their rheological properties to the applied shear rates. Fly ash acts more as a filler early on, and seems to have a diluting effect.
- The influence of chemical admixtures follows the same principles as for the other mixtures, but the influence of the applied shear rate seems to be additionally affected by the working mechanisms of the dispersing and viscosity-modifying agents.
- The above conclusions are only valid for well-dispersed systems. Increasing w/cm, and decreasing the dispersing admixture content modify the behavior of the paste. Research is ongoing to explain the difference between the observations in well-dispersed and not well-dispersed pastes.
- The obtained results can be strongly related to the sensitivity of concrete rheological properties to the mixing energy, or the occurrence of substantial shearing. However, the stipulations in this paper also indicate potential sensitivity of assessing workability loss to the timing of the measurements, as

well as additional difficulties in analyzing rheological properties of mortar or concrete when the shear rate in the paste is variable.

ACKNOWLEDGMENT

The authors would like to acknowledge the RE-CAST Tier 1 University Transportation Center (US DOT) at the Missouri University of Science and Technology (grant DTRT13-G-UTC45) and the center for infrastructure engineering studies (CIES) at Missouri S&T for the financial support, as well as Lafarge-Holcim, BASF, the Euclid Chemical Company, and Rolla Ready Mix for the donation of materials.

CONFLICT OF INTEREST

The authors declare no conflict of interest. The funding agency as well as the donors of materials had no influence in the experiments, analysis and interpretation of the data.

Table 1. Mix design of the evaluated mixtures. All units are expressed in g/l of paste. The values for the SP content and the initial mini slump flow for the reference mixture is the average of five mixtures.

	PC	Fly ash	Silica Fume	Water	SP 1	SP 2	VMA 1	VMA 2	Initial mini SF
Reference (5 times)	989	342	34.5	520	4.96				330 mm
High T (37°C)	990	342	34.6	521	4.18				335 mm
Low T (7°C)	988	342	34.5	520	6.16				330 mm
OPC + FA	1035	341		519	5.06				335 mm
OPC + SiF	1445		34.7	523	6.56				315 mm
Pure OPC	1498			520	5.95				340 mm
REF + VMA	989	342	34.5	520	4.48		0.84		310 mm
REF + Diff SP	989	342	34.5	520		5.28			315 mm
REF Diff SP + VMA	985	341	34.4	518		7.92		0.84	330 mm

Table 2. Rheological properties of the mixtures at 60 min, for the different applied shear rates.

		Applied shear rate			
		12.5 s^{-1}	25 s^{-1}	50 s^{-1}	100 s^{-1}
Reference repeat 1	τ at 5 s^{-1}	8.29 Pa	8.21 Pa	8.23 Pa	7.85 Pa
	μ_{diff} at 10 s^{-1}	0.582 Pas	0.542 Pas	0.474 Pas	0.390 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.583 Pas	0.539 Pas	0.497 Pas	0.437 Pas
Reference repeat 2	τ at 5 s^{-1}	7.58 Pa	7.56 Pa	7.33 Pa	7.12 Pa
	μ_{diff} at 10 s^{-1}	0.519 Pas	0.470 Pas	0.412 Pas	0.345 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.519 Pas	0.455 Pas	0.432 Pas	0.385 Pas
Reference repeat 3	τ at 5 s^{-1}	7.60 Pa	7.54 Pa	7.19 Pa	6.67 Pa
	μ_{diff} at 10 s^{-1}	0.538 Pas	0.493 Pas	0.400 Pas	0.316 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.539 Pas	0.491 Pas	0.431 Pas	0.364 Pas
Reference repeat 4	τ at 5 s^{-1}	11.83 Pa	11.02 Pa	9.96 Pa	9.33 Pa
	μ_{diff} at 10 s^{-1}	0.682 Pas	0.752 Pas	0.674 Pas	0.540 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.684 Pas	0.752 Pas	0.706 Pas	0.591 Pas
Reference repeat 5	τ at 5 s^{-1}	7.27 Pa	7.10 Pa	6.76 Pa	6.36 Pa
	μ_{diff} at 10 s^{-1}	0.536 Pas	0.490 Pas	0.426 Pas	0.315 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.532 Pas	0.488 Pas	0.443 Pas	0.366 Pas
Reference High T	τ at 5 s^{-1}	18.96 Pa	17.30 Pa	16.67 Pa	15.27 Pa
	μ_{diff} at 10 s^{-1}	1.202 Pas	0.788 Pas	0.645 Pas	0.455 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	1.157 Pas	0.788 Pas	0.735 Pas	0.614 Pas
Reference Low T	τ at 5 s^{-1}	5.44 Pa	5.39 Pa	5.32 Pa	5.26 Pa
	μ_{diff} at 10 s^{-1}	0.478 Pas	0.471 Pas	0.442 Pas	0.391 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.476 Pas	0.472 Pas	0.454 Pas	0.416 Pas
OPC + FA	τ at 5 s^{-1}	3.99 Pa	3.85 Pa	3.88 Pa	4.03 Pa
	μ_{diff} at 10 s^{-1}	0.376 Pas	0.367 Pas	0.334 Pas	0.287 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.376 Pas	0.369 Pas	0.342 Pas	0.291 Pas
OPC + SiF	τ at 5 s^{-1}	11.28 Pa	11.59 Pa	11.61 Pa	11.25 Pa
	μ_{diff} at 10 s^{-1}	0.640 Pas	0.668 Pas	0.524 Pas	0.399 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.644 Pas	0.638 Pas	0.584 Pas	0.517 Pas
Pure OPC	τ at 5 s^{-1}	6.97 Pa	6.83 Pa	6.69 Pa	5.99 Pa
	μ_{diff} at 10 s^{-1}	0.555 Pas	0.527 Pas	0.463 Pas	0.450 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.540 Pas	0.530 Pas	0.485 Pas	0.472 Pas
REF + VMA	τ at 5 s^{-1}	11.95 Pa	11.84 Pa	11.50 Pa	10.67 Pa
	μ_{diff} at 10 s^{-1}	0.766 Pas	0.684 Pas	0.570 Pas	0.427 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	0.776 Pas	0.686 Pas	0.627 Pas	0.529 Pas
REF + Diff SP	τ at 5 s^{-1}	20.95 Pa	19.50 Pa	18.71 Pa	18.61 Pa
	μ_{diff} at 10 s^{-1}	1.252 Pas	1.299 Pas	1.193 Pas	0.860 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	1.257 Pas	1.294 Pas	1.279 Pas	1.160 Pas
REF Diff SP + VMA	τ at 5 s^{-1}	11.97 Pa	11.69 Pa	10.96 Pa	9.41 Pa
	μ_{diff} at 10 s^{-1}	1.024 Pas	0.892 Pas	0.719 Pas	0.509 Pas
	μ_{ave} btw 8 and 12.5 s^{-1}	1.105 Pas	0.903 Pas	0.772 Pas	0.596 Pas

Table 3. Workability loss from 15 to 90 min (slope of shear stress at 5 s^{-1} and differential viscosity at 52.5 s^{-1} with time), and structural build-up (A_{thix}) of the evaluated mixtures.

	Shear stress at 5 s^{-1} mPa/min	Differential viscosity at 52.5 s^{-1} mPas/min	A_{thix} Pa/min
REF Average	85.4	3.53	2.45
REF StDev	*19.0*	*1.58*	*0.42*
REF High T	246.4	5.77	9.76
REF Low T	35.3	3.27	0.40
OPC + FA	32.7	1.46	0.54
OPC + SiF	126.6	2.76	1.47
100% OPC	80.0	3.00	0.54
REF + VMA	103.4	3.68	3.67
REF + Diff SP	173.3	6.89	4.37
REF Diff SP + VMA	86.7	3.28	1.85

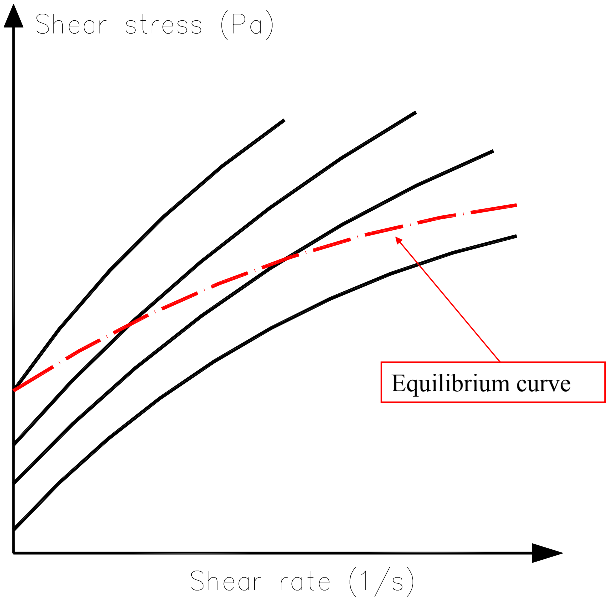


Figure 1. Dependency of rheological properties on the applied shear rate for thixotropic materials. The dashed line represents the equilibrium curve, for which dλ/dt = 0 at each measurement point. Each solid line correspond to a unique set of rheological properties at each reference state. The lowest curve corresponds to the highest applied shear rate. Figure after [29].

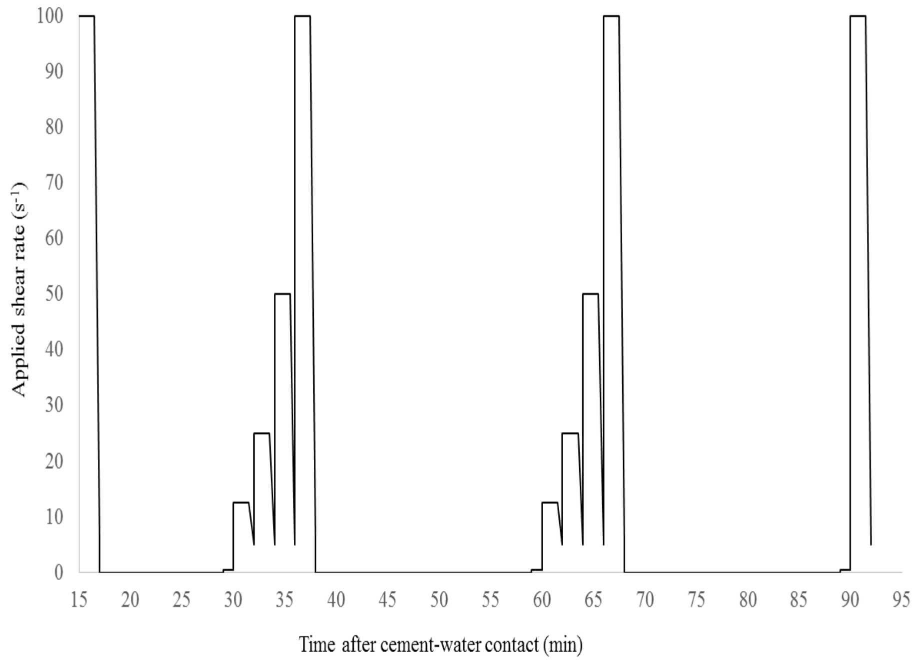


Figure 2. Measurement protocol. The shear rate for the static yield stress measurements is slightly exaggerated for better visibility.

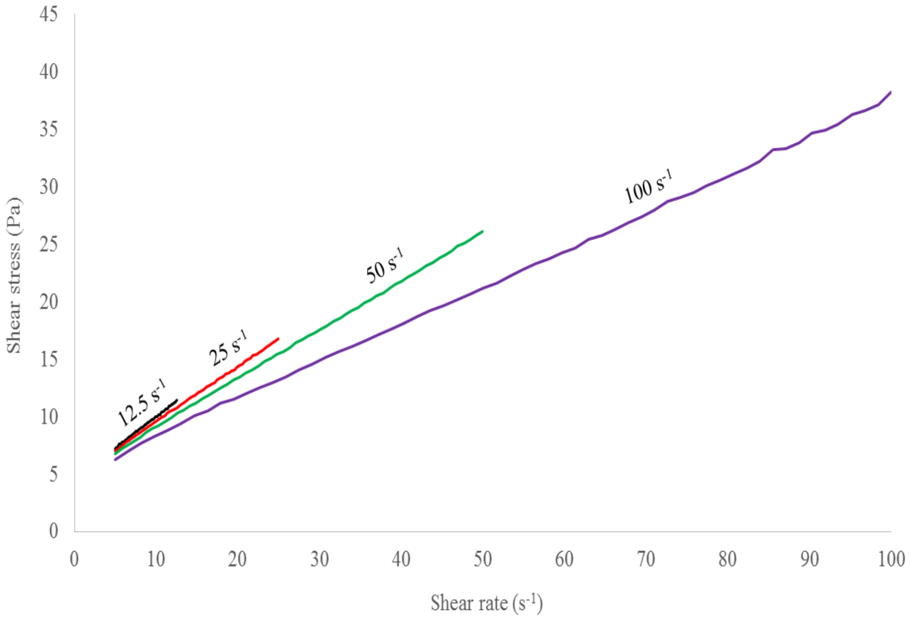


Figure 3. Example of flow curves obtained at 60 min for one of the reference mixtures.

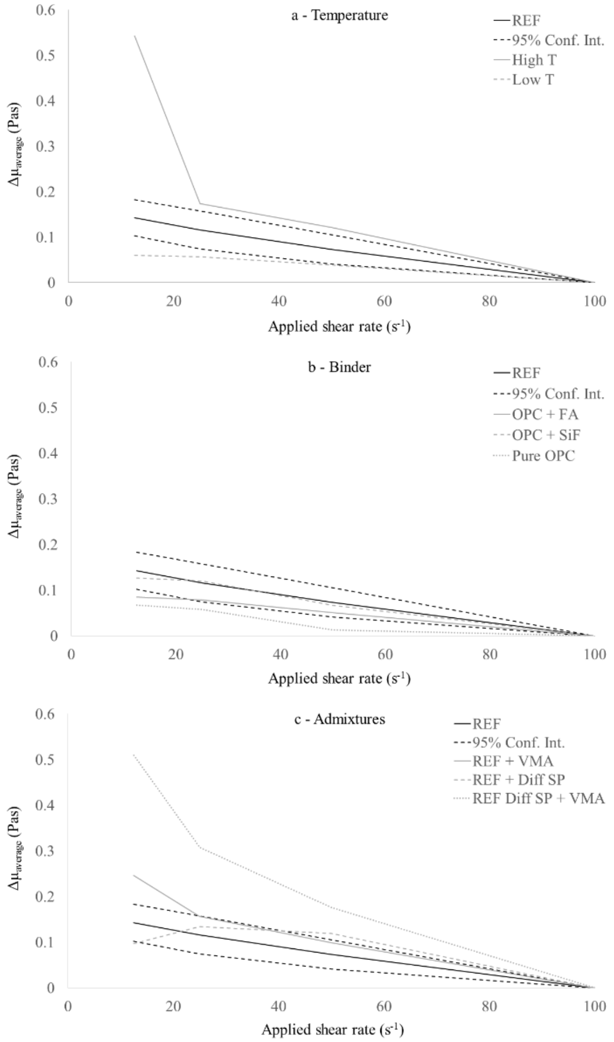


Figure 4. Influence of applied shear rate on the average differential viscosity between 8 and 12.5 s^{-1}, based on a 6^{th} order polynomial applied on the flow curve. The graphs show the difference between the average viscosity at a certain shear rate and the corresponding value at 100 s^{-1}. All figures show the average and 95% confidence interval of the reference mixture. Figure 4a shows the effect of temperature, Figure 4b the effect of binder composition and Figure 4c the effect of the admixtures.

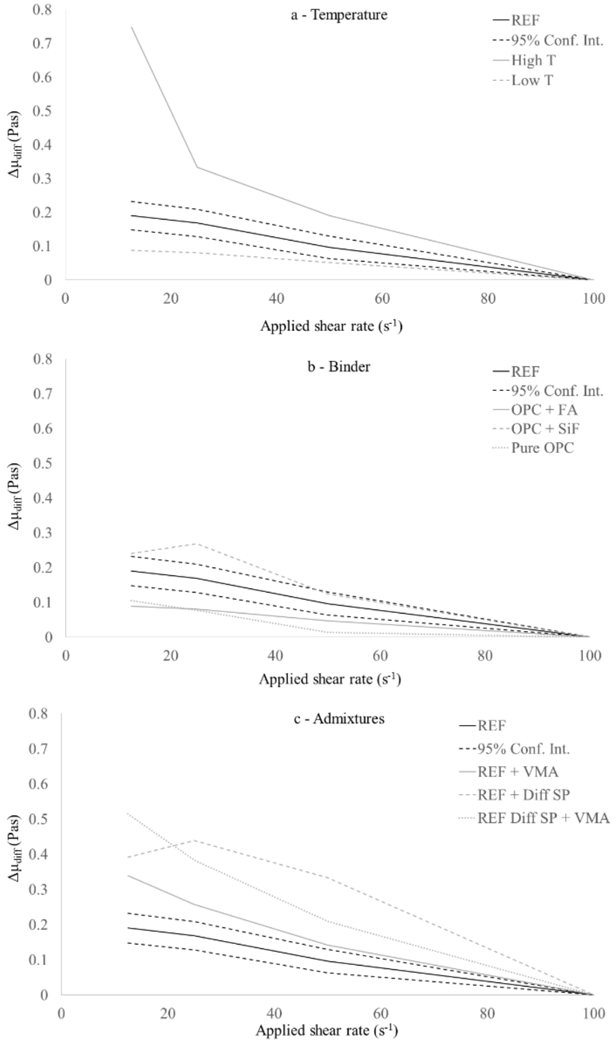


Figure 5. Dependency of modified Bingham differential viscosity at 10 s^{-1} on the applied shear rate. All figures show the average and 95% confidence interval of the reference mixture. Figure 5a shows the effect of temperature, Figure 5b the effect of binder composition and Figure 5c the effect of the admixtures.

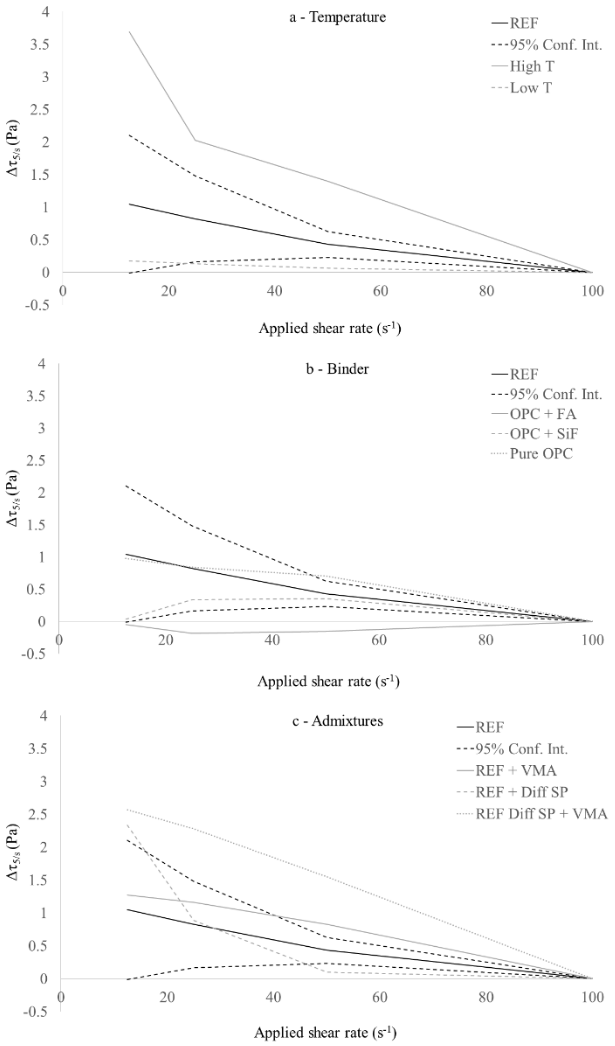


Figure 6. Dependency of shear stress at 5 s^{-1} on the applied shear rate. All figures show the average and 95% confidence interval of the reference mixture. Figure 6a shows the effect of temperature, Figure 6b the effect of binder composition and Figure 6c the effect of the admixtures.

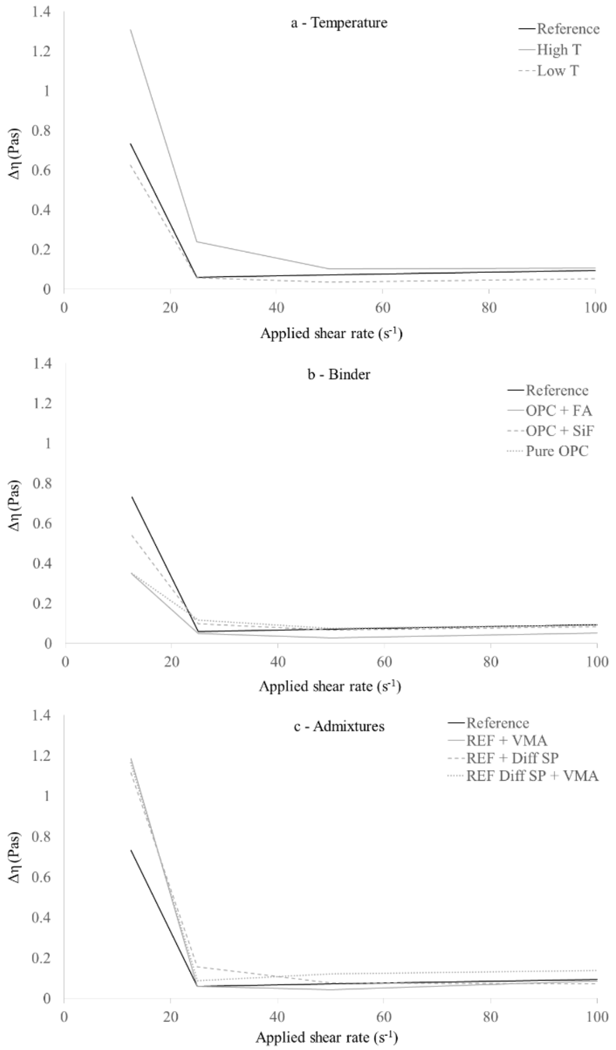


Figure 7: Change in apparent viscosity at each preshear step. The Δη values show the difference between the apparent viscosity at the first second during each preshear period and the average apparent viscosity during the last five seconds of each preshear period

REFERENCES

[1] Tattersall, G.H. and Banfill, P.F., 1983. *The rheology of fresh concrete,* London: Pitman.

[2] Roussel, N. ed., 2012. *Understanding the rheology of concrete*. Woodhead Publishing, Cambridge.

[3] Yammine, J., Chaouche, M., Guerinet, M., Moranville, M. and Roussel, N., 2008. From ordinary rhelogy concrete to self compacting concrete: A transition between frictional and hydrodynamic interactions. *Cement and Concrete Research*, *38*(7), pp.890-896.

[4] Gadala Maria, F. and Acrivos, A., 1980. Shear□Induced Structure in a Concentrated Suspension of Solid Spheres. *Journal of Rheology*, *24*(6), pp.799-814.

[5] Kaplan, D., de Larrard, F. and Sedran, T., 2005. Design of concrete pumping circuit. *Materials Journal*, *102*(2), pp.110-117.

[6] Chapdelaine, F., 2007. *Fundamental and practical study on pumping of concrete*, PhD dissertation, Université Laval, Québec.

[7] Feys, D., Khayat, K.H., Perez-Schell, A. and Khatib, R., 2014. Development of a tribometer to characterize lubrication layer properties of self-consolidating concrete. *Cement and Concrete Composites*, *54*, pp.40-52.

[8] Le, H.D., Kadri, E.H., Aggoun, S., Vierendeels, J., Troch, P. and De Schutter, G., 2015. Effect of lubrication layer on velocity profile of concrete in a pumping pipe. *Materials and Structures*, *48*(12), pp.3991-4003.

[9] Choi, M., Roussel, N., Kim, Y. and Kim, J., 2013. Lubrication layer properties during concrete pumping. *Cement and Concrete Research*, *45*, pp.69-78.

[10] Phillips, R.J., Armstrong, R.C., Brown, R.A., Graham, A.L. and Abbott, J.R., 1992. A constitutive equation for concentrated suspensions that accounts for shear-induced particle migration. *Physics of Fluids A: Fluid Dynamics*, *4*(1), pp.30-40.

[11] Feys, D. and Khayat, K.H., 2017. Particle migration during concrete rheometry: How bad is it?. *Materials and Structures*, *50*(2), p.122.

[12] Hattori, K. and Izumi, K., 1990, March. A New Viscosity Equation for Non-Newtonian Suspensions and Its Application, Rheology of Fresh Cement and Concrete. In *Proceedings of The International Conference Organized by The British Society of Rheology, University of Liverpool.*

[13] Wallevik, J.E., 2003. *Rheology of particle suspensions: fresh concrete, mortar and cement paste with various types of lignosulfonates*. Ph-D dissertation, the Norwegian Institute for science and technology, Trondheim, Norway.

[14] Wallevik, J.E., 2009. Rheological properties of cement paste: thixotropic behavior and structural breakdown. *Cement and Concrete Research*, *39*(1), pp.14-29.

[15] Kim, B.G., Jiang, S., Jolicoeur, C. and Aïtcin, P.C., 2000. The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste. *Cement and Concrete research*, *30*(6), pp.887-893.

[16] Hanna, E., Luke, K., Perraton, D. and Aitcin, P.C., 1989. Rheological Behavior of Portland Cement in the Presence of a Super Plasticizer. *Special Publication*, *119*, pp.171-188.

[17] Ferrari, L., Kaufmann, J., Winnefeld, F. and Plank, J., 2010. Interaction of cement model systems with superplasticizers investigated by atomic force microscopy, zeta potential, and adsorption measurements. *Journal of Colloid and Interface Science*, *347*(1), pp.15-24.

[18] Flatt, R.J. and Houst, Y.F., 2001. A simplified view on chemical effects perturbing the action of superplasticizers. *Cement and concrete research*, *31*(8), pp.1169-1176.

[19] Plank, J. and Hirsch, C., 2007. Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cement and Concrete Research*, *37*(4), pp.537-542.

[20] Khayat, K.H., 1998. Viscosity-enhancing admixtures for cement-based materials—an overview. Cement and Concrete Composites, 20(2-3), pp.171-188.

[21] Neville, A.M., 1995. *Properties of concrete* (Vol. 5). London: Pearson.

[22] Nachbaur, L., Mutin, J.C., Nonat, A. and Choplin, L., 2001. Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting. *Cement and Concrete Research*, *31*(2), pp.183-192.

[23] Petit, J.Y., Khayat, K.H. and Wirquin, E., 2006. Coupled effect of time and temperature on variations of yield value of highly flowable mortar. *Cement and Concrete Research*, *36*(5), pp.832-841.

[24] Petit, J.Y., Khayat, K.H. and Wirquin, E., 2009. Coupled effect of time and temperature on variations of plastic viscosity of highly flowable mortar. *Cement and Concrete Research*, *39*(3), pp.165-170.

[25] Barnes, H.A., 1997. Thixotropy—a review. *Journal of Non-Newtonian fluid mechanics*, *70*(1-2), pp.1-33.

[26] Mewis, J. and Wagner, N.J., 2012. *Colloidal suspension rheology*. Cambridge University Press.

[27] Roussel, N., 2006. A thixotropy model for fresh fluid concretes: theory, validation and applications. *Cement and Concrete Research*, *36*(10), pp.1797-1806.

[28] Jarny, S., Roussel, N., Rodts, S., Bertrand, F., Le Roy, R. and Coussot, P., 2005. Rheological behavior of cement pastes from MRI velocimetry. *Cement and Concrete Research*, *35*(10), pp.1873-1881.

[29] Cheng, D.H., 1967. Hysteresis loop experiments and the determination of thixotropic properties. *Nature*, *216*(5120), pp.1099-1100.

[30] Wallevik, O.H., Feys, D., Wallevik, J.E. and Khayat, K.H., 2015. Avoiding inaccurate interpretations of rheological measurements for cement-based materials. *Cement and Concrete Research*, *78*, pp.100-109.

[31] Feys, D., Cepuritis, R., Jacobsen, S., Lesage, K., Secrieru, E. and Yahia, A., 2018. Measuring rheological properties of cement pastes: most common techniques, procedures and challenges. *Rilem Technical Letters*, *2*, pp.129-135.

[32] Roussel, N., Ovarlez, G., Garrault, S. and Brumaud, C., 2012. The origins of thixotropy of fresh cement pastes. *Cement and Concrete Research*, *42*(1), pp.148-157.

[33] Ferron, R.D., Shah, S., Fuente, E. and Negro, C., 2013. Aggregation and breakage kinetics of fresh cement paste. *Cement and Concrete Research*, *50*, pp.1-10.

[34] Tattersall, G.H., 1955. Structural breakdown of cement pastes at constant rate of shear. *Nature*, *175*(4447), pp.166-166.

[35] Yahia, A. and Khayat, K.H., 2001. Analytical models for estimating yield stress of high-performance pseudoplastic grout. *Cement and Concrete Research*, *31*(5), pp.731-738.

[36] Billberg, P., 2006. *Form pressure generated by self-compacting concrete: influence of thixotropy and structural behaviour at rest,* Ph-D dissertation, School of Architecture and Built Environment, Stockholm, Sweden.

[37] Roussel, N., Le Roy, R. and Coussot, P., 2004. Thixotropy modelling at local and macroscopic scales. *Journal of non-newtonian fluid mechanics*, *117*(2), pp.85-95.

[38] Oertel, T., Hutter, F., Tänzer, R., Helbig, U. and Sextl, G., 2013. Primary particle size and agglomerate size effects of amorphous silica in ultra-high performance concrete. *Cement and Concrete Composites*, *37*, pp.61-67.

[39] Plank, J., Schroefl, C., Gruber, M., Lesti, M. and Sieber, R., 2009. Effectiveness of polycarboxylate superplasticizers in ultra-high strength concrete: the importance of PCE compatibility with silica fume. *Journal of Advanced Concrete Technology*, *7*(1), pp.5-12.

[40] Meng, W., Lunkad, P., Kumar, A. and Khayat, K., 2016. Influence of Silica Fume and Polycarboxylate Ether Dispersant on Hydration Mechanisms of Cement. *The Journal of Physical Chemistry C*, *120*(47), pp.26814-26823.

[41] Ridi, F., Fratini, E., Luciani, P., Winnefeld, F. and Baglioni, P., 2012. Tricalcium silicate hydration reaction in the presence of comb-shaped superplasticizers: boundary nucleation and growth model applied to polymer-modified pastes. *The Journal of Physical Chemistry C*, *116*(20), pp.10887-10895.

[42] Cheung, J., Jeknavorian, A., Roberts, L. and Silva, D., 2011. Impact of admixtures on the hydration kinetics of Portland cement. *Cement and concrete research*, *43*(12), pp.1289-1309.

[43] Schießl, P., Mazanec, O. and Lowke, D., 2007. SCC and UHPC—effect of mixing technology on fresh concrete properties. *Advances in Construction Materials 2007*, pp.513-522.

[44] Han, D. and Ferron, R.D., 2015. Effect of mixing method on microstructure and rheology of cement paste. *Construction and Building Materials*, *93*, pp.278-288.

[45] Cazacliu, B. and Roquet, N., 2009. Concrete mixing kinetics by means of power measurement. *Cement and Concrete Research*, *39*(3), pp.182-194.

[46] Feys, D., De Schutter, G., Khayat, K.H. and Verhoeven, R., 2016. Changes in rheology of self-consolidating concrete induced by pumping. *Materials and Structures*, *49*(11), pp.4657-4677.

SECTION

3. SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

3.1. SUMMARY OF RESEARCH

This research was conducted to establish the fundamental of rheological robustness of cement pastes with SCC consistency to be implemented for SCC pavements with less cost and more durability.

The first paper represented a unique up-to-date study for evaluate the influence of amount of water, amount of SP, mixing time, mixing speed and addition time of SP on cement pastes with SCC consistency by means of rheology.

The second paper represented the influence of addition time of SP on the initial rheological properties of two different mix designs (VMA mix design and Powder type mix designs) and determine why the VMA mix designs are more robust compare to Powder mix designs by changing the addition time of SP.

The third paper demonstrated the results of a study to evaluate the change of yield stress and viscosity over time (first hours) of cement pastes with SCC consistency. Three study parameters are included: Material Proportions, Material Properties and Mixing Procedure.

The fourth paper investigated the consequences of applying different shear rates (from 12.5 s^{-1} to 100 s^{-1}), after a rest period, on cement paste with SCC consistency to evaluate the rheological properties of cement pastes.

3.2. CONCLUSIONS

This section summarizes the conclusions from the three different phases of experimental studies to determine the most important factors influencing the initial and over time rheological properties of cement pastes with SCC consistency, and their variations over time. Regarding to the experimental studies, the following conclusions are presented:

- Variations in water, amount of SP, variations in the adding time of the SP (with the mixing water or delayed by 2 min), variations in mixing time and speed (mixing energy) all have significant influence on the measured viscosity and yield stress. Also, for the variations imposed, the selected powder-type mix designs appear more robust than the selected VMA-type.
- For the powder-type cement paste with w/p = 0.275, the changing water and SP content, result in the largest variations in yield stress and viscosity.
- Increasing w/p to 0.315 (by increasing the water content and decreasing the relative amount of limestone filler) has revealed that the influence of a change in water content is similar or even inferior to some of the other parameters tested. In this case, the influence of mixing speed appeared more important, while the adding time of the SP and increasing mixing time had similar influence as changing the water content, especially for the viscosity.
- For the selected VMA-type cement paste, the adding time of the SP and the resulting change in rheological properties was larger than the changes induced by varying the water content.

- The source of the PCE-SP appears to play a minor but important role, as mixtures with a long workability-retaining admixture (SP 2) appeared more sensitive to the adding time of the SP.
- Omitting VMA reduces the sensitivity of viscosity of the cement paste, regardless of the VMA manufacturer. For the yield stress, different results were obtained.
- The presence of silica fume and fly ash renders the viscosity of the tested VMA-type mixture very sensitive to a change in adding time, while for cement paste without SCMs, the yield stress is more affected. Replacing a part of the binder with limestone filler reduces the variations in rheological properties due to the adding time of the SP.
- In most cases, the viscosity of the mixture was more affected than the yield stress due to a delayed addition of SP.
- For the VMA-type mixtures made with the long workability-retention SP, the change in yield stress and viscosity with time appears not significantly affected by either a change in water or SP content.
- For the mixtures with the short workability retention SP: A change in water content significantly affects the increase (or decrease) of both yield stress and viscosity with time: a reduction in water content results in a faster increase in rheology, while an increase in water results in a slower increase in rheology.). This can be attributed to the increased inter-particle spacing when more water is added, resulting in less connections growing between cement particles.

- The adding time of the SP is the second most important factor influencing the change of yield stress and viscosity with time: in the case of a delayed addition, these properties increase faster with time. As a result, the beneficial effect of delaying the SP addition on the initial rheological properties is reduced or even removed over time. Immediate addition of SP results in more intercalation of the SP in between hydration products immediately after mixing. This renders a delayed addition more efficient. However, with time, more hydration products are formed and as more of the SP is “active” in case of a delayed addition, it is speculated that more SP gets overgrown with time.
- For mix designs 1 and 3 (SP 1), increasing the amount of SP results in a faster increase in yield stress with time, however, the change of yield stress increase with time is too small to compensate for the significant change in initial yield stress due to an increase in SP addition. The hypothesis for this behavior is similar to the differences between immediate and delayed addition: if more SP is added, more SP can be overgrown, resulting in a faster decline in efficiency. The changes in the increase of viscosity with time are of minor importance.
- Changing the mixing energy appeared to have a minor, less significant importance on the change in rheological properties with time. A reduction in mixing energy could lead to more entrapped water as less flocs of cement particles are broken, and a faster increase in viscosity with time was noted for mix design 2 (the changes for mix designs 1 and 3 were insignificant). However, less deflocculated particles results in less exposed surface, and thus a reduction in the adsorbed SP in the system.

- In a shear stress – shear rate diagram, the flow curves are not coinciding: the higher the applied shear rate, the lower the flow curve on the diagram. Increasing the applied shear rate breaks down more connections, regardless whether they are physical or chemical in nature, resulting in a decrease in rheological properties.
- A large influence of the applied maximum shear rate on the viscosity of the mixtures has been observed, showing sometimes more than a factor 2 difference between the viscosity at 12.5 and at 100 s^{-1}. Similarly, the difference between the initial stress and the equilibrium stress during the pre-shear period demonstrates the breakdown of internal structure.
- The dependency of the viscosity on the applied shear rate seems largely dependent on the temperature, as both flocculation and hydration are accelerated with increasing temperature. The workability loss and the structural build up prove the accelerated formation of connections between particles, resulting in more connections being broken when shearing at higher temperature.
- The binder composition appears to affect the dependency of the rheological properties on time and the applied shear rate according to their influence on thixotropy and the hydration reaction. Silica fume promotes flocculation due to its small size and facilitates hydration due to the abundance of nucleation sites for the hydration products. Mixtures with silica fume appear to show more sensitivity of their rheological properties to the applied shear rates. Fly ash acts more as a filler early on, and seems to have a diluting effect.

- The influence of chemical admixtures follows the same principles as for the other mixtures, but the influence of the applied shear rate seems to be additionally affected by the working mechanisms of the dispersing and viscosity-modifying agents.

3.3. RECOMMENDATIONS

Based on the objective and scope of work of this study, the following aspects are recommended for future research:

1. Studying the robustness of cement-based materials, with cements have similar physical (e.g. grain size distribution) or chemical (e.g. chemical composition) properties to control variation in deliveries of cement (from the same manufacturer or from different producers).
2. In this project, the study was limited to two different PCE-SP, showing different results related to the SP type. The research can thus be developed to other SP types, from the same (PCE) and other subgroups (PNS, etc.). In this way, simple quality control guidelines can be established to evaluate the variation in fresh properties of SCC, increasing the application of this novel concrete type and decreasing time and cost for quality control.
3. The research can further perform to investigate the sensitivity of rheological properties to use of different type of VMA (the adding sequence of VMA was not investigated) and AEA.
4. Further study can be focused on the variations between different deliveries of chemical admixtures.

5. Further Research is needed to explain the difference between the observations in well-dispersed and not well-dispersed pastes.
6. Further study can be performed to analyze the rheological properties of mortar or concrete when the shear rate in the paste is variable

REFERENCES

Aiad, I. (2003). Influence of time addition of superplasticizers on the rheological properties of fresh cement pastes. *Cement and Concrete Research*,*33*, 1229–1234

Aiad, I., Abd El-Aleem, S., & El-Didamony, H. (2002). Effect of delaying addi- tion of some concrete admixtures on the rheological properties of cement pastes. *Cement and Concrete Research*,*32*, 1839–1843.

Aitcin, P.C.A., Jolicoeur, C., & McGregor, J.G. (1994). Superplasticizers: How they work and why they occasionally don't. *Concrete International*, *16*(5), 45-52.

Asghari, A., Ley Hernandez, A.M., Feys, D., & De Schutter, G. (2016). Which parameters, other than the water content, influence the robustness of cement paste with SCC consistency?. *Construction and Building Materials*, *124*, 95-103.

Ball, R.C., & Melrose, J.R. (1995). Lubrication breakdown in hydrodynamic simulations of concentrated colloids. *Adv Colloid Interface Sci. 59*, 19–30.

Banfill, P.F.G. (1979). A discussion of the paper Rheological properties of cements mixes. *Cement and Concrete Research*, *9*(6), 795–796.

Banfill, P.F.G. (1981). A Viscometric Study of Cement Pastes Containing Superplasticizers with a Note on Experimental Techniques. *Magazine of Concrete Research*, *33(*114), 37-47.

Barnes, H.A. (1997). Thixotropy—a review. *Journal of Non-Newtonian fluid mechanics*, *70*(1-2), 1-33.

Barret, P., Bertrandie, D., & Menetrier, D. (1980). *7th ICCC Paris*, vol. II, pp. II–261. Paris.

Bartos, P.J.M., Sonebi, M., Tamimi, A.K. (Eds.) (2002). Workability and Rheology of Fresh Concrete: Compendium of Tests. RILEM, Cachan, France.

Batchelor, G.K., & Green, J.T. (1972). The hydrodynamic interaction of two small freely moving spheres in a linear flow field. *J Fluid Mech*., 56, 375–400.

Beedle, S.S., Groves, G.W., & Rodger, S.A. (1989). The effect of fine pozzolanic and other particles on hydration of C3S. *Adv. Cem. Res*. *2*(5), 3–8.

Benstead J., & Ghosh S.N. (Ed.) (1983). *Advances in Cement Technology*, (Oxford : Pergamon Press.

BIBM, CEMBUREAU, ERMCO, EFCA, & EFNARC (2005). European Guidelines for Self Consolidating Concrete: Specification, Production and Use. 63 pp. http://www.efnarc.org/pdf/SCCGuidelinesMay2005.pdf.

Billberg, P. (2006). *Form pressure generated by self-compacting concrete: influence of thixotropy and structural behaviour at rest.* Ph-D dissertation, School of Architecture and Built Environment, Stockholm, Sweden.

Billberg, P., (2009), Increase of SCC Robustness to Varying Aggregate Moisture Content Using VMA, *Proceedings of the Second International Symposium on Design, Performance, and Use of Self-Consolidating Concrete (SCC)*, China, 473-493.

Billberg, P. (2011). Influence of powder type and VMA combination on certain key fresh properties of SCC. *9th International Symposium on High Performance Concrete*, Rotorua, New Zealand.

Billberg, P., & Khayat, K.H. (2008). Use of Viscosity-Modifying Admixtures to Enhance Robustness. *Proceedings of the Third North American Conference on the Design and Use of Self-Consolidating Concrete*, Chicago, IL.

Billberg, P., & Westerholm, M. (2008). Robustness of fresh VMA-modified SCC to varying aggregate moisture. *NCR J.*, *38*(7), 103-119.

Bokan-Bosiljkov, V., Gasperic, N., & Zevnik, L. (2013). New type of superplasticizer for SCC mixtures with increased robustness. in: Proc. of the *7th Int. RILEM Symp. on Self-Compacting Concrete*, Paris, France.

Bonen, D., & Sarkar, S.L. (1995). The superplasticizer adsorption capacity of cement pastes pore solution composition and parameters affecting flow loss. *Cement and Concrete Research*, *25*, 1423–1434.

Bonen, D., & Shah, S.P. (2005). Fresh and hardened properties of self-consolidating concrete. *Progress in Structural Engineering Materials Journal*, *7*(1), 14-26.

Bonen, D., Deshpande, Y., Olek, J., Shen, L., Struble, L., Lange, D., & Khayat, K.H. (2007). Robustness of Self-Consolidating Concrete,.Proc. of the 5th Int. RILEM Symposium on SCC, Ghent, Belgium, 33-42.

Bossis, G., & Brady, J.F. (1989). The rheology of Brownian suspensions. *J. Chem. Phys. 91*(3), 1866-1874.

Brady, J.F., & Bossis, G. (1988). Stokesian dynamics. *Ann Rev Fluid Mech*., *20,* 111–57.

Brady, J.F., & Morris, J.F. (1977). Microstructure of strongly sheared suspensions and its impact on rheology and diffusion. *J Fluid Mech. 348*, 103–39.

Carlsward., J., Emborg, M, Utsi, S., & Oberg, P.,(2003). Effects of constituents on the workability and rheology of self-compacting concrete. 143-153, Proc. 3rd *Intern. RILEM Symp. on self-compacting concrete,* Eds. Wallevik O, Nielsson I, RILEM Publications S.A.R.L.

Cazacliu, B., & Roquet, N. (2009). Concrete mixing kinetics by means of power measurement. *Cement and Concrete Research*, *39*(3), 182-194.

Chapdelaine, F. (2007). *Fundamental and practical study on pumping of concrete*, PhD dissertation, Université Laval, Québec.

Chen, S., & Doolen, G.D. (1998). Lattice Boltzmann method for fluid flows. *Annu Rev Fluid Mech. 30*, 329–64.

Cheng, D.H., (1967). Hysteresis loop experiments and the determination of thixotropic properties. *Nature*, *216*(5120), 1099-1100.

Cheung, J., Jeknavorian, A., Roberts, L. & Silva, D. (2011). Impact of admixtures on the hydration kinetics of Portland cement. *Cement and concrete research*, *43*(12), 1289-1309.

Choi, M., Roussel, N., Kim, Y. & Kim, J. (2013). Lubrication layer properties during concrete pumping. *Cement and Concrete Research*, *45*, 69-78.

Chong, J.S., Christiansen, E.B., & Baer, A.D. (1971). Rheology of concentrated suspensions. *J Appl Polym Sci. 15*, 2007–21.

Chow, A.W., Sinton, S.W., JIwamiya, J.H., & Stephens, T.S. (1994) Shear-induced particle migration in Couette and parallel-plate viscometers: NMR imaging an stress measurements. *Phys Fluids. 6*(8), 2561–76.

Collepardi, M. (1998). Admixtures Used to Enhance Placing Characteristics of Concrete. *Cem Concr. Comp. 20*(2-3), 103-112.

De Jong, J.G.M., Stein, H.N., & Stevels, J.M. (1967). Hydration of tricalcium silicate. *J. Appl. Chem*. *17*(9), 246-250.

De Kruif, C.G., vanIersel, E.M.F., Vrij A., & Russel, W.B. (1986). Hard sphere colloidal dispersions: Viscosity as a function of shear rate and volume fraction. *J Chem Phys*. *83*, 4717–25.

De Schutter, G., Bartos, P.J.M., Domone, P., & Gibbs, J. (2008). Self-compacting concrete, Whittles Publishing. Caithness.

Derjaguin, D., & Landau, L. (1941). Theory of the stability of strongly charged lyophobic sols and the adhesion of strongly charged particles in solution of electrolytes. *Acta Physicochim. URSS 14*, 633-662.

Double, D.D., Thomas, N.L., & Jameson, D.A. (1980).*7th ICCC Paris,* vol. II, pp. II–256. Paris.

Douglas, R., Gregori, A., Sun, Z., Bonen, D., & Shah, S.P. (2005). The Effect of ingredients and shear history on the thixotropic rate of rebuilding of SCC. *Proc. Of 2nd North American Confer. & 4th Intern. RILEM Confer. On Self-Consolidating Concrete*, Chicago, IL, 591-596.

Dratler, D.I., & Schowalter, W. (1996) Dynamic simulation of suspensions of non-Brownian hard spheres. *J Fluid Mech. 325*, 53–77.

Einstein, A. (1906). Eine neue Bestimmung der Moleküldimensionen, Annalen der Physik, 19 , 289-306.

Emborg, M., Simonsson, P., Carlswärd, J., & Nilsson, M. (2007). Industrial Production Methods and Materials, like a Robust SCC, Utilizing Lean Construction Principles. *Proc. of the 5th Int. RILEM Symposium on SCC*, Ghent, Belgium, 485-491.

Erdogan, T.S., (2005). Determination of aggregate shape properties using X-ray tomographic methods and the effect of shape on concrete rheology, PhD thesis, University of Texas at Austin.

Fernandez-Altable, V., Casanova, I., (2006), Influence of mixing sequence and superplasticiser dosage on the rheological response of cement pastes at different temperatures. *Cement and Concrete Research*,*36*, 1222–1230.

Ferrari, L., Kaufmann, J., Winnefeld, F., Plank, J. (2010). Interaction of Cement Model Systems with Superplasticizers Investigated by Atomic Force Microscopy, Zeta Potential, and Adsorption Measurements. *J. Colloid Interface Sc. 347*(1), 15-24.

Ferraris, C.F., Gaidis, J.M. (1992). Connection between the rheology of concrete and rheology of cement paste, *ACI Mat. J. 89*(4), 388-393.

Ferraris, C.F., Obla,, K.H., & Hill, R. (2001). The influence of mineral admixtures on the rheology of cement paste and concrete. *Cement and Concrete Research*, *31*(2), 245–255.

Ferron, R.D., Shah, S., Fuente, E. & Negro, C. (2013). Aggregation and breakage kinetics of fresh cement paste. *Cement and Concrete Research*, *50*, 1-10.

Feys ,D., Verhoeven, R., & De Schutter, G. (2007). Evaluation of time independent rheological models applicable to fresh Self-Compacting Concrete. *Appl. Rheol. 17*(5), 56244.

Feys, D. & Khayat, K.H. (2017). Particle migration during concrete rheometry: How bad is it?. *Materials and Structures*, *50*(2), p.122.

Feys, D., Cepuritis, R., Jacobsen, S., Lesage, K., Secrieru, E. & Yahia, A. (2018). Measuring rheological properties of cement pastes: most common techniques, procedures and challenges. *Rilem Technical Letters*, *2*, 129-135.

Feys, D., De Schutter, G., Khayat, K.H. & Verhoeven, R. (2016). Changes in rheology of self-consolidating concrete induced by pumping. *Materials and Structures*, *49*(11), 4657-4677.

Feys, D., Heirman, G., De Schutter, G., Verhoeven, R., Vandewalle, L., & Van Gemert, D. (2007). Comparison of two concrete rheometers for shear thickening behaviour of SCC. *Proc 5th Int RILEM Symp SCC*, Ghent, 365–370.

Feys, D., Khayat, K.H., Perez-Schell, A. and Khatib, R. (2014). Development of a tribometer to characterize lubrication layer properties of self-consolidating concrete. *Cement and Concrete Composites*, *54*, 40-52.

Feys, D., Verhoeven, R., & De Schutter, G. (2008). Fresh self compacting concrete: a shear thickening material. *Cement Concrete Research, 38*, 920–929.

Feys, D., Wallevik, J.E., Yahia, A., Khayat, K.H., & Wallevik, O.H. (2013). Extension of the Reiner–Riwlin equation to determine modified Bingham parameters measured in coaxial cylinders rheometers. *Mat. Struct. 46*, 289-311.

Flatt, R.J. (2004). Towards a prediction of superplasticized concrete rheology. *Materials and Structures*, *37*(5), 289–300.

Flatt, R.J., & Bowen, P. (2006). Yodel: A yield stress model for suspensions. *Journal of the American Ceramic Society*, *89*(4), 1244–1256.

Flatt, R.J., & Bowen, P. (2007). Yield stress of multimodal powder suspensions: An extension of the YODEL (yield stress model). *J. Am. Ceram. Soc., 90*(4), 1038–1044.

Flatt, R.J., & Houst, Y. (2011). A simplified view on chemical effects perturbing the action of superplasticizers. *Cement and Concrete Research, 31*, 1169–1176

Flatt, R.J., & Schober, I. (2012). Superplasticizers and the rheology of concrete: In: Understanding the rheology of concrete. Ed: Roussel N, Woodhead Publishing Ltd, Oxford.

Flatt, R.J., Bowen, P., Houst, Y.F., & Hofmann, H. (2003). Modelling interparticle forces and yield stress of cement suspensions. *Proceedings of the 11th International Congress on the Chemistry of Cement (ICCC)* , Durban, South Africa.

Fuji, K., & Kondo, R. (1974). Kinetics of the Hydration of Tricalcium Silicate, J. *Am. Ceram. Soc.*, *57*(11), 492

Gadala-Maria, F., & Acrivos, A. (1980). Shear-induced structure in a concentrated suspension of solid spheres. *J Rheol*. *24*, 799–814.

Gadala‐Maria, F., & Acrivos, A.1(980). Shear‐Induced Structure in a Concentrated Suspension of Solid Spheres. *Journal of Rheology*, *24*(6), 799-814.

Geiker, M.R., Brandl, M., Thrane, L.N., & Nielsen, L.F. (2002). On the effect of coarse aggregate fraction and shape on the rheological properties of self-compacting concrete. *Cem. Concr. Aggr. 24*, 3–6.

Gettu, R., Shareef, S.N., & Ernest, K.J.D. (2009). Evaluation of the robustness of SCC. *The Indian Concrete Journal, 83*(6), 13-19.

Glasser, F.P., & Marinko, M.B. (1984). *Proc. Brit. Ceram. Soc*., 35, 221-227.

Golaszewski, J., & Szwabowski, J. (2004). Influence of superplasticizers on rheological behavior of fresh cement mortars. *Cement and Concrete Research*,*34*(2), 235–248.

Haldenwang, R., & Fester, V.G. (2011). The influence of different superplasticisers on the flowability and reproducibility of a SCC mix. In *Proc. of at the 9th Int. Symp. on High Performance Concrete*, Rotorua, New Zealand.

Hampton, R.E., Mammoli, A.A., Graham A.L., & Tetlow, N. (1997) Migration of particles undergoing pressure-driven flow in a circular conduit. *J Rheol*. *41*, 621–40.

Han, D., & Ferron, R.D. (2015). Effect of mixing method on microstructure and rheology of cement paste. *Construction and Building Materials*, *93*, 278-288.

Han, S., Yan, P.Y., & Kong, X.M. (2011). Study on the compatibility of cement-superplasticizer system based on the amount of free solution. *Science China Technological Sciences*, *54*(1), 183–189.

Hanehara, S., Yamada, K. (1999). Interaction between cement and chemical admixtures from the points of cement hydration, admixture adsorption and paste rheology. *Cement and Concrete Research*, *29*(8), 1158-1165.

Hanna, E., Lake, K., Perraton, D., Aitcin, P.C. (1989). Rheological behavior of Portland cement paste in the presence of a superplasticizer. *ACI SP-119:* V.M. Malhotra (Ed.), *3rd International Conference on Superplasticizers and other Chemicals Admixtures in Concrete*, ACI, Ottawa 171 – 188.

Hanna, E., Lake, K., Perraton, D., & Aitcin, P.C. (1989). Rheological behavior of Portland cement paste in the presence of a superplasticizer. *Proc. 3rd International Conference on Superplasticizers and other Chemicals Admixtures in Concrete*, ACI SP 119, Ottawa, pp. 171–188.

Hattori, K. & Izumi, K. (1990). A New Viscosity Equation for Non-Newtonian Suspensions and Its Application, Rheology of Fresh Cement and Concrete. In *Proceedings of The International Conference Organized by The British Society of Rheology, University of Liverpool*.

Heikal, M., Morsy, M.S., & Aiad, I. (2005). Effect of treatment temperature on the early hydration characteristics of superplasticized silica fume blended cement pastes. *Cement and Concrete Research*, *35*(4), 680–687.

Hidalgo, J., Chen, C.T., Struble L.J. (2008). Correlation between paste and concrete flow behavior. *ACI Mat. J. 105*(3), 281-288.

Hiemenz, P.C., & Rajagopalan, R. (1997) *Principles of Colloid and Surface Chemistry.* 3rd ed., (New York: Marcel Dekker Press).

Hous,t Y.F., Flatt, R.J., Bowen, P., Hofmann, H., Mäder , U., Widmer, J., Sulser, U., Bürge, T.A., & Sika, A.G. (1999). Influence of Superplasticizer Adsorption on the Rheology of Cement Paste. *Proceedings of the International Conference, The Role of Chemical Admixtures in high Performance Concrete,* Monterrey, Mexico, 387-402.

Hsu, K.C., Chiu, J.J., Chen, S.D., & Tseng, Y.C. (1999). Effect of Addition Time of a Superplasticizer on Cement Adsorption and on Concrete Workability. *Cem. Concr. Comp. 21*(5-6), 425-430.

Hunter, R.J. (1981) *Zeta Potential in Colloid Science* (London: Academic Press).

Jarny, S., Roussel, N., Rodts, S., Bertrand, F., Le Roy, R. and Coussot, P. (2005). Rheological behavior of cement pastes from MRI velocimetry. *Cement and Concrete Research*, *35*(10), 1873-1881.

Jawed, L., Skalny, J., & Young, J.F. (1983). In: Barnes, P. (eds.) *Structure and Performance of Cements*, chapter 6 p. 250. (London: Applied Science Publication).

Jolicoeur, C., & Simard, M.A. (1998). Chemical admixture-cement interactions: Phenomenology and physico-chemical concepts. *Cement and Concrete Composites*, *20*(2), 87–101.

Jolicoeur, C., Sharman, J., Otis, N., Lebel, A., Simard, M.A., & Page, M. (1997). The influence of temperature on the rheological properties of super- plasticized cement pastes. *5th International Conference on Super- plasticizer and other Chemical Admixtures in Concrete*, Rome, 379–406.

Jones, T.E.R., & Taylor, S.A. (1977). Mathematical model for the flow curve of cement paste. *Magazine of Concrete Research*, *29*(101), 207-212.

Kaplan, D., de Larrard, F. & Sedran, T. (2005). Design of concrete pumping circuit. *Materials Journal*, *102*(2), 110-117.

Khayat, K.H. (1999). Workability, Testing, and Performance of Self-Consolidating Concrete. *ACI Mat. J.* 96-3, 346-353.

Khayat, K.H., (1998). Viscosity-enhancing admixtures for cement-based materials—an overview. Cement and Concrete Composites, 20(2-3), 171-188.

Khayat, K.H., Manai, K., & Trudel, A. (1997). In Situ Mechanical Properties of Wall Elements Cast Using Self-Consolidating Concrete. *ACI Mat. J. 94*(6), 491-500.

Kim, B.G., Jiang, S., Jolicoeur, C., & Aitcin, P.C. (2000). The adsorption behavior of PNS superplasticizer and its relation to fluidity of cement paste. *Cement and Concrete Research*, *30*(6), 887–893.

Kim, S., & Karrila, S.J. (1991). *Microhydrodynamics: Principles and Selected Applications* (Stoneham, MA: Butterworth-Heinemann).

Kong, X., Zhang, Y., & Hou, S. (2013). Study on the rheological properties of portland cement pastes with polycarboxylate superplasticizers. *Rheol. Acta*, *52*(7), 707–718.

Kreppelt, F., Weibel, M., Zampini, D., & Romer, M. (2002). Influence of solution chemistry on the hydration of polished clinker surfaces—A study of different types of polycarboxylic acid-based admixtures. *Cem. Concr. Res.*, *32*(2), 187–198.

Krieger, I.M. (1972). Rheology of monodisperse lattices. *Adv Colloid Interface Science, 3*(2), 111-136.

Kubens, S. (2010). Interaction of cement and admixtures and its effect on rheological properties, PhD dissertation, Bauhaus-Universität Weimar – Reykjavik University, Götingen - Reykjavik.

Kurdowski, W. (2014). *Cement and Concrete Chemistry*. 699p., Springer.

Kurdowski, W., Nocuń, W., Miśkiewicz, K., & Szuba, J. (1986). *8th ICCC Rio de Janeiro*, vol. III, p. 179. Rio de Janeiro.

Kuroiwa, S., Matsuoka, Y., Hayakawa, M., & Shindoh, T. (1993). Application of Super Workable Concrete to Construction of a 20-Story Building. In ACI SP-140: High Performance Concrete in Severe Environments, Zia P, Ed., Detroit, MI: American Concrete Institute, 147-161.

Kwan, A.K.H., & Ng, I.Y.T. (2009). Optimum superplasticiser dosage and aggregate proportions for SCC, *Mag. Conc. Res. 61*(4), 281-292.

Kwan, A.K.H., Ng, I.Y.T. (2010). Improving performance and robustness of SCC by adding supplementary cementitious materials. *Constr. Build. Mat. 24*, 2260–2266.

Ladd A.J.C. (1994). Numerical simulations of particulate suspensions via a discretized Boltzmann equation: 2. Numerical results. *J Fluid Mech*., 271, 311–39.

Laun, H.M. (1984) Rheological properties of aqueous polymer dispersions. *Angew Makro-mol Chem.123*(1), 335–59.

Le, H.D., Kadri, E.H., Aggoun, S., Vierendeels, J., Troch, P. & De Schutter, G. (2015). Effect of lubrication layer on velocity profile of concrete in a pumping pipe. *Materials and Structures*, *48*(12), 3991-4003.

Leemann, A., & Winnefeld, F.,(2007). The effect of viscosity modifying agents on mortar and concrete. *Cem. Conc. Comp. 29*(5), 341-349.

Lei, L., & Plank, J. (2011). Synthesis, working mechanism and effectiveness of a novel cycloaliphatic superplasticizer for concrete. *Cement and Concrete Research*, *42*(1),118–123.

Leighton, D., & Acrivos, A. (1987). The shear-induced migration of particles in concentrated suspensions. *J Fluid Mech. 181*, 415–39.

Li, L.G., Kwan, A.K.H. (2013). Concrete mix design based on water film thickness and paste film thickness. *Cem. Conc. Comp. 39*(5), 33-42.

Lowke, D., Schiessl, P. (2005). Effect of mixing energy on fresh properties of SCC. *2th North American Conference on the Design and Use of Self-consolidating Concrete / 4th International RILEM Symposium on Self-Compacting Concrete*, Chicago, IL, USA.

Lyon, M.K., & Leal, L.G. (1998). An experimental study of the motion of concentrated suspensions in two-dimensional channel flow: 1. Monodisperse systems. *J Fluid Mech. 363*, 25–56.

Macosko, C.W. (1994). *Rheology Principles, Measurements and Applications.* (NewYork: Wiley-VCH Press).

Mahaut, F., Mokéddem, S., Chateau, X., Roussel, R., & Ovarlez, G. (2008). Effect of coarse particle volume fraction on the yield stress and thixotropy of cementitious materials. *Cement and Concrete Research*,*38*(11), 1276–1285.

Maranzano B.J., & Wagner, N.J.(2000) Thermodynamic properties and rheology of sterically stabilized colloidal dispersions. *Rheol Acta*.,*39*(5), 483–94.

Maranzano, B.J., & Wagner, N.J. (2001). The effects of particle-size on reversible shear thickening of concentrated colloidal dispersions. *J Chem Phys. 114*(23), 10514–27.

Martys, N.S(2005). Study of a dissipative particle dynamics based approach for modeling suspensions. *J Rheol.*, *49*(2), 401–24.

Matas, J.P., Morris, J.F., & Guazzelli, E. (2004) Inertial migration of rigid spherical particles in Poiseuille flow. *J Fluid Mech. 515*, 171–95.

Ménétrier, D., Jawed, I., Sun, T.S., & Skalny, J. (1979). *Cement and Concrete Research*,*9*, 473-482

Meng, W., Lunkad, P., Kumar, A., & Khayat, K. (2016). Influence of Silica Fume and Polycarboxylate Ether Dispersant on Hydration Mechanisms of Cement. *The Journal of Physical Chemistry C*, *120*(47), 26814-26823.

Mewis, J. & Wagner, N.J. (2012). *Colloidal suspension rheology*. Cambridge University Press.

Mewis, J., & Wagner, N.J. (2012). *Colloidal Suspension Rheology*. (Cambridge: Cambridge University Press).

Mohan K., & Taylor H.F.W. (1981). Paste of Iricalcium silicate with fly ash analytical electron microscopy, trimethylsilitation and other studies, Effect of fly ash incorporation in cement and concrete. *Proceedings of Annual Meeting of the Materials Research Society,* Boston, MA.

Nachbaur, L., Mutin, J.C., Nonat, A. and Choplin, L. (2001). Dynamic mode rheology of cement and tricalcium silicate pastes from mixing to setting. *Cement and Concrete Research*, *31*(2), 183-192.

Naji, S., Hwang, S.D., & Khayat, K.H. (2011). Robustness of self-consolidating concrete incorporating different viscosity-enhancing admixtures. *ACI Materials Journal*, *108*(4), 432-438.

Neville, A.M. (1995). *Properties of concrete* (Vol. 5). London: Pearson.

Nguyen, N.Q., & Ladd, A.J.C. (2005). Sedimentation of hard-sphere suspensions at low Reynolds number. *J Fluid Mech*. 525, 73–104.

Nunes, S., Figueiras, H., Oliveira, P.M., Coutinho, J.S., & Figueiras, J. (2006). A Methodology to Assess Robustness of SCC Mixtures. *Cement and Concrete Research*, *36*, 2115-2122.

Nunes, S., Oliveira, P.M., Coutinho, J.S., & Figueiras, J. (2011). Rheological characterization of SCC mortars and pastes with changes induced by cement delivery. *Cem. Conc. Comp. 33*(1), 103-115.

Oertel, T., Hutter, F., Tänzer, R., Helbig, U. and Sextl, G. (2013). Primary particle size and agglomerate size effects of amorphous silica in ultra-high performance concrete. *Cement and Concrete Composites*, *37*, 61-67.

Okamura, H., & Ouchi, M. (2003). Self-compacting concrete, *J. of Advance Concrete Technology*, *1*, 5-15.

Ovarlez, G., Bertrand, F., & Rodts, S. (2006). Local determination of the constitutive law of a dense suspension of non colloidal particles through magnetic resonance imaging. *J Rheol*. *50*(3), 259–92.

Perrin, J. (1916). Atoms, translated by Hammick D.L., Van Nostrand, New York.

Petit, J.Y., Khayat, K.H. and Wirquin, E. (2009). Coupled effect of time and temperature on variations of plastic viscosity of highly flowable mortar. *Cement and Concrete Research*, *39*(3),165-170.

Petit, J.Y., Khayat, K.H., & Wirquin, E. (2006). Coupled effect of time and temperature on variations of yield value of highly flowable mortar. *Cement and Concrete Research*, *36*, 832–841.

Petit, J.Y., Wirquin, E., & Duthoit, B. (2005). Influence of temperature on yield value of highly flowable micromortars made with sulfonate-based superplasticizers. *Cement and Concrete Research*, *35*(2), 256-266.

Phillips, R.J., Armstrong, R.C., Brown, R.A., Graham, A.L. & Abbott, J.R. (1992). A constitutive equation for concentrated suspensions that accounts for shear‐induced particle migration. *Physics of Fluids A: Fluid Dynamics*, *4*(1),30-40.

Phyfferoen, A., Monty, H., Skags, B., Sakata, N., Yanai, S., & Yoshizaki, M. (2002). Evaluation of the biopolymer, diutan gum, for use in self-compacting concrete. In *Proc. of the 1st North American Conference on the Design and Use of Self-Consolidating Concrete*, Evanston, IL, USA.

Plank, J., & Hirsch, C. (2007). Impact of ζ-potential of Early Cement Hydration Phases on Superplasticizer Adsorption. *Cement and Concrete Research*, *37*(4), 537-542.

Plank, J., & Hirsch, C. (2007). Impact of zeta potential of early cement hydration phases on superplasticizer adsorption. *Cement and Concrete Research*, *37*(4), 537-542.

Plank, J., Schroefl, C., Gruber, M., Lesti, M. and Sieber, R. (2009). Effectiveness of polycarboxylate superplasticizers in ultra-high strength concrete: the importance of PCE compatibility with silica fume. *Journal of Advanced Concrete Technology*, *7*(1), 5-12.

Plowman C., & Cabrera J.G. (1981) The hydration reaction of calcium aluminate, *In Proceedings of Cement and Concrete Symposium*, Annual Meeting, 71–81.

Pöllmann H., & Stöber S. (1997). *10th ICCC Goeteborg,* vol. III, p. 3iii032. Goeteborg.

Pöllmann H. (1989). 11th Conf. on Cement Microscopy, New Orleans, 286-291.

Ramachandran V.S. (1973). Action of triethanolamine on the hydration of tricalcium aluminate. *Cement and Concrete Research*,*3*(1), 41-54.

Ramachandran, A., & Leighton, D.T. (2007) Viscous resuspension in a tube: The impact of secondary flows resulting from second normal stress differences. *Phys Fluids*. *19*(5), 053301.

Reiner, M. (1949). Deformation and flow. An elementary introduction to theoretical rheology. H.K. Lewis & Co, Limited, Great Britain.

Ridi, F., Fratini, E., Luciani, P., Winnefeld, F. and Baglioni, P. (2012). Tricalcium silicate hydration reaction in the presence of comb-shaped superplasticizers: boundary nucleation and growth model applied to polymer-modified pastes. *The Journal of Physical Chemistry C*, *116*(20), 10887-10895.

Rigueira, J.W., García-Taengua, E., & Serna-Ros, P. (2009). Self-Consolidating Concrete in Continuous Production Regarding Fresh and Hardened State Properties. *ACI Materials Journal*, *106*(3), 301-307.

Roussel, N., 2006. A thixotropy model for fresh fluid concretes: theory, validation and applications. *Cement and Concrete Research*, *36*(10), pp.1797-1806.

Roussel, N. (2012). *Understanding the rheology of concrete*. Woodhead Publishing, Cambridge.

Roussel, N., Le Roy, R. & Coussot, P. (2004). Thixotropy modelling at local and macroscopic scales. *Journal of non-newtonian fluid mechanics*. *117*(2), 85-95.

Roussel, N., Ovarlez, G., Garrault, S., & Brumaud, C. (2012). The origins of thixotropy of fresh cement pastes, *Cement and Concrete Research*. *42*(1), 148-57.

Roy, D.M., & Asaga, K. (1979). Rheological properties of cement mixes: III The effects of mixing procedures on viscometric properties of mixes containing superplasticizers, *Cement and Concrete Research*, *9*, 731-739.

Rubio-Hernández, F.J., Velázquez-Navarro, J.F., & Ordonez-Belloc, L.M. (2013). Rheology of concrete: A study case based upon the use of the concrete equivalent mortar. *Materials and Structures*, *46*(4), 587–605.

Sahmaran, M., Yurtseven, A., Yaman, I.O. (2005). Workability of hybrid fiber reinforced self-compacting concrete, *Building and Environment*, *40*(12), 1672–1677.

Sakai, E., Yamada, K., & Ohta, A. (2003). Molecular structure and dispersion-adsorption mechanisms of comb-type superplasticizers used in Japan. *J. of Advanced Concrete Technology*, *1*(1), 16-25.

Sakata, N., Yanai, S., Yoshizaki, M., Phyfferoen, A., & Monty, H. (2001). Evaluation of S-657 Biopolymer as a new viscosity-modifying admixture for self-compacting concrete. *presented at the Second International Symposium on Self-Compacting Concrete*, Tokyo, Japan.

Schiessl, P., Mazanec, O., & Lowke, D. (2007). SCC and UHPC - Effect of mixing technology on fresh concrete properties. *Advances in Construction Materials*, Ed: Grosse CU, Heidelberg, Germany, 513-522.

Scott G.D., & Kilgour, D.M. (1969) The density of random close packing of spheres. *Brit J Appl Phys*. *2*, 863–6.

Segree, G., & Silberberg, A. (1962) Behaviour of macroscopic rigid spheres in Poiseuilled interpretation. *J Fluid Mech*. *14*, 136-57.

Shapiro, A.H., & Probstein, R.F. (1992) Random packings of spheres and fluidity limits of monodisperse and bidisperse suspensions. *Phys Rev Lett*. *68*(9) 1422–5.

Shapley, N.C., Armstrong, R.C., & Brown, R.A. (2002). Laser Doppler velocimetry measurements of particle velocity fluctuations in a concentrated suspension. *J Rheol., 46*(1), 241–72.

Sheinn, A.M., Ho, D.W., & Tam, C.T. (2002). Rheological model for self-compacting concrete-paste rheology. *Proc. 27th Conf. on Our World in Concrete and Structures*, CI-Premier, Singapore.

Sierou, A., & Brady, J.F. (2011) Accelerated Stokesian dynamic simulations. *J Fluid Mech. 448*, 115–46.

Sierou, A., & Brady, J.F. (2002). Rheology and microstructure in concentrated noncolloidal suspensions. *J Rheol. 46*(5), 1031–56.

Simard, M.A., Nkinamubanzi, P.C., & Jolicoeur, C. (1993). Calorimetry, rheology, and compressive strength of superplasticized cement pastes. *Cement and Concrete Research*, *23*, 939–950.

Sinton S.W., & Chow, A.W. (1991) NMR flow imaging of fluids and solid suspension sin Poiseuille flow. *J Rheol. 35*, 735–72.

Skalny J., & Young J.F. (1980) Mechanism of Portland cement hydration. In *Proceedings of 7th International Congress on the Chemistry of Cement*, Paris, France, Editions Septima, Paris, France, Vol. 1, Sub-Themeil, 1–45.

Stein, H.N., & Stevels, J.M. (1964). Influence of silica on the hydration of $3CaO.SoO_2$. *J. Appl. Chem., 14*, 338–346.

Stöber S., & Pöllmann H. (1999). Synthesis of a lamellar calcium aluminate hydrate (AFm phase) containing benzenesulfonic acid ions. *Cement and Concrete Research*,*29*(11), 1841-1845.

Struble, L., & Sun, G.K. (1995). Viscosity of Portland cement paste as a function of concentration. *Advances in Cement Based Materials*, *2*(2), 62–69.

Takemoto K., & Uchikawa H. (1980) Hydration of pozzolanic cement. In *Proceedings of 7th International Congress on the Chemistry of Cement*, Paris, France, Editions Septima, Paris, France, Sub-Theme IV-2, 1–28.

Tattersall, G.H., & Banfill, P.F. (1983). *The rheology of fresh concrete,* London: Pitman.

Tattersall, G.H. (1955). Structural breakdown of cement pastes at constant rate of shear. *Nature*, *175*(4447),166-166.

Tetlow, N., Graham, M.S., Ingber *et al.* (1998). Particle migration in a Couette apparatus: Experiment and modeling. *J Rheol.*, *42*, 307–27.

Torquato, S., Truskett, T.M., & Debenedetti, P.G. (2000) Is random close packing of spheres well defined? *Phys Rev Lett. 84*(10), 2064–7.

Toutou, Z., & Roussel, R. (2006). Multi scale experimental study of concrete rheology: from water scale to gravel scale. *Mat. Struct. 37*, 167–176.

Uchikawa, H., Sawaki, D., Hanehara, S. (1995). Influence of kind and added timing of organic admixture on the composition, structure and property of fresh cement pastes. *Cement and Concrete Research*, *25*, 353–364.

Verwey, E.J.W., & Overbeek, J.T.G. (1984). *Theory of the Stability of Lyophobic Colloids*, (Amsterdam: Elsevier Press).

Wallevik, J.E. (2003). Rh*eology of particle suspensions, Fresh concrete, mortar and cement paste with various types of lignosulfonates*. Ph-D dissertation, the Norwegian University of Science and Technology, Trondheim.

Wallevik, J.E. (2009). Rheological properties of cement paste: Thixotropic behavior and structural breakdown. *Cement and Concrete Research*, *39*, 14–29.

Wallevik, O.H., & Wallevik, J.E. (2011). Rheology as a tool in concrete science: The use of rheographs and workability boxes. *Cement and Concrete Research*,41, 1279-1288.

Wallevik, O.H., Feys, D., Wallevik, J.E. and Khayat, K.H. (2015). Avoiding inaccurate interpretations of rheological measurements for cement-based materials. *Cement and Concrete Research*, *78*,100-109.

Wallevik, O.H., Kubens, S., Müller, F. (2007). Influence of cement-admixture interaction on the stability of production properties of SCC. In *Proc. of the 5th Int. RILEM Symp. on Self-Compacting Concrete*, Ghent, Belgium.

Williamson, R.V. (1931). Some unusual properties of colloidal dispersions. *J Phys* Chem. 35(1), 354–9.

Yahia, A. & Khayat, K.H. (2001). Analytical models for estimating yield stress of high-performance pseudoplastic grout. *Cement and Concrete Research*, *31*(5), 731-738.

Yamada, K., & Hanehara, S. (2001). Interaction mechanism of cement and superplasticizers - The roles of polymer adsorption and ionic conditions of aqueous phase. *Concrete Science and Engineering, 3*(11), 135- 145.

Yamada, K., Hanehara, S., & Honma, K. (1998). The effect of naphthalene sulfonate type and polycarboxylate type superplasticizers on the fluidity of belite-rich cement. *Proceeding of Self-Compacting Concrete Workshop*, Kochi, 201 – 210.

Yamada, K., Ogawa, S., & Hanehara, S. (2000). Influence of Silica Fume/Fly Ash/Superplasticizer Combinations in Powder-Like Complex Modifiers on Cement Paste Porosity and Concrete Properties, *Proc. 6th CANMET/ACI International Conference on Superplasticizers and Other Chemical Admixtures in Concrete,* ACI SP 195, Nice, p. 367.

Yamada, K., Ogawa, S., & Hanehara, S. (2001). Controlling of the adsorption and dispersing force of polycarboxylate-type superplasticizer by sulfate ion concentration in aqueous phase. *Cement and Concrete Research*, *31*(3), 375-383.

Yamada, K., Ogawa, S., & Takahashi, T. (2001). Improvement of the compatibility between cement and superplasticizer by optimizing the chemical structure of the polycarboxylate-typ superplasticizer. In *Proc. of the 2nd Int. Symp. on Self-Compacting Concrete*, Tokyo, Japan.

Yammine, J., Chaouche, M., Guerinet, M., Moranville, M. & Roussel, N. (2008). From ordinary rhelogy concrete to self compacting concrete: A transition between frictional and hydrodynamic interactions. *Cement and Concrete Research*, *38*(7), 890-896.

Yoshioka, K., Sakai, E., Daimon, M., & Kitahara, A. (1997). Role of steric hindrance in the performance of superplasticizers for concrete. *J. of the American Ceramic Society*, *80*(10), 2667-2671.

Yurugi, M., Sakai, G., &Sakata, N. (1995). Viscosity Agent and Mineral Admixtures for Highly Fluidized Concrete. *Proceedings, Concrete under Severe Conditions, Environmental and Loading*, 995-1004.

Zhang, Y., Kong, X., Lu, Z., Hou, S. (2015). Effects of the charge characteristics of polycarboxylate superplasticizers on the adsorption and the retardation in cement pastes. *Cement and Concrete Research*, 67, 184–196.

Zingg, A., Winnefeld, F., Holzer, L., Pakusch, J., Becker, S., & Gauckler, L. (2008). Adsorption of polyelectrolytes and its influence on the rheology, zeta potential, and microstructure of various cement and hydrate phases. *Journal of Colloid Interface Science*, *323*(2), 301–312.

VITA

Azadehalsadat Asghari was born in Babolsar, IRAN in 1982. She received her bachelor in Civil Engineering and master's degree in Structural Engineering both with distinction from University of Mazandaran - IRAN in 2005 and 2009 respectively. She started her graduate studies with research focused on the shear strength of RC deep beams in September 2006. She published her masters' research titled "Evaluation of shear behavior in RC deep made of lightweight concrete strengthened with FRP" in different Journals and international conferences.

She worked as a lecturer at the Azad University of Mahmud Abad, College of Engineering, civil department. During her career, she taught several classes and coached her students to different concrete competitions like ACI.

In 2013, she got a scholarship to complete her PhD in Missouri University of Science and Technology and started her Ph.D. program in Civil Engineering. Her research focused on the "Sensitivity of Rheological Properties of Cement Pastes with SCC Consistency". She published several papers in Elsevier such as Construction & Building Materials and ACI journal and presented her research in different conferences. She received her PhD in Civil Engineering from Missouri University of Science and Technology in December 2018.