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1 **Recent advances on yield stress and elasticity of fresh cement-**
2 **based materials.**

3
4 Roussel, N.¹, Bessaies-Bey¹, H, Kawashima, S.², Marchon; D.³, Vasilic, K.⁴, Wolfs, R.⁵

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6 ¹ IFSTTAR, East Paris University, France

7 ² Department of Civil Engineering and Engineering Mechanics, Columbia University, New
8 York, NY, United States

9 ³ Department of Civil and Environmental Engineering, University of California, Berkeley,
10 CA, United States.

11 ⁴ German Society for Concrete and Construction Technology (DBV), Berlin, Germany.

12 ⁵ Department of the Built Environment, Eindhoven University of Technology, Eindhoven,
13 The Netherlands.

14

15 **Abstract**

16 The interest in the elastic and yielding properties of fresh cement-based materials has
17 recently grown due to the development of new processing techniques, which avoid the
18 use of standard formworks. Without support, the material shaping relies only on the
19 mechanical properties of the fresh material. Within this frame, the point of this paper is
20 to gather the accepted knowledge along with the most recent advances on both yield
21 stress and elasticity of fresh cement- base materials. In the first part, we will go through
22 the physical and chemical origin of these macroscopic properties and their evolutions. In
23 the second part, we will describe the way they can be measured while the third part will
24 deal with the way they can be controlled and tuned. Finally, the most recent models for
25 both properties prediction from mix design and processing modeling from rheological
26 measurements will be described.

27

1 1. Introduction

2 The rheological behavior of fresh cement-based materials has been an important field of
3 research for decades. It has, however, over the years primarily focused on the way fresh
4 cement based materials flow. As concrete, mortar or grouts processing mostly involves
5 sub-processes such as mixing, pumping, spraying and pouring, non-Newtonian **fluids**
6 mechanics was considered to be the sub-field of mechanical sciences that could improve
7 our understanding of fresh cement-based materials processing.

8 The elasto-plastic behavior and the material ductility were therefore features that were
9 considered to belong to the set of mechanical properties that only hardened concrete
10 was concerned with and fresh cement-based materials were classified as non-
11 Newtonian granular fluids.

12 It is interesting enough to note that beginning of setting was, within this frame,
13 historically defined as the time required for the material to display an elastic modulus. It
14 was however shown that fresh cement-based materials do display an elastic behavior
15 for observations times as short as a few seconds after the end of mixing (L. Nachbauch
16 et al., 2001) (N. Roussel et al., 2012). After such short time scales, the percolated
17 network of interacting particles indeed display an elastic modulus of the order of several
18 hundreds of Pa and a strength of the order of a few tens of Pa. 28 days and an extremely
19 complex hydration reaction later, this strength has turned into several tens of MPa. As a
20 force sensor able to measure a strength variation over 6 orders of magnitude does not
21 exist, beginning of setting was therefore defined as the time required for the material to
22 display an elastic modulus that was measurable using a standard concrete compression
23 testing machine (*i.e.* unable to measure the low values of elastic modulus and strength
24 typical of fresh materials). This contributed into strengthening the idea that fresh-
25 cement based materials were pasty fluids with neglectable elasticity.

26 It has however to be acknowledged that, until recently, the knowledge of the elastic
27 behavior of fresh cement-based materials was of little interest as they were supposed to
28 flow from the mixer to the formwork, fill it properly under the sole effect of gravity and
29 set. In order to ensure that the material properly fills the formwork along with the

1 centimetric porosity between the reinforcing steel bars, high energy vibrating pokers
2 (vibration amplitude of the order of a couple mms for frequencies of the order of couple
3 hundreds Hz) were used to apply accelerations roughly ten times higher than the natural
4 gravity acceleration to the fresh material. At such a level of stress, any interactions or
5 elastic inter-particle network is destroyed and the material behaves indeed as a non-
6 Newtonian liquid.

7 Only recently, with the increased industrial use of extremely fluid cement-based
8 materials such as self-compacting or self-leveling mortars, concretes or floor screeds,
9 elasticity and yield stress started to matter. Without vibration, the filling degree or the
10 shape conformity was shown to depend on the competition between gravity and yield
11 stress (N. Roussel, 2007a) whereas some features such as pressure formwork were
12 related to the elasticity and structuration (*i.e.* the increase in elastic modulus or yield
13 stress with resting time) of the fresh material (P. Billberg, 2003), (G. Orvarlez et al.,
14 2007).

15 Even more recently, the development of 3D printing technologies for and by the
16 concrete industry stressed the need for a better assessment and understanding of the
17 elastic and yield properties of fresh cement-based materials. Most 3D printing
18 applications and demonstrators are based on extrusion, where a cement-based material
19 is extruded to form sequential layers via a digitally controlled nozzle mounted on a
20 robot arm, gantry or crane. The processes are similar to conventional Additive
21 Manufacturing processes except that the material and scale of manufacture generate
22 unique challenges and questions: the formulation of mixes that are pumpable, yet stable
23 in shape once placed without formwork; the production of reliable interlayer bonding;
24 and how to control the geometry of printed parts within appropriate geometrical
25 tolerances. All these questions relate to the yield stress and elasticity of fresh cement-
26 based materials.

27 Within such a frame, the point of this paper is to gather the accepted knowledge along
28 with the most recent advances on these features. In the first part, we will go through
29 the physical and chemical origin of these macroscopic properties in the fresh state and

1 their evolutions. In the second part, we will describe the way they can be measured
2 while the third part will deal with the way they can be controlled and tuned. Finally, the
3 most recent models for both properties prediction from mix design and process
4 modeling from rheological measurements will be described.

6 **2. Yield stress and elasticity in fresh cement-based materials: physical origin**

7 **2.1. Brownian motion, Van der Waals forces and buoyancy**

8 It is now accepted that the dominant interactions in a fresh cement paste are the
9 following: colloidal attractive forces, gravity forces and Brownian effects (N. Roussel et
10 al., 2010). Hydrodynamic forces (including laminar viscous dissipation, particle kinetic
11 energy and lubrication) only occurs when the system is sheared and flows. Note that,
12 once mixing is over and the interstitial fluid is forming a continuous phase, capillary
13 forces in cement-based systems can be neglected.

14 The main competition in the system at rest involves therefore colloidal attractive forces,
15 Brownian motion and gravity forces. This competition was reported to result in one of
16 the following regimes (A. Perrot et al., 2012):

17 If **colloidal attractive forces dominate Brownian motion**, which is the case for most
18 cementitious materials in industry, a percolated network of interacting particles appears
19 within the suspension. It is able to withstand an external stress up to a critical value
20 called yield stress. Because it originates from the attractive van der Waals forces (Flatt,
21 R.J. et al., 2004), this yield stress scales with the inverse power two of the inter-particle
22 separating distance and is therefore strongly dependent on the presence of adsorbed
23 polymers at pseudo-contact points between particles (see section 3). This percolated
24 interaction network has a rigidity, which dictates in turn the material elasticity
25 (Nachbauch et al., 2001); (W.G. Lei and L.J. Struble, 1997), (N. Roussel et al., 2012).

26 If **Brownian motion dominates colloidal attractive forces** (in the case of diluted systems
27 or systems at high admixture concentration (see section 3)), the suspension does not
28 have any yield stress. The network of attractive colloidal interactions is instantaneously
29 destroyed by Brownian agitation and is not able to withstand any external stress. In this

1 particular case, Brownian motion could dominate gravity forces. The result would be a
2 stable Newtonian viscous suspension. However, according to the order of magnitudes of
3 the two phenomena, this cannot happen in the case of typical cementitious materials.
4 Suspensions, in which Brownian motion dominates colloidal forces, shall therefore
5 always be unstable and display high levels of sedimentation (N. Roussel et al., 2010), (N.
6 Massoussi et al., 2017).

7 If **colloidal attractive forces dominate gravity forces**, particles are trapped in the
8 colloidal interactions network and are therefore not able to rearrange their relative
9 positions. The suspension is stable. There is neither bleeding nor sedimentation and the
10 fresh paste stays homogeneous.

11 If **gravity forces dominate colloidal attractive forces**, particles may settle. This induces a
12 relative displacement of the cement particles within the interstitial fluid or a relative
13 displacement of the interstitial fluid between the cement particles. This phenomenon
14 called “bleeding” in practice is time driven and is influenced by the viscosity of the
15 interstitial fluid and the permeability of the porous medium formed by the interacting
16 cement grains (which mainly depends on the solid volume fraction and on the average
17 diameter of the grains (Picandet et al., 2011)). It was shown recently that bleeding
18 relates to the formation of preferred water extraction channels resulting from a local
19 and partial rearrangement of the cement particles configuration (N. Massoussi et al.,
20 2017). As such, it is a heterogeneous process in contrast to the former approach in
21 literature describing bleeding as a homogeneous consolidation phenomenon (L.
22 Josserand et al., 2006). Within very specific conditions, bleeding may be adequately
23 limited by the above mix design factors. It is in this regime only that fluid cement pastes
24 allowing for the production of fluid concrete can be mix designed.

25

26 **2.2. Hydrates nucleation, thixotropy and structuration**

27 Casting of concrete occurs within the induction period, which is generally considered to
28 be a period of little chemical activity. However, there are still the effects of cement
29 hydration, where early hydrates form and subsequently impact the workability or

1 rheology of the fresh suspension. This has been more precisely tied to C-S-H nucleation
2 in both cement (Lei and Struble 1997) and tricalcium silicate (L. Nachbaur et al. 2001)
3 systems, and more recently supported by (N. Roussel et al. 2012) through a description
4 of structuration and thixotropy. In this latter study, the general behavior of fresh
5 cement-based systems at rest was described, and it is again presented here in Fig. 1
6 through yield stress evolution and a microstructural view of cement interaction and C-S-
7 H nucleation and growth. Immediately after mixing, the cement particles are in a
8 dispersed state, where the degree of dispersion is dependent on mixing energy (Fig. 1a).
9 Once at rest, the non-contact, colloidal interactions discussed in Sec 2.1 lead to early
10 (few sec) flocculation of the fresh suspension (Fig. 1b). From there, C-S-H nucleation
11 occurs and forms bridges between cement particles/flocs (Fig. 1c), and gives rise to an
12 increasingly interconnected, rigid structure through continued C-S-H nucleation and
13 growth (Fig. 1d). This structure underlies increase in yield stress (flow onset) and
14 elasticity over time.

15 Thixotropy – structural breakdown and build-up – is theoretically a completely
16 reversible phenomenon. However, this is not the case for cement-based materials due
17 to the continuous progression of hydration. Cement thixotropy arises from a
18 combination of general flocculation/deflocculation behavior, as well as
19 formation/breakage of C-S-H bridges (J.E. Wallevik 2009) (N. Roussel et al. 2012). If
20 there is sufficient shearing energy (i.e. mixing, pumping, casting), the aforementioned C-
21 S-H bridges can be broken down and flow can be restored. At the same time, some C-S-
22 H bridges will be irreversible under the given shearing conditions and a corresponding
23 level of structure will remain. Over time, the presence of irreversible C-S-H bridges will
24 increase (in size and frequency) (Jiang et al., 1995), (A. Nonat et al., 1997), which gives
25 rise to an increase in yield stress associated with flow onset.

26 Role of hydration on workability has been of practical significance for workability loss,
27 where mixing/shearing can no longer restore flowability. And thixotropy has been of
28 practical significance for select applications, e.g. SCC formwork pressure where it is now
29 well accepted that structural build-up behavior of the fresh SCC has a direct effect on

1 lateral pressure exerted on the formwork wall [G. Ovarlez and N. Roussel 2006), (J.
2 Assaad et al. 2003a), (J. Assaad et al. 2003b). More recently, the connection between
3 structural build-up behavior and C-S-H nucleation has been shown (T. Lecompte and A.
4 Perrot, 2017) (Ma et al., 2018), (D. Lowke 2018). The role of C-S-H nucleation on
5 structural build-up kinetics (both flow onset and elasticity) becomes critically more
6 important for AM, as recently summarized by (L. Reiter et al 2018). Short-term kinetics
7 are important in controlling material shape stability immediately after deposition, while
8 long-term kinetics (approaching setting) is important for determining building rate. It
9 has been shown that yield stress evolution goes from linear to nonlinear over longer
10 periods (A. Perrot et al., 2015), which has more recently been tied to increase in solid
11 volume fraction and decrease in packing fraction by C-S-H nucleation (T. Lecompte and
12 A. Perrot, 2017). This linear to non-linear yield stress evolution has been incorporated
13 into a theoretical framework to predict building rate for AM (A. Perrot et al., 2015). It
14 can finally be noted that the behavior of the material becomes closer to the one of a
15 brittle solid and further from the one of a plastic paste (Mettler et al., 2016).

16

17 **2.3. From cement paste to mortars and concretes**

18 Adding particles such as sand and/or coarse aggregates to a cement paste to produce a
19 mortar or a concrete can conceptually be considered as adding rigid inert non-Brownian
20 non-colloidal particles into a yield stress fluid as long as the typical size of the
21 constitutive elements of the paste (*i.e.* cement grains of average size of 10 micrometers)
22 can be neglected in front of the typical size of the particles (*i.e.* sand or coarse
23 aggregates of respective average size of 1 or 10 mm). In this specific case, the
24 rheological properties of the suspension shall depend only on the rheological properties
25 of the suspending fluid (as long as the presence of the particles do not affect it) and on
26 the particle volume fraction, shape and size distribution. With the aim of providing such
27 generic results, (F. Mahaut *et al.*, 2008a) have performed an experimental study on a
28 broad range of materials. They have suspended beads of various sizes and made of
29 various materials in very different pastes whose common point was to exhibit a yield

1 stress. They showed that the dimensionless yield stress of such mono-disperse
2 suspensions indeed relates to the particle volume fraction only. It should be noted that
3 this should apply to any homogeneous and isotropic suspension of particles in a yield
4 stress fluid as long as the particles have only mechanical interactions with the paste (*i.e.*
5 when there are no specific physicochemical interactions between the particles, and
6 between the particles and the paste). The same authors have moreover studied
7 suspensions of coarse spherical particles in a cement paste and demonstrated that they
8 behave exactly as any other suspension once all artifacts have been ruled out by
9 adequate experimental protocols (F. Mahaut *et al.*, 2008b). All the above studies
10 emphasize the fundamental role played by the packing properties of the inclusions
11 added to the cement paste (J. Yamine *et al.*, 2008).
12 From a thixotropy point of view, it was also shown that it is sufficient to know how the
13 interstitial cement paste evolves in time to predict the mortar or concrete evolution
14 (assuming there is no water absorption). As a consequence, if the mechanical impact of
15 the non-colloidal particles is to increase the yield stress by a given factor, then their
16 impact on the structuration rate of the paste is to increase by the same factor. It is thus
17 sufficient to measure the cement paste yield stress evolution in time and to measure
18 the increase of yield stress with volume fraction for a single resting time to infer the
19 value of the structuration rate of the mortar or concrete at any time (F. Mahaut *et al.*,
20 2008b).

21

22 **3. Yield stress and elasticity in fresh cement-based materials: measurements**

23 **3.1. Industrial test for yield stress measurements**

24 Regardless of the exact standards or geometry of slump, slump flow, L-Box or J-ring
25 tests, the following general procedure is common for these tests: a mold or reservoir of
26 a given standard shape or volume is filled with the cementitious material to be tested.
27 The material is poured, a mold is lifted or a gate is opened and flow occurs if the shear
28 stress generated by gravity inside the sample is higher than the yield stress of the
29 material. As the material is flowing, the thickness of the sample and, therefore, the

1 stress generated by gravity decrease. If the stress in the tested sample becomes lower
2 than the yield stress of the tested material, flow stops. The shape at stoppage is
3 therefore directly linked to the yield stress of the tested material if inertia or surface
4 tension effects can be neglected. Several correlations between the measured
5 geometrical quantities such as slump flow and slump and yield stress can be found in
6 literature (J. Murata, 1984), (N. Pashias et al., 1996), (Schowalter, 1998), (S. Clayton et
7 al., 2003), (A.W. Saak et al., 2004) (W.R. Schowalter and G. Christensen, 1998) (N.
8 Roussel and P. Coussot, 2005), (N. Roussel et al. 2005) (N. Roussel, 2006), (N. Roussel,
9 2007) (T.L.H. Nguyen et al., 2006).

10 11 **3.2. Rheometry: flow onset and critical strain measurements**

12 When the flow onset and critical strain of fresh cement-based materials are of interest,
13 a typical measurement consists of using a rheometer and applying a constant low shear
14 rate, starting from rest, and then observing the characteristic stress peak and critical
15 strain associated with flow onset. However, as these materials are thixotropic, their
16 rheological behavior depends on the flow history and their characterization requires a
17 rigorous procedure to ensure reproducibility. Before starting the measurement, the
18 suspension has to be pre-sheared to ensure that all tests start from the same destructed
19 state (D. Feys et al, 2017). Moreover, in order to study in detail the evolution of shear
20 stress over a large range of strains, a compromise must be reached between the
21 duration of the test and its accuracy.

22 A specific measurement protocol has been developed by (N. Roussel et al., 2012) for
23 cement suspensions. First, the sample is pre-sheared at 150 s^{-1} for 200s. After 5 minutes
24 of resting time, a constant shear rate of 0.005 s^{-1} is applied to the sample.

25 This protocol allows for the measurement of a linear increase of shear stress
26 corresponding to the elastic behavior of the material in its solid regime. Above a critical
27 strain around a few % and when shear stress reaches yield stress, the material starts to
28 yield and flow (see Fig. 3a). This stress peak is associated to the breakage of the network
29 of attractive colloidal interactions between cement particles. At a critical shear strain of

the order of few hundredth of %, another peak can be identified and is associated to the breakage of the hydrates formed between flocculated cement grains (see Fig. 3b).

3.3. Rheometry: oscillations

Small amplitude oscillatory shear (SAOS) is a common way to probe the viscoelastic properties of soft materials, and it has been found to be suitable for fresh cement pastes to study hydration and stiffening behavior (or what we now term structuration) [A. Papo and B. Caufin, 1991), (P.Banfill et al. 1991), (Schultz et al., 1993); (Z. Sun et al. 2006). In SAOS, a small sinusoidal strain is applied to the material to obtain a stress response. The storage modulus (G') is the in-phase, elastic component of the response while the loss modulus (G'') is the out-of-phase, viscous component. The complex modulus ($G^* = G' + G''i$) and phase lag provide further description of viscoelasticity. Through performing a strain sweep, i.e. progressively increasing amplitude, we can obtain a measure of critical strain, which marks the end of the linear viscoelastic regime (LVR) – theoretically the limit of the material's ability to respond elastically and keep its structure intact. Within the LVR, G' remains constant and independent of applied strain. If the critical strain is exceeded, there is a significant drop in G' , indicating the structure has been irreversibly broken. A frequency of 1Hz is commonly used for cement pastes and found to be within the LVR. And the critical strain is typically found to be in the order of 10^{-4} , which corresponds to the scale of C-S-H bridges that form between cement particles during the early stages of hydration (N. Roussel et al. 2012). Therefore, SAOS can be used as a tool to probe the rigid structure formed progressively through C-S-H nucleation and growth, discussed in Sec 2.2.

By applying a sinusoidal strain within the LVR, we can obtain a continuous measure of structural build-up of a material at rest. For cement-based systems, it is well accepted that monitoring G' provides a measure of structure due to rigidification and, since the material is probed within the LVR, resultant elasticity. Further, G' is related to instantaneous (or apparent) shear modulus, which is the slope of the shear stress-strain curve obtained by applying a sufficiently low shear rate. Importantly, it should be noted

1 that short-term (few sec) increase in G' is tied to colloidal interactions, while long-term
2 linear increase in G' is due to C-S-H nucleation (N. Roussel et al., 2012). This has more
3 recently been supported by (A.M. Mostafa and A. Yahia, 2016) in comparing G' and
4 phase angle evolution between cement versus model calcium carbonate suspensions –
5 in the latter there was a short-term increase in G' and decrease in phase lag due to
6 percolation, and no long-term increase due to the absence of hydration and
7 corresponding rigidification. A physico-chemical model has been proposed that can
8 predict structural build-up due to colloidal interactions and chemical rigidification based
9 on mix parameters (A.M. Mostafa and A. Yahia, 2017).

10 It has been shown that increase in G' does not necessarily coincide with an increase in
11 static yield stress due to differing mechanisms (S. Ma et al., 2018), i.e. G' arises from C-S-
12 H bridges while yield stress arises from a combination of colloidal interactions and C-S-H
13 bridges that remain unbroken at higher applied strains. However, since C-S-H nucleation
14 is an overlapping mechanism, these parameters have also been found to be similar (Q.
15 Yuan et al., 2017). In evaluating structuration, it is therefore necessary to measure both
16 yield stress (through flow onset) and elasticity (through oscillations). This becomes
17 particularly important for AM, as we are interested in the contribution of both colloidal
18 and hydration effects on the development of the undisturbed structure for controlling
19 shape stability of the layer, building rate, and ultimately buckling stability of the layered
20 structure. It should be noted that the potential of large amplitude oscillatory shear to
21 characterize fresh cement pastes has recently been demonstrated (T. Conte and M.
22 Chaouche, 2016). Although it can be a powerful characterization tool for evaluating
23 thixotropy, its suitability for cements and quantitative interpretation of data needs
24 further exploration.

26 **4. Yield stress in fresh cement-based materials: effects of admixtures**

27 **4.1. Repulsive inter-particle forces and decrease in yield stress**

28 Several types of admixtures can decrease the strength of the flocculated network of
29 cement particles in a paste by generating repulsive forces between particles and

1 increasing therefore the average inter-particle distance (see section 2.1) (J. Gelardi et
2 al., 2015). For instance, when adsorbed on cement surfaces, concrete dispersants can
3 provide electrostatic and/or steric repulsion between particles. The most efficient and
4 famous ones are the comb-shaped polycarboxylate ether (PCE) super-plasticizers that
5 have a negatively charged backbone adsorbing on particles surface and non-adsorbing
6 side chains inducing steric hindrance (J. Gelardi et al. 2015), (R.J. Flatt and Schober,
7 2012).

8 At equilibrium, adsorbed macromolecules have a preferred conformation of adsorption
9 on the surface of cement particles (R.J. Flatt et al., 2009). As soon as two covered
10 particles approach and the layers of polymer overlap, a repulsive steric force occurs
11 between the particles. This comes from a change of adsorption conformation of the
12 polymer, which results in a loss of entropy, together with a rise of osmotic pressure
13 coming from an increase of the concentration of polymer between the two approaching
14 particles, which prevents them from approaching further (J. Gelardi and R.J. Flatt, 2015).
15 The coverage degree and the thickness of the layer of adsorbed dispersants are
16 therefore of great importance as they dictate the minimum distance between two
17 particles before repulsion and impose therefore the value of the attractive Van der
18 Waals forces. This means that they rule the dispersion ability and therefore yield stress
19 and elasticity. They also depend on the dosage of polymer and on the surface occupied
20 by one molecule, which is itself dependent on the molecular structure of the polymer
21 (R.J. Flatt et al., 2009), (J. Gelardi and R.J. Flatt, 2015).

22

23 **4.2. Attractive inter-particle forces and increase in yield stress**

24 ***Bridging forces***

25 Bridging forces arise when a polymer chain adsorbs simultaneously at the surface of two
26 or more particles. For bridging to occur, the polymer chain must be long enough to
27 reach the surface of at least two particles and must have an affinity with the surface
28 particle. It was shown by [Tadros et al., 2012] that an optimal bridging flocculation is
29 attained at half particles surface coverage. At higher concentrations, an adsorbed

1 polymer on one particle might not find an empty site on another particle. In cement
2 based materials, most viscosity modifying admixtures (VMA) are able to bridge cement
3 particles, which increases the macroscopic yield stress of the suspension to a certain
4 extent (C. Brumaud et al., 2014), (H. Bessaies-Bey et al.,2015) (see Fig. 4). Some VMAs
5 also strongly modify the critical strain of cement paste. By comparing the flow onset of
6 the reference cement paste and cement pastes containing polyacrylamide and cellulose
7 ethers, we note that cellulose ether were found to allow for the mix design of softer
8 systems (i.e. lower elastic modulus) in comparison with the reference cement paste and
9 the cement containing polyacrylamide (C. Brumaud et al., 2014), (H. Bessaies-Bey et al.,
10 2015]. On the other hand, pastes containing polyacrylamide were found to exhibit a
11 higher elastic modulus. Such organic admixtures are essential for promoting particle
12 flocculation for shotcrete applications, mono-layer render mortar or tile adhesives (C.
13 Brumaud et al., 2011) along with additive manufacturing of concrete (D. Marchon et al.,
14 2018).

15

16 **Attractive depletion forces**

17 Fig. 5 shows the evolution of a cement paste yield stress as a function of PCE dosage. In
18 the first regime (i.e. low dosages), we note a decrease in yield stress as PCE dosage
19 increases. However, above a critical concentration, the latter trend is inverted and an
20 increase in PCE dosage leads to an increase in yield stress. For this PCE and in this
21 dosage range, cement particle surfaces are fully covered by adsorbed PCE and any
22 additional PCE remains in the suspending fluid. These results suggest that excess in
23 super-plasticizer may be at the origin of attractive depletion forces, which causes a
24 fluidity loss.

25 It is now accepted in the literature of colloidal particles that the addition of non-
26 adsorbing polymer to a suspension can generate depletion attractive forces, which may
27 cause particle flocculation (S. Asakura et al., 1954), (S. Asakura et al., 1958). When a
28 polymer has no affinity with a surface it is excluded leading to a formation of a region of
29 pure solvent. The differences in osmotic pressure between the polymer depleted (or

1 pure solvent) region and the bulk polymer solution lead to an attraction between the
2 particles. In cement based materials, (H. Bessaies-bey et al, 2018) showed recently that
3 non-adsorbed polymers induce attractive depletion forces, which may lead to an
4 increase in cement paste yield stress. These forces mainly depend on the polymer
5 concentration rather than their molecular weight.

6 It should be kept in mind that, in the absence of super-plasticizers, Van der Waals
7 attractive forces dominate depletion forces and the consequence of non-adsorbing
8 polymers on yield stress is negligible. However, in the presence of super-plasticizers, the
9 magnitude of the attractive van der Waals forces decreases (see section 4.1) and
10 attractive depletion forces induced by non-adsorbing polymers become important and
11 greatly contribute to yield stress and elasticity.

12

13 ***Hydrophobic forces***

14 Although surfactant molecules are mainly incorporated in cement based materials to
15 stabilize aqueous foams, it was recently shown by (B. Feneuil et al., 2017) that these
16 molecules can adsorb on the surface of cement particles and introduce attractive
17 hydrophobic forces in the system.

18 When adsorbed at the surface of cement particles, surfactants can turn the surface
19 hydrophobic. As hydrophobic surfaces tend to attract each other (J. Israelachvili et al.,
20 1984), (E. Meyer et al., 2006), the suspension flocculates and the yield stress increases.
21 It should be kept in mind that, above a critical concentration of surfactant in solution,
22 micelles may form and affect the mechanism of action of the surfactant.

23

24 **4.3. Competitive adsorption between admixtures**

25 Modern cement-based materials tend to include more than one type of admixture in
26 order to achieve required rheological properties. However, the blending of these
27 chemical admixtures has to be well controlled to limit incompatibilities and to achieve
28 the intended effect. As shown in the above sections, the mechanism of action of most
29 chemical admixtures is very sensitive to their adsorption on the surface of cement

1 particles. The blending of these chemical admixtures can generate a competitive
2 adsorption on particles surface, which will, in turn, influence their performances. Many
3 examples of competitive adsorption between a superplasticizer and sulfate ions (K.
4 Yamada et al., 2001), (R.J. Flatt et al., 2009], hydroxides (R.J. Flatt et al., 2015), (D.
5 Marchon et al., 2013), citrates (J. Plank et al., 2008) and other organic admixtures (J.
6 Plank et al., 2007), (J. Plank et al., 2010), (H. Bessaies-Bey et al., 2016) have been studied
7 in literature. By occupying the adsorbing sites at the surface of cement particles, so-
8 called “displacers” restrict the adsorption of super-plasticizer and considerably affect
9 their dispersion efficiency as shown in **Error! Reference source not found.**6 in presence
10 of sodium gluconate. Depending on the industrial application, competitive adsorption
11 can also be an advantage leading to synergetic effects between adsorbing species.
12 Indeed, it was observed in (H. Bessaies-Bey et al., 2016) that a super-plasticizer can
13 inhibit the adsorption of VMAs, which, in turn, enhances their stabilizing effects.
14 In addition, adsorption and desorption kinetics could be at the origin of the evolution of
15 material rheological behavior over time. In some cases, the exchange could be rapid, as
16 the desorption of a superplasticizer by sulfate (K. Yamada et al., 2001) or sodium
17 gluconate (H. Bessaies-Bey et al, 2016). However, as the desorption of an already
18 adsorbed macromolecule requires the simultaneous desorption of the anchor groups,
19 the exchange could also be a very slow process in the order of hours, days or even years
20 (J.A. Kling et al., 1998).
21 To control the outcome of competitive adsorption, several recent studies focused on the
22 modification of the chemical structure and surface affinity of the organic admixtures (W.
23 Fan et al., 2012), (S. Pourchet et al., 2012), (F. Dalas et al., 2015). Moreover, it should be
24 kept in mind that competitive adsorption is only observed at high surface saturation (i.e.
25 high surface coverage) where there are not enough sites for adsorbing species. The
26 extent of this regime can therefore be controlled by tuning the polymer dosage,
27 adsorbed conformation or adsorption energy.

28

29 **4.4. Admixtures, hydration and structuration**

1 Admixtures do not only modify the colloidal interactions at the origin of the yield stress
2 and elasticity of the material. They may also affect the hydration reaction in the
3 induction period and modify therefore the structuration at rest of the fresh suspension
4 and the associated evolutions in yield stress and elastic modulus (see Section 2.2.). As
5 for most of the admixtures that have the ability to adsorb on cement particles, PCEs, for
6 example, affect hydration by delaying the setting and disturbing the chemical balance
7 between the cement phases (Cheung et al., 2011), (D. Marchon and R.J. Flatt, 2015), (L.
8 Berodier et al., 2018), (Jansen et al., 2012). Among them, C_3S and C_3A are the most
9 reactive and therefore the most relevant phases regarding the influence of their
10 hydration on the evolution of the rheological properties. In the first minutes after
11 contact with water, the principal hydration mechanisms are their dissolution and the
12 nucleation and growth of their hydrates. C_3A reacts with calcium sulfate and water to
13 form ettringite, and C_3S hydration produces portlandite and C-S-H, for which we have
14 seen in section 2.2. the major role in the structuration of cement-based materials at
15 rest.

16 Several reasons were mentioned for the delay of hydration caused by PCEs: the
17 complexation with Ca-ion, the perturbation of hydrates formation and the slowing down
18 of C_3S dissolution (D. Marchon and R.J. Flatt, 2015). Recent findings firstly highlight the
19 blocking of active dissolution sites by adsorbed molecules as the most realistic
20 explanation for the change of hydration kinetics that leads to a delay of cement setting
21 (D. Marchon et al., 2017). Secondly, a direct quantified correlation was found between
22 the retardation and the molecular structure and dosage of the PCEs (Fig. 7). This led for
23 the first time to the possibility of mastering both rheological properties and side effects
24 of using PCEs with respect to their molecular characteristics and therefore to an
25 optimization of the molecular design (D. Marchon et al, 2019a), (D. Marchon et al,
26 2019b).

27 Although the ions complexation and the inhibition or change of hydrates precipitation
28 seem to have less impact on the decrease of reaction rate of cement, their influence on
29 the location and the way hydrates develop is of great relevance regarding structuration

1 build-up and microstructure development (P.J.M. Monteiro et al., 2019). In C_3S pastes,
2 nano-clusters composed of calcium and polymer complexes were observed in the pore
3 solution (Sowoidnich et al., 2015). This might be linked to the recent findings that PCEs
4 stabilize globular precursors of purely synthesized C-S-H before they convert to the
5 more commonly observed nano-foil like structure (Schönlein and Plank, 2018).
6 Nanoparticles composed of polymer and hydrate phases were also observed in pore
7 solution of cement pastes (Caruso et al. 2017). The presence of such particles in the
8 aqueous solution dispersed by the PCEs could most probably be at the origin of a
9 transition from a heterogeneous to homogeneous nucleation (Valentini et al., 2016),
10 that would affect the bridging effect of C-S-H mentioned earlier as well as the final
11 spatial distribution of the phases in the microstructure (Artioli et al., 2014).
12 Finally, a recent study focusing on the workability loss of cement pastes containing PCEs
13 highlighted two very distinct and successive regimes (S. Mantellato et al., 2019). The
14 first one occurring along the induction period shows a linear evolution of the yield stress
15 that is independent of hydration reactions, illustrating the thixotropic behavior of the
16 system. After a so-called onset, the measured exponential increase in yield stress is
17 directly proportional to the heat rate and to the specific surface area of the system. This
18 correlation points out the dependency of rheological properties on the strong
19 precipitation of hydrates in the acceleration period. With respect to PCEs influence, it
20 was observed that this proportionality changes in presence of the polymer, due to the
21 retardation effect, but does not seem to closely depend on the molecular structure of
22 the PCEs.
23 More generally, admixtures are essential for applications such as concrete 3D printing,
24 where a structural build-up is needed right after deposition of the concrete and
25 followed by a fast stiffening to sustain subsequent layers (L. Reiter et al., 2018). Playing
26 along with admixtures and targeting silicates along with aluminates seem to show great
27 potential for printing concrete (D. Marchon et al., 2018). For example, this can be done
28 by enhancing ettringite precipitation with shotcrete accelerators or blended cements
29 with calcium aluminate cement for a fast surface development and rapid strength gain.

1 However, the challenge is to choose the perfect mixture proportions between the
2 different systems that are available to avoid an uncontrolled expansion or to not disturb
3 the balance between the main phases of the system. Indeed, provoking ettringite
4 nucleation or having a high aluminate content might strongly influence the sulfate
5 consumption and silicate hydration (Cheung et al., 2011) (L. Berodier et al., 2018). In
6 term of chemistry of hydration, the sulfate depletion is strongly accelerated and if it
7 occurs before the strong precipitation of C-S-H, the presence of a very high content of
8 aluminum in the pore solution inhibits the dissolution of the silicate phase and therefore
9 delays the precipitation of C-S-H that is the source of the mechanical strength (N.
10 Tenoutasse, 1968), (E. Pustovgar et al., 2017). This has a detrimental impact on the early
11 as well as on the late mechanical strength. In term of rheology, this causes a very rapid
12 stiffening, called flash set, and subsequent loss of fluidity.

13

14 **4.5. Nanoparticles and structuration**

15 It was shown by (P. Juilland et al., 2012) that the mechanical action of mixing of cement
16 paste results in the detachment of C-S-H from the surface of particles leading to the
17 enhancement of the main heat peak of hydration. Recent work by (F. Caruso et al.,
18 2017) highlighted the formation of nanoparticles in cement pore solution containing
19 super-plasticizers. They asserted that these nano-size particles are either nano-C-S-H,
20 nano-ettringite, nano-AFm, or intramolecular complexes of polymer and cations. More
21 recently, (A. Vandenberg et al., 2018) showed that an appropriate combination of
22 mixing energy and super-plasticizer dosage promotes the scratching of nanoparticles
23 from the surface of cement particles and their stabilization in the suspending fluid and
24 hence generates additional nucleation surfaces. These generated nanoparticles enhance
25 the thixotropic behavior of cement-based materials and promote structuration.

1 In addition, it is possible to further tailor nucleation and structuration by introducing
 2 nanoparticles as additives. Highly purified attapulgite nanoclays have been
 3 demonstrated to be effective in enhancing thixotropy at relatively low additions (S.
 4 Kawashima et al., 2013), (Z. Quanji et al., 2014), (Y. Qian and S. Kawashima, 2016). Their
 5 effect has been tied to the colloidal strain regime, which supports that the clays are
 6 enhancing electrostatic interactions between cement particles to enhance yield stress
 7 recovery immediately after shear (S. Ma et al., 2018). Due to their high specific surface
 8 area, nanoparticles can introduce additional CSH nucleation sites to accelerate
 9 hydration, termed seeding effect, (F. Sanchez and K. Sobolev, 2010), which can in turn
 10 enhance structuration in the fresh state. One challenge of incorporating any
 11 nanoparticle type in cement systems is dispersion, where dispersion degree will
 12 significantly impact the working mechanism. Therefore the seeding effect is sensitive to
 13 processing parameters, i.e. dispersion technique and mixing. This is the underlying
 14 reason why, in contrast to flow onset results where increase in yield stress is
 15 consistently observed, the effect of nanoclay on SAOS results is much more dependent
 16 on processing and pre-shear conditions (S. Kawashima et al., 2013), (T. Conte and M.
 17 Chaouche, 2016), (S. Ma et al., 2018).

18

19 **5. Yield stress and elasticity in fresh cement-based materials: modeling**

20 **5.1. Yield stress modeling and YODEL**

21 The YODEL is a first principle analysis of yield stress of colloidal particles suspension,
 22 which was shown to successfully predict the main parametric dependencies of cement
 23 suspensions yield stress (R.J. Flatt and P. Bowen, 2006), (R.J. Flatt and P. Bowen, 2007)
 24 (A. Perrot et al., 2012), (J. Hot et al., 2014). This model writes:

$$\tau_p \cong m \frac{A_0 a^* \varphi_c^2 (\varphi_c - \varphi_{perc})}{d^2 H^2 \varphi_{cm} (\varphi_{cm} - \varphi_c)} \quad (1)$$

25 *Where we have 5 material parameters:*

26 *m is a pre-factor, which depends on the cement particle size distribution; It can be*
 27 *computed from a measurement of the particle size distribution.*

1 A_0 is the non-retarded Hamaker constant taken as 1.6×10^{-20} J;
2 a^* is typical size of the surface defects of cement grains and is of the order of several
3 hundreds of nm (A. Perrot et al., 2012);
4 d is the cement particle average diameter d_{50} and is of the order of $10 \mu\text{m}$
5 φ_{cm} is the maximum packing fraction of cement grains.
6 And 3 mixture variables:
7 φ_c is the solid volume fraction of the cement particles in cement paste
8 φ_{perc} is the percolation volume fraction; It results from the competition between
9 Brownian motion and colloidal attractive forces between cement particles, which, in
10 turn, depend on the admixture dosage (A. Perrot et al., 2012).
11 H is the average surface-to-surface separating distance between flocculated cement
12 particles; It depends on the admixture dosage.

13

14 **5.2. Flow and processing modeling**

15 The previous sections have introduced the experiments allowing for the measurement
16 of yield stress and the model allowing for the prediction of yield stress as a function of
17 components properties and dosage. The present section refers to the mathematical
18 models that link yield stress to the macroscopic flow behaviour, by introducing its value
19 into macroscopic flow equations. As mentioned in the introduction, the common
20 approach to model fresh cementitious materials is based on non-Newtonian fluid
21 mechanics. Here, the macroscopic flow behaviour is expressed by constitutive
22 equations, which give relation between the shear stresses and velocity gradients (J.D.
23 Anderson, 1992). The commonly accepted constitutive relations for fresh cement-based
24 materials are Bingham and Herschel-Bulkley (C.F. Ferraris, 1999). The Bingham model
25 (Equation 2) captures a linear viscous behaviour if the applied stress is higher than the
26 yield value (E.C. Bingham, 1922), while the Herschel-Bulkley approach (W.H. Herschel
27 and R. Bulkley, 1926) assumes that the material behaves non-linearly if the stresses are
28 above yield stress value (Equation 3):

$$\tau = \tau_0 + \eta_{pl} \cdot \dot{\gamma} \quad (2)$$

$$\tau = \tau_0 + k \cdot \dot{\gamma}^n \quad (3)$$

1 where τ is shear stress, τ_0 is yield stress of the material, η_{pl} is plastic viscosity of the
 2 material, $\dot{\gamma}$ is the shear rate, k is consistency index and n is power law index. The
 3 constitutive relations are integrated into the conservation equations, which govern the
 4 fluid flow.

5 The abovementioned mathematical models found practical applications in numerical
 6 concrete flow simulations (N. Roussel and A. Gram, 2014), (A. Gram and J. Silfwerbrand,
 7 2011), (L.N. Thrane, 2012). Due to the computational limits, a complete flow simulation
 8 that account for all concrete phases is still not possible; therefore, the above authors
 9 used different approximate models that aim to describe the macroscopic flow behavior
 10 (rather than its microstructure). Recently, in (N. Roussel et al., 2016) the researchers
 11 studied numerically the effect of yield stress on the final shape in two concrete filling
 12 ability tests: slump and channel flow. They compared the numerical predictions of these
 13 benchmark flows obtained by several research teams, who used various numerical tools.
 14 The comparison demonstrated that, if segregation does not occur, the compared
 15 numerical simulations are able to accurately predict the benchmark flows, and concrete
 16 filling ability. The numerical results were in agreement with the analytical solutions
 17 proposed in (N. Roussel, 2007), (N. Roussel and P. Coussot, 2005), which claim that final
 18 shape and flow distance of a yield-stress material are determined by its density and the
 19 yield stress value, only.

20 The findings of this numerical benchmark study are of particular interest for the
 21 practical application of numerical simulations to predict industrial processes. The
 22 purpose of a numerical prediction is not to perfectly depict the process itself, but to
 23 predict its result (for instance, in case of concreting on site, one aims to predict if the
 24 formwork will be properly filled or not). Consequently, such a simulation focuses on the
 25 flow at stoppage, where the shear rates are rather low, and the contribution of the
 26 second part of the equations 2 and 3 is negligible. It is therefore not crucial if the
 27 material behaves linearly or non-linearly at the higher shear rates – at the low shear
 28 rates at stoppage the yield stress is the dominating factor, that finally determines the

1 flow length or the filling degree of a mold. This was recently demonstrated in (K. Vasilic
2 et al. 2016), through large scale-laboratory castings and corresponding numerical
3 simulations: for non-blocking cases, yield stress determines the final shape of the
4 material and the proper filling of the form in practical applications.

5 6 **5.3. Stability modeling of printed cement-based materials**

7 The successful deposition of consecutive layers in a 3D printing process lead to an
8 increment of gravity-induced stresses as an object is created. As the resistance of the
9 printing material is initially low (i.e. in the order of the loads acting on the material) and
10 no confining formwork is present, this increment in stress may lead to structural failure
11 during the printing process, by either *elastic buckling* (illustrated in Figure 9) or *plastic*
12 *collapse*. In this phase, when the fresh concrete is generally at rest, the elastic-plastic
13 behavior of the early age material, and its structuration kinetics, are critical to control
14 such failure (N. Roussel et al., 2012), (L. Reiter et al., 2018).

15 In a recent paper, the rheological requirements to prevent both material yielding as well
16 as self-buckling have been outlined (N. Roussel, 2018). It was shown that, for a typical
17 wall of 2.5 m height, the gravity-induced stresses gradually increase with the rising
18 height of the object, and reach a value of around 30 kPa in the critical bottom layer at
19 the end of printing.

20 Consequently, in addition to an initial material yield stress required to control the layer
21 shape immediately after extrusion (typically in the order of a couple tens to thousands
22 of Pa), a structuration rate A_{thix} (N. Roussel, 2006) is imposed to prevent plastic collapse
23 when consecutive layers are placed. The minimum rate is dependent on the rising speed
24 of the object, and may follow both a linear and non-linear trend (A. Perrot et al., 2015),
25 (T. Wangler et al., 2016). Likewise, the initial elasticity and its evolution rate required to
26 avoid elastic buckling, a common failure mode for the dominantly vertical slender
27 shapes created by 3D printing, are imposed by the rising speed of the object, as well as
28 its geometrical features. The rising speed, in turn, follows from the printing velocity,

1 contour length, and layer dimensions. Thus, the rheological requirements of 3D printed
2 concrete are fully process dependent.

3 The occurrence of failure by elastic buckling in a 3D concrete printing process was for
4 the first time shown in a recent paper (R. Wolfs et al., 2018). To assess the process
5 dependent structural failure of an object during 3D printing, the authors proposed a
6 numerical approach based on Finite Element Method (FEM) modelling. This approach
7 includes the development of both the geometry and the material properties throughout
8 a printing process, and thus, may predict if, and how, an object may collapse. The
9 numerical simulations were validated by means of printing experiments. With a similar
10 aim, a mechanistic model has recently been presented, to explore the influence of
11 various process parameters on the mechanical performance of 3D printed wall
12 structures (A.S.J. Suiker, 2018).

13 The recent developments in the field of 3D concrete printing highlight the need to
14 assess both yield stress and elasticity beyond the range commonly considered for fresh
15 concrete. Whereas the rheological properties of concrete are often studied in the range
16 of several Pa, they may reach the order of several tens to thousands of kPa in a 3D
17 printing process. In this range, standard rheometers may not be adequate, which has led
18 to the adoption of mechanical tests to characterize the early age properties. The results
19 of such experiments additionally demonstrate a decrease of the critical strain with time
20 at rest, which indicates a transition from plastic towards brittle failure as the material
21 ages (L.K. Mettler et al., 2016), (R. Wolfs et al. 2018). Consequently, where fresh
22 concrete is often considered as a non-Newtonian fluid with a Von Mises yield criterion,
23 at later ages, a solid mechanics approach based on a Mohr-Coulomb or Drucker-Prager
24 criterion may be more suitable to assess plastic collapse in 3D printing processes.

25

1 6. CONCLUSION

2

3 This paper gathered the accepted knowledge along with the most recent advances on
4 yield stress and elasticity of fresh cement-based materials. In the first part, the physical
5 and chemical origins of these macroscopic properties and their evolutions were
6 described. The second part of the paper focused on the way these properties can be
7 measured while the third part dealt with the way they can be controlled and tuned.
8 Finally, the most recent models for both properties prediction from mix design and
9 processing modeling from rheological measurements were described.

10 The clear distinction in the research community between non-Newtonian fluid
11 mechanics and fresh cement-based materials on one side and solid mechanics and
12 hardened ones on the other side lasted for decades. However, it can be concluded from
13 the above research trends that, nowadays, the boundary between these two fields is
14 becoming narrow.

15 Because of the need to measure, understand and tune rheological properties of
16 printable materials, the rheology and processing community is now exploring
17 consistency and strength regimes that used to be considered as typical of a hardening
18 material. In parallel, the hydration community keeps on improving its understanding of
19 the setting process. Although being an extremely short phenomena relative to the life
20 period of a concrete element, yield stress, elasticity, thixotropy, structuration and
21 setting seem to be progressively described in literature as a continuous transition with
22 the same physico-chemical origin.

23

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Figure 1. General behavior of fresh cement-based systems at rest described through yield stress evolution and underlying cement particle interaction and C-S-H nucleation and growth. The freshly sheared suspension starts in a dispersed state (a), then exhibits initial flocculation due to non-contact interactions. C-S-H nucleation occurs, forms bridges between cement particles/flocs (c), and gives rise to an increasingly interconnected, rigid structure (d). Reproduced from (N. Roussel et al. 2012).

Figure 2. Dimensionless yield stress (i.e. the ratio between the yield stress of the suspension for a given volume fraction of beads and the yield stress of the suspending fluid) as a function of beads volume fraction for various suspending yield stress fluids including cement pastes (reproduced from (F. Mahaut et al., 2008b)).

Figure 3. Shear stress as a function of shear strain during a Vane test on a cement paste with a water to cement ratio of 0.4. (a) Linear shear strain scale from 0 to 15%; (b) Linear shear strain scale from 0 to 0.4%. Extracted from [Roussel et al., 2012]

Figure 4. Flow onset measurements for a reference cement paste and pastes containing Polyacrylamide and Cellulose ether (mass dosages).

Figure 5. Yield stress of cement paste as a function of PCE dosage ($W/C=0,3$) (extracted from (H. Bessaies-Bey et al., 2018))

Figure 6. Desorption of a superplasticizer (polycarboxylate ether) in the presence of a retarder (sodium gluconate) (left y axis) and consequences on the yield stress (right y axis). The relative yield stress is the ratio between the yield stress of the cement paste with admixtures and the yield stress of the reference cement paste. Adapted from (H. Bessaies et al., 2016).

Figure 7. Abacus of retardation showing the ratios $\Delta t_1 / \Delta t_2$ function of N_1 / N_2 Ratio. N is the number of monomers in the backbone for one side chain and P the number of monomer in one side chain. This plot shows the evolution of the retardation as a function of changes of structural parameters with respect to a reference polymer dosed to achieve the same dispersion ability. The reference is polymer 1 with $N_1=4$ and $P_1=23$. The black dot represents the case where polymer 2 has the same structural parameters as polymer 1. The curved lines determine the ratio of retardation $\Delta t_1 / \Delta t_2$ for different side chain lengths. The vertical dashed line represents the case where $N_1=N_2$. The star represents a polymer that was used to experimentally prove that the prediction offered by this plot is realistic (reproduced from (D. Marchon et al, 2019b).

Figure 8. Yield stress as a function of cement volume fraction for various dosages of High Range Water Reducing Admixtures (HRWRA). Experimental data points along with YODEL prediction (lines). Reproduced from (A. Perrot et al., 2012).

Figure 9. Elastic buckling during a 3D printing process.