

Investigation of Mobility Parameters in Rheological Behaviour of Low Cement Content Mortars

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Abstract

The construction industry is closely tied to economic development economies, and increasing demand also presents a significant contribution to environmental degradation. The construction industry's impact to climate change is led by the 8% contribution from the production of concrete mixtures, more specifically, the production of cement. The combination of using advanced mix-design techniques (e.g., particle packing models -PPM) and more sustainable ingredients poses as a promising alternative to overcome concrete environmental impact. However, there is a lack of studies regarding the fresh state difficulties arising from the aforementioned combination. Therefore, this work appraises the use of mobility parameters to overcome the fresh state issue raised when mix-designing mortar mixtures through PPM and with high volume of limestone filler. Twelve mixtures were developed with distinct cement content ranging from 150 kg/m³ to 320 kg/m³. To produce sustainable mortar, besides using PPM, cement content was replaced by limestone filler. Time dependent fresh state analysis was performed using mortar slump flow and a rheological profile. In the hardened states, the compressive strength, porosity, surface electrical resistivity tests were performed. The main findings of the project observed a strong correlation between mobility parameters and five distinct rheological parameters: flow behaviour parameter, high shear rate viscosity and shear stress, low shear rate viscosity and shear stress. Additionally, in the hardened state, a dilution parameter IPS_{cement} was used to appraise the dilution and filler effect of the mortar mixtures. The works highlighted a promising method to produce eco-efficient mortars.

Keywords: Rheology, shear stress, viscosity, mobility parameters, particle packing models, inter-particle separation distance, maximum paste thickness, limestone filler, low cement content.

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Table of Contents

Chapter 1. Introduction	1
1.1. Background.....	1
1.2. Research Objectives	3
1.3. Thesis Organization.....	4
1.4. References	5
Chapter 2. Introduction	9
2.1. Concrete mix-design.....	9
2.2. Rheological behaviour of concrete	18
2.3. Mobility parameters.....	20
2.4. The use of inert filler in cementitious mixtures.....	22
2.5. Hardened state evaluation of packed concrete mixtures	25
2.6. Eco Efficiency/BI factor	26
2.7. References	28
Chapter 3. Investigation the Impact of Mobility Parameters on the Rheological and Hardened Behaviour of Low Cement Content Concrete Mixtures.....	37
3.1. Introduction	38
3.2. Literature Review	39
3.3. Scope of the Work	45
3.4. Materials and Methods	46
3.5. Results	52
3.6. Discussion.....	61
3.7. Conclusion.....	71
3.8. References	72
Chapter 4. Conclusion and future recommendations.....	77
4.1. Conclusions	77
4.2. Future recommendations	78
Chapter 5. References	80

List of Figures

Figure 2.1: ACI mix design input vs output.	10
Figure 2.2: Various system impacts in discrete packing models.....	13
Figure 2.3: Depiction of the similarity condition in continuous packing models.....	14
Figure 2.4: Andreasan distribution modulus n and its suggested applications.	15
Figure 2.5: Distribution modulus n (q in this paper) and corresponding porosity.....	17
Figure 2.6: Various types of rheological behaviours w.r.t shear rate.	18
Figure 2.7: IPS and MPT from Innocentini.	22
Figure 2.8: Various rheological implications because of increasing limestone replacement.	25
Figure 2.9: Binder intensity for worldwide mixture.	27
Figure 3.10: Particle size distribution of mortar components.....	47
Figure 3.11: a) revised Mortar IBB Rheometer dimensions and b) Rheometer 2-cycle testing shear ramp profile.....	51
Figure 3.12: Slump Loss in a) Phase 1 mixtures and b) Phase 2 mixtures.	54
Figure 3.13: Raw rheometer data for a) Mixtures from phase 1, b) eco-efficient mixtures from phase 2, c) initial torque (0 s^{-1}) and d) high shear rate torque (0.7 s^{-1}) for Phase 1 and Phase 2 mixtures.....	56
Figure 3.14: Time dependent rheological data for shear rates corresponding to a) 0 s^{-1} and b) 0.7 s^{-1} ..	58
Figure 3.15: Compressive strength over time for all mixtures.	59
Figure 3.16: a) 28-day capillary porosity and surface electrical resistivity and b) 28-day dynamic modulus of elasticity.....	61
Figure 3.17: Rheological models (Bingham, MB and HB) in a) Group1 and b) Group2 mixtures.....	63
Figure 3.18: Real viscosity of non-Newtonian mixtures calculated through Herschel-Bulkley model, where a) Phase1 and b) Phase 2 mixtures are presented.....	64
Figure 3.19: Correlation between MPT of sustainable mixtures and a) flow behaviour factor from Herschel Bulkley model, b) initial torque (at 0.1 s^{-1}) and final torque (at 0.7 s^{-1}), and c) initial viscosity (at 0.1 s^{-1}) and final viscosity (at 0.7 s^{-1})	67
Figure 3.20: Compressive strength vs. a) w/f and b) w/c compared between Phases.	68
Figure 3.21: Combined dilution model employing IPS_{cement} and MPT_{Larrard}	70
Figure 3.22 : Sustainability appraisal of mortar mixtures.....	71

List of Tables

Table 1.1: GHG contribution by major components in concrete.....	1
Table 2.1: Various packing models, discrete and continuous.....	13
Table 2.2: Estimated shear rates for various concrete placement activities.	18
Table 2.3: Various rheological models for estimation of shear stresses.....	19
Table 3.1: Description of acronyms used in the background of this research.	39
Table 3.2: Material characterization data.....	47
Table 3.3: Mix design for the eco-efficient concrete mixtures being evaluated.....	48
Table 3.4: Fresh state properties of the various mixtures.	53
Table 3.5: Compared rheological models.	62

List of Symbols/Abbreviations

$\dot{\gamma}$	Shear Rate
τ	Shear Stress Applied to A Fluid
τ_0	Yield Stress of Fluid
a_i	Apparent Volume of i^{th} size particle
b_i	Binder Intensity
CSR	Class Size Ratio Between Two Consecutives Particle Sizes
D_l	Largest Dimension of a Mixture's Dry Matrix
D_p	Particle Size in Question
D_s	Smallest Dimension of a Mixture's Dry Matrix
f'_c	Compressive Strength
I	Discrete particle size in question
K_{hb}	Viscosity Constant
N	Flow Behaviour Parameter
P_d	Packing Density
p_f	Packing Factor
p_{of}	Apparent Porosity
$P_{of(\text{cement})}$	Dry Porosity of Cement
q	Distribution Modulus for Alfred Model
SSA	Specific Surface Area
V	Total Volume
V_a	Maximum value of V_{ai}
V_{ai}	Apparent Volume of Particle
V_s	Volume of Solids
$V_{s(\text{cement})}$	Solid Volume of Cement
VSA	Volume Surface Area, Material $d_p < 100 \mu\text{m}$
VSA_c	Volume Surface Area, Material $d_p > 150 \mu\text{m}$
VSA_{cement}	Volume Surface Area of Cement
x_i	Mass Fraction of the i^{th} sized particle
ACI	American Concrete Institute
ASTM	American Society of Testing Materials
BRE	Building Research Establishment
CaCO_3	Calcium Carbonate
CaO	Lime
CO_2	Carbon Dioxide
CPFT	Cumulative Percent Finer Than

GHG	Greenhouse Gases
HB	Herschel Bulkley Model for Fluids
IF	Inert Filler
IPS	Inter-Particle Separation Distance
IPS _{cement}	Inter-Particle Separation Distance of Cement Particles
MPT	Maximum Paste Thickness
PC	Portland Cement
PSD	Particle Size Distribution
SCC	Self Consolidating Concrete
SCM	Supplementary Cementitious Materials
w/c	Water-to-Cement Ratio
w/f	Water-to-fine Ratio

1.1.**Background**

Environmentally motivated initiatives have been gaining momentum in the developing world, with the rate of temperature increase being tied to greenhouse gas emissions. Many of these initiatives limit the quantity of carbon dioxide (CO₂) produced by distinct industries to mitigate the impact to our environment. One of the primary contributors to the global CO₂ production is the construction industry. Concrete, the most commonly used building material in the construction industry, contributes upwards of 8.5% of the overall anthropogenic CO₂ [1–3]. This CO₂ contribution is continuing to rise, with an 80% increase in demand from current levels towards 2050 [3,4]. This demand increase is tied to burgeoning economies and aging infrastructure projects dominating the global landscape [2,5–9]. Concrete production ranges between 250-312 kg CO₂ eq/m³, with 88.5% (Table 1.1) of overall greenhouse gas emissions directly from the cement production [3,10–13].

Table 1.1: GHG contribution by major components in concrete.

	GHG EMISSIONS (% OF CONCRETE)
ORDINARY PORTLAND CEMENT	88.5
MINERAL ADMIXTURES (E.G., SCMS)	0.7
AGGREGATES	10.1
CHEMICAL ADMIXTURE	0.6
BATCHING ACTIVITY	0.1

The production of cement is inherently not a sustainable material. It is produced when lime (CaO) is liberated from a calcium carbonate (CaCO₃) through calcination at elevated temperatures (~1400 degrees) releasing almost a half tonne of CO₂ per tonne of cement produced. The two essential processes (calcination, fuel consumption) contributes to 90% of overall CO₂ release from cement

production (i.e., calcination and fuel consumption produces 50% and 40% of CO₂, respectively) [2,14–16]. Therefore, cement reduction is a key factor to increase sustainability of concrete. Additionally, zero emissions policies propose a reduction of 24% from cement related CO₂, the increasing cement demand of 23% will pose a problem [2,8,17].

At the cement production level, two main types of CO₂ reductions are commonly proposed: 1) renewable fuel sources; 2) carbon capture and storage [2,18,19]. The use of alternative fuel sources does not solve the stoichiometric release of carbon dioxide from calcination of calcium carbonate materials [2,3,20]. Additionally, Kajaste [11] suggests that the carbon capture is still an alternative too costly for widespread immediate implementation. While these methods offer potential long term solutions, various authors suggest that CO₂ reductions performed by cementitious replacement with supplementary cementitious materials (SCMs) are more realistic in the immediate future [3,11,21–23]. A recent report by Gray [24] noted that increasing environmental policy restrictions are changing the quality of commonly available SCM's for use in concrete, changing the applicability of these materials as cementitious replacements. Furthermore, production of SCMs, is not expected to meet the increasing cement demand as a replacement material [25–27]. Use of an inert limestone filler (non-calcinated CaCO₃) is recognized as a novel and promising method of increasing cementitious efficiency due its production capacity, as well as its enhancement to a concrete mixture's microstructure [23,28,29]. Previous works noted mechanical enhancements, reduced environmental impact, and improved workability through inert limestone use. More efficient cement use in concrete/mortar mixtures can still be further broken down into two main focuses: 1) ultra high strength concrete mixtures [30,31] and 2) use of distinct mix-design methodologies [13,30,32–35]. While increased design strength may offer a solution, the benefit from the reduced overall concrete volume is not reflected in conventional concrete

supply [30,36]. Alternatively, novel mix design methodologies are promising but result in complications to fresh state in conventional concrete mixtures (mechanical capacity of 20-40 MPa). Methods evaluating the embodied energy (CO₂) noted a significant decrease in efficiency of these conventional concrete mix designs, and the effective use of inert limestone fillers can aid in solving the fresh state problems, while possessing adequate readily available supply. This has led to a distinct gap in knowledge in the conventional concrete mixture supply, most notably in the fresh state. Additionally, a common theme amongst these various methods is the inability to design when considering the wide spectrum of a concrete mixture's potential application.

1.2. Research Objectives

The main objective of this research project is to evaluate the use of mobility parameters (i.e., interparticle separation distance and maximum paste thickness) to appraise the fresh and hardened properties of mortar mixtures, particularly fresh state properties.

In this research program, twelve mortar fractions of concrete were designed with decreasing cement contents and constant values for the changing mobility parameters. To produce eco-efficient mortar mixtures the cement content was reduced from 324 to 150 kg/m³. It is worth noting that this work is focused on (currently in-efficient) conventional strength concrete mixtures (20-40 MPa) placed by pumping or placement (slump ~100mm). The rheology (e.g., time dependent rheological profile, mortar slump flow, etc.) and mechanical (compressive strength, ultrasonic pulse velocity, porosity, and surface electrical resistivity) are used to assess the hardened state and microstructural characteristics. The various techniques are performed and considerations for future research are proposed.

1.3.

Thesis Organization

This thesis is divided into four chapters. Chapter 1 consists of an overview of the concrete industry and its impact on the environment, as well as the importance of reducing cement to produce eco-efficient cement-based materials. Moreover, Chapter 1 shows the research objectives and thesis organization. Chapter 2 presents a detailed literature review of the following topics: concrete mix-design, particle packing models, mobility parameters, and rheology. This chapter also provide a summary of various techniques currently used in the field to estimate and describe both pumpability and rheology.

Chapter 3 consists of a journal paper, which focuses on the appraisal of mobility parameters on the rheological behaviour of low cement content mortars.

Chapter 4 summarizes the conclusions of the work and provides for suggestions, limitations, and future work yet to be completed.

1.4.

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2.1.**Concrete mix-design**

As mentioned in Section 1, overall use of concrete as a building material continues to dwarf other construction building materials due to its interesting mechanical, economical and production characteristics. Concrete is a phasic material composed of; water, powders, aggregates (fine and coarse) and is arranged in a variety of methods based on input design parameters. The mixture proportioning and the ratios between the aggregates are subject to rigorous empirical tests and methodologies to achieve the desired design parameters. Figure 2.1 [1] shows the intermediate design process based on certain desired inputs and the outcome of mix design parameters. Normally, the inputs values are: strength (i.e., MPa); slump (mm); and durability (i.e., minimum w/c) whereas the output values are quantities of each ingredient (i.e. cement, water, fine aggregate, coarse aggregate in kg/m³). The empirical mix-design methodology most used is the American Concrete Institute (ACI) method, in which tables were developed based on amelioration techniques and field testing to facilitate the mix-design of conventional concrete [2–4]. However, many researchers suggest that mix-design and proportioning is more of an art form which is very unique from one production plant to another [4–6].

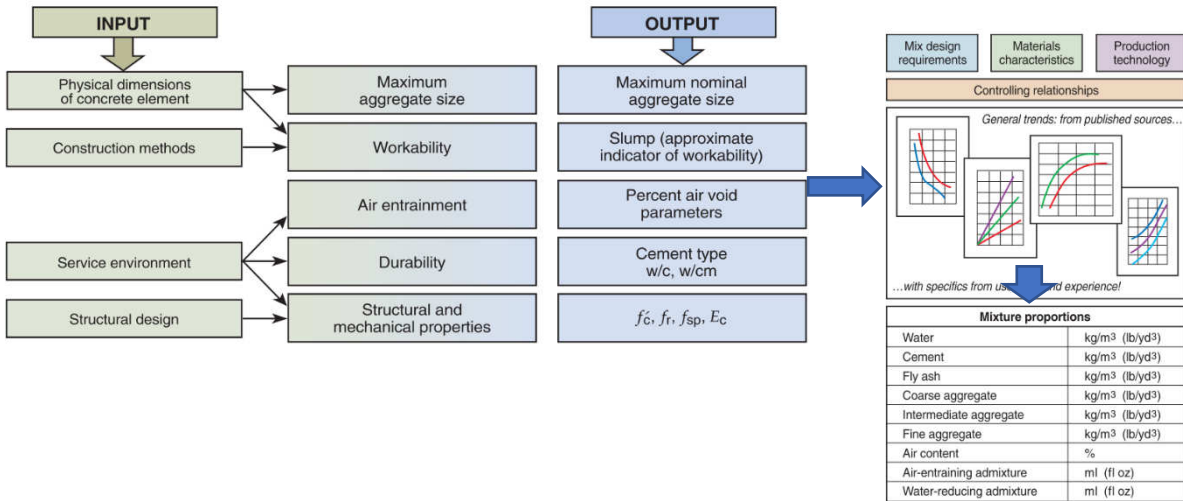


Figure 2.1: ACI mix design input vs output.

The ACI method begins by assessing the exposure conditions, and selecting the strength requirement [1]. The mixture proportions are then prescribed based on; 1) desired workability (i.e., slump); 2) fineness of sand; rodded volume of coarse. Use of mix optimization procedures commonly used to relate the mix proportions and suggest small tweaks to mix design [7,8]. The use of the ACI method considers the physical packing and resistance to bleeding and segregation in their works, by analyzing the solid volume of the coarse aggregate as the primary step in defining the water/paste volume. Finally, the remaining voids are filled with sand (called the absolute volume method). According to many authors ACI presents a robust method that incorporates for skeleton packing through the use of the absolute volume methodology in the coarse fraction [2,9]. Some of the drawbacks of this method are: 1) lack of addressing shape of aggregates; 2) lack of accountability for packing in the fines portion; 3) reliance on minimum w/c achieve durability (furthermore not accounting for packing in fines); 4) definition of slump for fresh state description. The shape of aggregates is accounted using in two distinct classifications, crushed or natural, which define their production method rather than their impact to packing density (and consequently impact to workability. Kosmatka notes that a 25kg/m³ is used when a natural coarse

aggregate is used, irrespective of its actual contribution to lubricant requirement. From a sustainability aspect, the indifference to packing in the fines (PSD <100 µm, cement replacement and reduction), is a large drawback, and the variable impacts can drastically change the fresh state behaviour [2]. Jiao [10] noted highly variable fresh state impacts in published works when fines packing was unaccounted for. John proposed using fillers as a part of binder content to account for the increased packing enhancement, but works have since disproven this theorization [11,12]. Wasserman noted that the minimum cement content had no impact on the durability of the concrete [13]. Furthermore, Hooton investigated the prescriptive requirements for minimum w/c in addressing durability and noted its inefficiency [14]. Lastly, the use of slump to define workability drastically underestimates the varying applications in the concrete manufacturing process. Banfill noted that [15] slump was not correlative with pumping ability, and proposed additional rheological parameters, notable viscosity, which has been gaining increasing popularity. ACI 304.2R notes slump provides a very limited capacity for estimating pump pressures [16]. Most designers use ACI as a first attempt and include for factory specific modifications based on input materials. The use of alternative mix design methods may offer a solution to some of the issues related with popular mix design methodologies. Packing model mix design has been growing in recent years due to its focus on improved packing in both the fines and coarse.

2.1.1. Particle packing models and their use in concrete mix-design

Although several particle packing model techniques are available in the literature, all of them aims to increase system's packing density (*Equation 2-1*); hence reducing its porosity. Particle packing models can be classified as: discrete and continuous.

$$P_d = \frac{V_s}{V} \quad \text{Equation 2-1}$$

Where: P_d is the packing density, V and V_s are the total volume and the volume of solids, respectively.

Discrete models estimate the porosity through inclusion of finer discrete sizes (i.e., gap-graded), thus increasing the packing. Furnas pioneered the discrete approach to packing models using a binary blend of materials with distinct sizes [17–19]. Works by Aim addressed the excess porosity when larger particles on the smaller particles through the proposed wall effect (Figure 2.2) [19]. When the finer particles were unable to fit into a voids in coarser particles, the loosening effect was additionally noted by Powers [17,18]. Works by Larrard, noted that experimental porosity of packing models required an additional compaction effort (i.e., energy imparted to obtain maximum packing) and this further deviates the application to workability of discrete packing models [2]. While able to achieve very high packing densities, discrete models present some drawbacks: 1) discrete models do not represent reality; 2) gap-graded models are prone to segregation; 3) discrete models require heavy computation efforts when increasing the number of discrete size classes. Romano noted elevated packing densities when comparing continuous models to Furnas's discrete model [20]. Various authors have noted that gap graded systems are prone to segregation, which poses a serious risk for pumping applications [16,21,22]. Fennis postulated that increasing the number of multi-modal sizes would significantly increase computation efforts for optimizing packing density [23]. In spite of the problems facing discrete models, their application is more common in literature, [2,17,24–27] (Table 2.1), however, Fennis's concluded that continuous models were much more practical and simpler to follow [23].

Table 2.1: Various packing models, discrete and continuous.

SNo	Year	Models	Packing system			Effect on packing		
			Binary	Ternary	Multi-modal	Wall effect	Loosening effect	Compaction effect
Discrete approach								
1	1929	Furnas	•					
2	1967	Aim and Goff	•					
3	1969	Powers	•				•	
4	1977	Toufar, Klose & Born	•	•		•		
5	1986	LPDM			•	•	•	
6	1994	SSM				•	•	
7	1997	Modified Toufar		•		•		•
8	1999	CPM			•	•		•
9	2000	Modified LPDM			•	•	•	•
Continuous approach								
1	1907	Fuller and Thomson			•			
2	1930	Andreassen			•			
3	1997	Modified Andreassen			•			

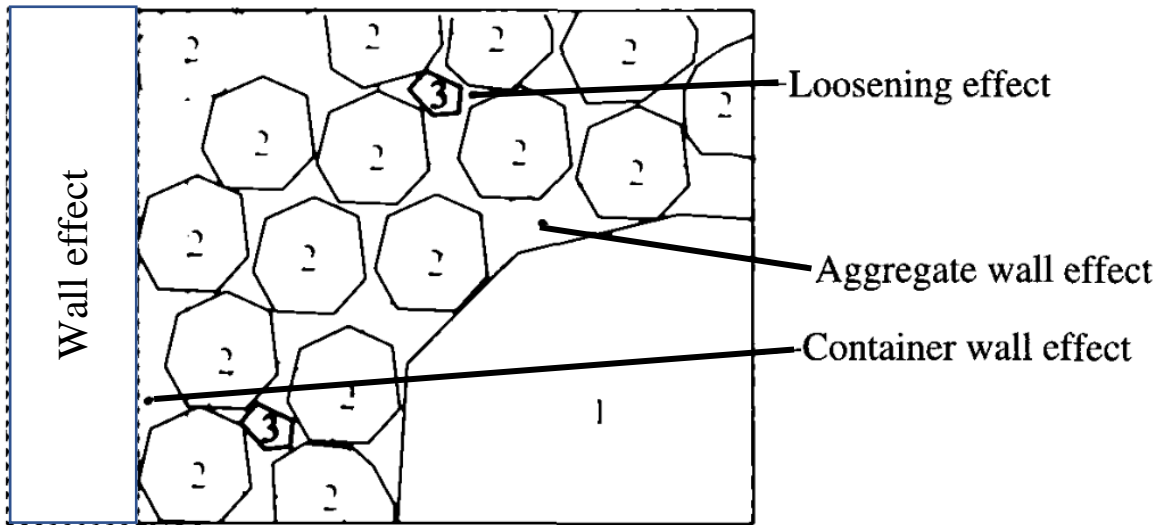


Figure 2.2: Various system impacts in discrete packing models[2][2][38][38].

Contradictory to discrete models, continuous particle packing models assume that there exists infinitely many sizes to achieve the desired filling effect [28]. The origin of these types of models was based on the work of Thompson and Fuller in the 1907 [28] and aptly named Fuller’s “ideal” curve (*Equation 2 2*). Andreassen proposed the existence of a similarity condition, also known as granulation image, which presents that regardless the scale analyzed, the same particle distribution can be seen as shown in Figure 2.3 [28–31].

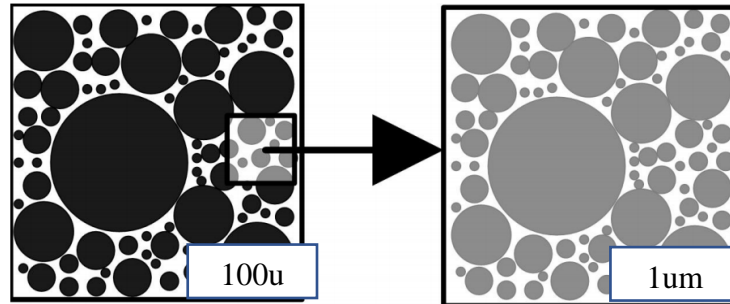


Figure 2.3: Depiction of the similarity condition in continuous packing models.

Andreasen's original equation, and his combined findings determined that the maximum packing density occurs when the distribution modulus, n , is between $1/3$ and $1/2$ [19,28]. The increase in the distribution modulus increases the quantity of relative coarser materials. This has shown to pose problems in fresh state behaviour, and for adequate workability, a distribution modulus of 0.2 to 0.3 generally produced more workable and flowable mixtures in works of refractory castables (Figure 2.4) [32].

$$CPFT = \left(\frac{D_i^n}{D_L^n} \right) \quad \text{Equation 2 2}$$

Where: CPFT is the cumulative percent finer than, D_i is the particle size of i^{th} particle in the assemblage, D_L is the largest particle size, and n is the distribution modulus.

Shaping technology	Dist. modulus
Slip casting and spray drying	0.19 – 0.21
Plastic forming	0.20 – 0.26
Refractory castables	0.2 – 0.3
	0.22 – 0.26
	0.26
	0.28 – 0.30
	0.32 – 0.42
	0.3 – 0.7
Dry pressing	0.33 – 0.5
	0.37
	> 0.5
	0.8 – 0.9

Figure 2.4: Andreasan distribution modulus n and its suggested applications.

Further works by Funk and Dinger noted that the system porosity was not reflected by only the maximum particle size, and they proposed the Modified Andreasan Model (*Equation 2 3*, *Equation 2 3*), which incorporates for the finest particle size in the distribution.

$$CPFT = \frac{(D^q - D_s^q)}{(D_L^q - D_s^q)} \quad \text{Equation 2 3}$$

Where: D_s is the smallest particle size, and q is the distribution modulus. Funk modelled the system porosity of the continuous distribution using a computer simulation based on the Westmann and Hugill model (*Equation 2 4*) [33].

$$\begin{aligned} V_{a1} &= a_1 x_1 \\ V_{a2} &= x_1 + a_2 x_2 \dots \\ V_{ai} &= \sum_{j=1}^{i-1} x_j + a_i x_i \dots \\ V_a &= \sum_{j=1}^{n-1} x_j + a_n x_n \end{aligned} \quad \text{Equation 2 4}$$

Where a_i is apparent volume of i^{th} size particle in mono-dispersion, x_i is the mass fraction of the i^{th} particles, V_{ai} is the apparent volume of i^{th} size particles, n is the number of particle sizes, and V_a is the maximum value of V_{ai} . A modification to the original algorithm [28] considers infinitely many particle sizes in continuous distribution consisting of a system. Funk used an small class sizes ratio (i.e., $i_1/i_2 < \sqrt{2}$) and modelled the packing density of the continuous packed particles. They calculated the system porosity (P_o) as per *Equation 2- 5* to *Equation 2- 7*;

$$P_f = 1 - \left(\frac{1}{CSR} \right)^{0.37} \quad \text{Equation 2- 5}$$

$$a_i = \frac{1}{P_f} \quad \text{Equation 2- 6}$$

$$P_o = 40\% \left(1 - \frac{1}{V_a} \right) \quad \text{Equation 2- 7}$$

Where P_f is the packing factor, CSR is the class size ratio between successive particle class sizes, and P_o is the system porosity, which can be determined when combining *Equation 2 4* to *Equation 2- 7*.

The results of Funk noted an absolute minimum at a distribution modulus (q) equal to 0.37, but, low values for system porosity (less than 5% for a wide PSD ranges) are apparent between 0.2 and 0.4 [28]. An important consideration is that the porosity mentioned by packing models are noted to be in the maximum packed condition, which is without any kind of lubricant and a completely dry system in perfect conditions.

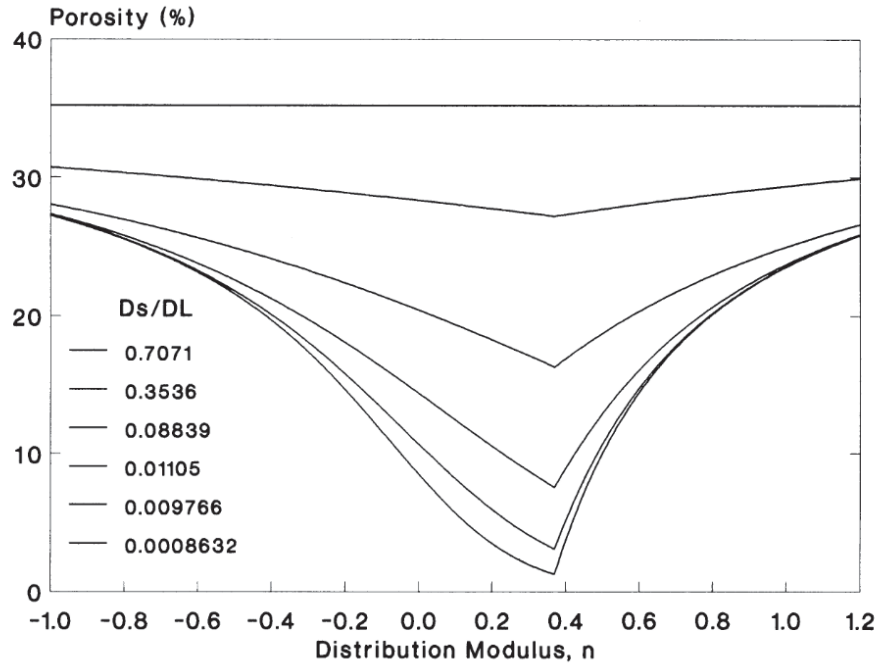


Figure 2.5: Distribution modulus n (q in this paper) and corresponding porosity.

With respect to practical applications, packing models have been successfully implemented to reduce the carbon footprint as well as produce high performance concretes [34–38], refractory castable [39,40]. While their use has shown to be environmentally friendly, there are some drawbacks to their applications in concrete: 1) optimal q values (i.e., 0.37) demonstrate poor fresh state performance); 2) appraisal of the workability has shown to be difficult. Romano noted that a distribution modulus of 0.37 resulted in undesirable fresh state behaviour (i.e., increased mixing energy) [20]. Similar results were obtained by Yousuf [41] who observed a 0-slump concrete with a distribution modulus of 0.37. Various works have also noted that use of lower distribution moduli improve the flowability of the mixtures [17,42]. In works by Yousuf [34] Works by Grazia [43] proposed the use of additional parameters for addressing the difficulty in appraising the rheology of highly packed systems. Additionally, current works into various workability parameters still focus on the slump of a mixture, which was shown not to be related to the application of a concrete mixture.

2.2.

Rheological behaviour of concrete

Besides the mechanical properties and durability characteristics, the slump of a fresh concrete mixture is a primary design parameter due its appraisal of field applicability. As early as 1918 with Abrams [6], the workability of the fresh concrete mixtures was designed according to a slump (consistency) of a material. This evaluation is currently still used in most mix-design methodologies due to its simplicity and availability for rapid testing. Roussel [44] attempted to correlate the slump to various concrete placing activities and noted that the slump test was lacking information to adequately describe the applicability of the concrete mixtures (Table 2.2). The approximate shear rate of the slump test is closer to 0 s⁻¹. Figure 2.6 [45] shows the various types of behaviours possible in fluids, and the base constitutive relationship is shown in *Equation 2- 8*

Table 2.2: Estimated shear rates for various concrete placement activities.

Flow pattern	Approximate maximum shear rate (s ⁻¹)
Mixing truck	10
Pumping	20–40
Casting	10

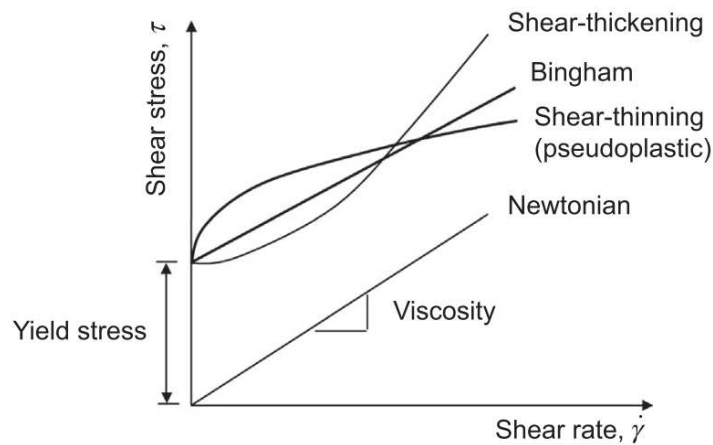


Figure 2.6: Various types of rheological behaviours w.r.t shear rate.

When addressing the rheology of a any mixture the general constitutive relationship is governed by *Equation 2- 8* (Newtonian liquid);

$$\tau = f(\dot{\gamma}) \quad \text{Equation 2- 8}$$

Where; τ is the shear stress, $\dot{\gamma}$ is the shear rate, and $f(\dot{\gamma})$ denotes the possibility for non-linear non-Newtonian mixtures. Additionally, fluids with a yield stress (i.e., energy required to initiate flow) are considered Bingham fluids (Equation 2-9 from Table 2.3). The curvature (i.e., non-linearity of the mixtures) describes the behaviour with respect to the increasing shear rates. Mixtures that require a decreasing and increasing shear stress as a function of increasing shear rates are labelled shear thinning and shear thickening, respectively. Shear thickening is linked to increased particle jamming, whereas shear thinning is related to preferential flow patterns in mixtures [46].

With the advent of various types and applications (e.g., no-slump, pumped, self-consolidating, roller-compacted, etc.), distinct models (e.g., Bingham, Herschel-Bulkley, Modified Bingham model) describe the shear stress of a fluid at a variety of shear rates ($\dot{\gamma}$, Table 2.3) [47–50].

Table 2.3: Various rheological models for estimation of shear stresses

Name	Equation	Equation Reference
Bingham	$\tau = \tau_0 + k_B \dot{\gamma}$	Equation 2-9
Modified Bingham	$\tau = \tau_0 + \mu_p \dot{\gamma} + c \dot{\gamma}^2$	Equation 2-10
Herschel Bulkley	$\tau = \tau_0 + k_{HB} \dot{\gamma}^n$	Equation 2-11

Where: τ is the shear stress, τ_0 is the yield stress, k_B is the viscosity constant of Bingham and $\dot{\gamma}$ is the shear-rate, μ_p is the modified Bingham viscosity, c is the modified Bingham constant, k_{HB} is the viscosity constant of Herschel-Bulkley and n is flow behaviour factor, which is $n < 1$ for suspensions presenting shear thinning behaviour and $n > 1$ for shear thickening ones [51].

The Bingham Model, Equation 2-9, was the commonly accepted model for describing the shear stress of concrete in relation to the shear rate. Cepuritis [52] postulated that for us in SCC's, where mineral and chemical additives are commonplace, the traditional Bingham model was insufficient

at higher shear rates. Further works have employed the Modified Bingham model, Equation 2-10, adequately describing the flow behaviour at increasing shear rates [53,54]. Works by Larrard noted negative yield stresses in Binghamian estimations and postulated that the Herschel Bulkley (Equation 2-11) model would better describe fresh concrete mixtures, observing <1% deviation from the measured data [48]. Various works including highly packed systems have noted shear thinning behaviours at shear rates between 0 and 1 s^{-1} [55,56]. In densely packed PPM's the use of mobility parameter has been suggested to appraise the full rheological picture by various authors [43,57–59].

2.3. Mobility parameters

As mentioned in Section 2.1.1, the increased packing density in particle packing model designed concrete mixtures can lead to problems in the fresh state [34,35,60]. In addition to being highly packed systems between the Alfred distribution modulus' of 0.21 to 0.37, their resultant rheological implications acts are not well understood [28,32,34]. The idea of fluid thicknesses governing the viscosity of a paste (with negligible yield stresses) has been proposed in various fashions as early as 1988 by Shaughnessy and Clark [61], but most research on the topic is based around physical testing of individual powders which adds a high experimental load per ingredient addition [62,63]. This has been experimentally re-iterated by many researchers over the years and various proposed methods of mobility parameters based on measured values are used in the determination of Kwan's [64] *water film thickness* (WFT) approach as well as in the determination of an iteration of the *inter-particle separation distance* (IPS) model from Hao [65] which showed an improved correlation with respect the predictive values. The original derivation of the IPS parameter (Equation 2- 12) was used to increase transport efficiency and better understand the flowability of coal-water slurries at high concentrations [28]. The proposed

parameter is based around the differentiation of two types of water; pore fluid forming the packed system, and fluid used as lubricant to allow for movement between particles.

$$IPS = \frac{2}{VSA} \left(\frac{1}{V_s} - \frac{1}{1 - P_{of}} \right) \quad \text{Equation 2- 12}$$

Where; VSA is the volume solids area m^2/cm^3 , V_s is the solids volume, and P_{of} is the system porosity as defined by the WH algorithm (*Equation 2 4*). Pileggi's work [66] use of IPS demonstrated a correlation when the solids fraction was kept constant.

Furthermore, works by Romano et. al [20] showed the possibility of use of a particle separation distance similar to IPS for use in the aggregate matrix termed the *maximum paste thickness* (MPT, *Equation 2- 13*). The main difference between the IPS and MPT is the analyzed force regime of the aggregate size, justified by works of Darby and Farris' particle size interactions[67,68]. By size contribution, the force regime of the IPS is governed by surface forces, whereas the MPT is governed predominantly by gravitational/frictional forces.

$$MPT = \frac{2}{VSA_c} \left(\frac{1}{V_{sc}} - \frac{1}{1 - P_{ofc}} \right) \quad \text{Equation 2- 13}$$

Where; VSA_c is the coarse aggregate volume surface area (m^2/cm^3), V_{sc} is the solids loading considering the paste volume fraction as interstitial fluid, and P_{ofc} is the WH (*Equation 2 4*) system porosity of the coarse aggregates.

The understanding between the relationship to the rheology of the concrete mix is still evident. The authors Innocentini [69] shows the two mobility parameters in conjunction with one another in Figure 2.7.

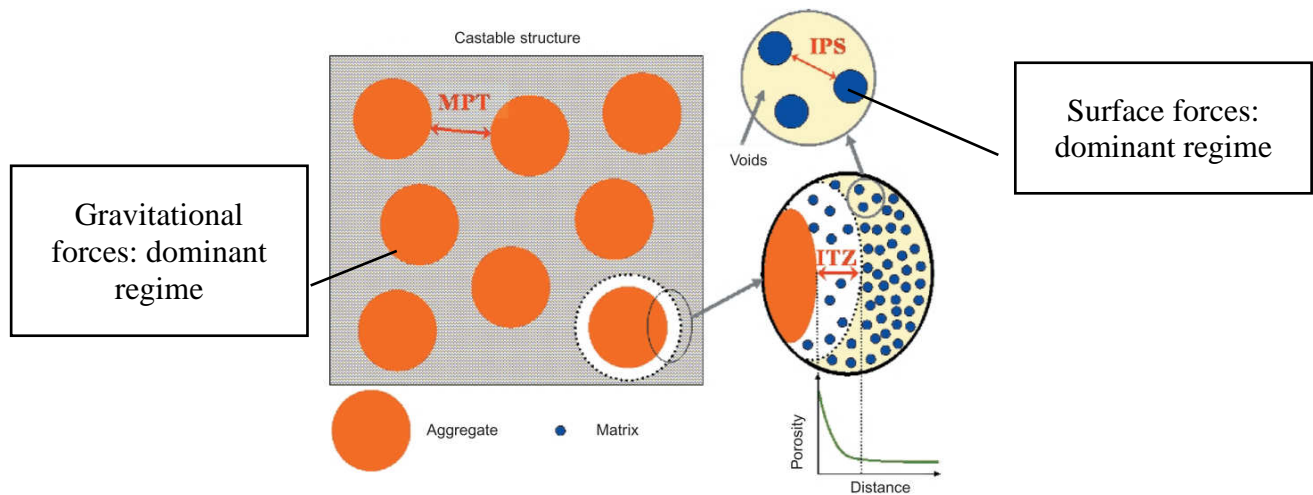


Figure 2.7: IPS and MPT from Innocentini.

Silva and Bonadia [70,71] noted that the increasing MPT(2.58 to 60.5, and 81.1 to 111.3 μm , respectively) increased the flowability and attributed this to the decrease in particle collisions.. . The values for IPS (0.2 and 0.81), and MPT (0.26-1.58) yielded different rheological behaviours as measured by the mixing energy applied [29,43]. Works by Menezes [58] who a strong relationship ($R^2=0.94$) between slump and the combined mobility parameters (MPT and IPS). Rebmann [72] proposed a predictive model using IPS and MPT for mixing torque, and final viscosity (RSE of 0.98 and 0.91, respectively). . The use of mobility parameters in concrete mix design to appraise eco-efficient mixtures, to the best of this authors knowledge, has not been comprehensively evaluated in increasingly eco-efficient mix design of highly packed systems. The inclusion of limestone fillers has shown promise in effectively replacement cement, and its impact on the mobility parameters in the fresh and hardened state is to be evaluated.

2.4. The use of inert filler in cementitious mixtures

Currently, the use of inert fillers are limited to around a 8% overall replacement of binder phase globally [11,73]. In North America, ASTM C33 limits to 15% of limestone filler [74,75] The use of limestone fillers in concrete presents an interesting opportunity to reduce the environmental

impact since their production is closely linked with the cement and aggregate production, and the non-calcined limestone does not produce the same CO₂ load as cement [76–79]. Inert filler addition into cement based systems are usually accompanied by three primary effects: 1) the nucleation/filler effect; 2) dilution effect; and 3) the packing effect [80].

2.4.1. Filler/nucleation effects

One of the first investigations into the nucleation effect was in 1976 by Soroka observing the reactivity of calcareous fillers from fine sand inclusions [81]. In 2014, Berodier et al. [82] coined the term “filler effect”, whereby the additional nucleation sites promoted the formation of CSH when fine (PSD < cement) limestone fillers were incorporated. The supplementation using limestone fillers increased the rate of heat generation as compared to other inert fillers such as quartz [82]. The filler effect was further investigated by Kumar on the hydration rate of C3S confirmed that limestone fillers increased nucleation of CSH [83]. The inclusion of these calcareous filler materials was further investigated by Bentz in 2015, and further observed that the various phases impacted the nucleation of CSH grains on the surface of the limestone [84]. The importance of the various impacts on the strength and microstructure are to be balanced when design concrete mixes, as various researches have shown that higher inclusions than current standards may not be detrimental to concrete and pose opportunity for efficient cement use [76,84,85].

While the filler effect was apparent at lower volumes of replacement, it was also noted that elevated levels of inclusion, a further effect, namely the dilution effect was apparent.

2.4.2. Dilution Effect

The impact of dilution on the strength of the concrete relates to the degree of hydration noted in the cementitious materials. Cyr [86] observed a marked reduction in strength at replacement rates of up to 75%. This was attributed to the increase in space between clinker hydration products, with a 13% increase in hydration degree of clinker grains using only 30% inert fillers [82,87]. This was further explained by which described the free water used as lubricant around the inert particles as hydration water for the clinker [88]. This theory was linked to the microstructure by Bonavetti's effective w/c ratio, which did not account for the filler enhancement through porosity reduction [89,90].

2.4.3. Packing Effect

Strength of materials is closely tied to the porosity of materials [22,91], and the enhanced packing through use of materials finer than cement enhance the physical skeleton and reduce the capillary spaces available for hydrate formation. The increased packing density through fine inert materials addition in the range of 10-15% has shown to enhance the mechanical performance of the concrete [85,92–95]. This effect is further optimized in PPM's as the physical optimization provides less space for hydrates, combined with the aforementioned similarity condition promoting efficiency of final product.

2.4.4. Limestone fillers and rheology

Jiao's comprehensive review [10] surveyed the use of limestone fillers in concrete and showed varying impacts on the rheology on specifically a mass basis (Figure 2.8). Zhang noted a decrease of viscosity and yield stress up to 10% mass replacement of limestone filler [96].

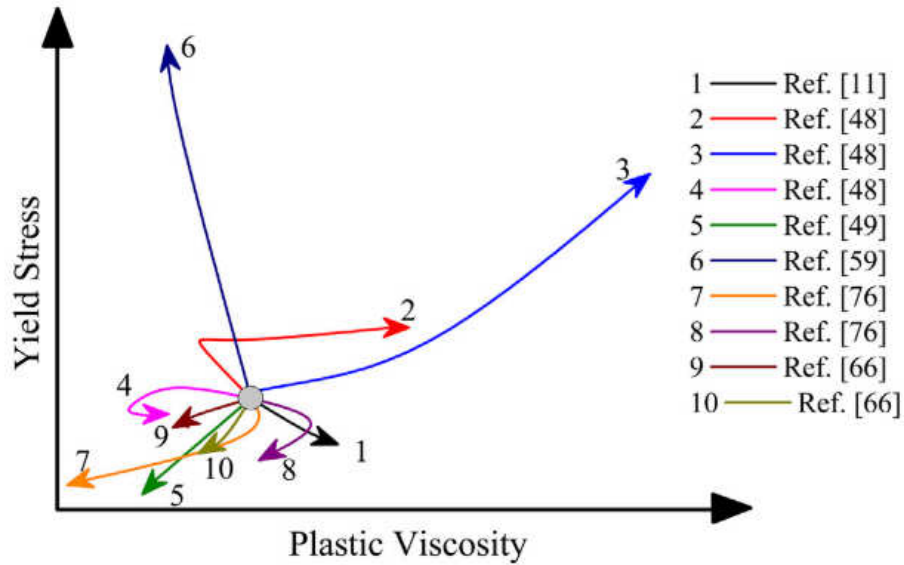


Figure 2.8: Various rheological implications because of increasing limestone replacement.

Vance noted a variable increase depending on type of limestone fillers (finer or coarser than the respective cement). Adjoudj [97] noted decreases to both plastic viscosity and yield stress as a result of 30% cement replacement with limestone filler at the same w/f ratio. The significant differences between the various studies were noted as being the PSD, SSA, and furthermore the packing density of the mixtures, which is accounted for in the combination of PPMs and mobility parameters. The previously mentioned works merely included for the limestone fillers at various rates, and a general conclusion was that the interparticle spacing, as affected by the various inclusions were the dominant factors in understanding the resultant impact to the workability [10,98].

2.5. Hardened state evaluation of packed concrete mixtures

While mobility parameters are predominantly related to the fresh state, some works have examined the hardened state as well. Works by Innocentini [69] evaluated the permeability, drying temperature as a function of both mobility parameters (i.e., IPS, and MPT) and noted they were

interrelated to the porosity/durability of the matrix. Alternatively, works by Romano et al [99] also showed a marked relationship between the MPT and the porosity, notably at constant paste volumes (constant IPS). Works of Shadkam [100] investigated the durability and noted that an increase in MPT provided a reduced transport capability for electrical ions and water. The work also noted that the paste density was an important parameter, and that the MPT alone was not able to predict the transport properties. Furthermore, the use of the predictive IPS_{cement} (Equation 3-14) dilution measurement [12] has also been shown to aid in correlating the compressive strength with inert fillers as a consideration for the distance between cementitious grains [82] in a packed system. This methodology accounts for the increased packing density from PF when compared to the pure cementitious counterparts[86].

$$IPS_{cement} * \frac{w}{f} = \frac{2}{VSA_{cement}} * \left(\frac{1}{V_{s(cement)}} * \frac{1}{1 - P_{of(cement)}} \right) \quad \text{Equation 3-14}$$

Where: IPS_{cement} is the spacing between the cement grains derived similarly to the IPS, w/f is the water to fines ratio considering the inert limestone as part of the fines fraction, VSA_{cement} is the volume surface area of the cement powder in m^2/cm^3 , $V_{s(cement)}$ is the volume of cement, considering the filler and water as the system lubricant, $P_{of(cement)}$ is the WH porosity as calculated in *Equation 2 4* [28]. The combined use of the dilution measurement to account for the decreased cement content will be examined for sustainability using an eco-efficiency measurement to evaluate its ability to assess the environmental impact to resulting mixtures.

2.6. Eco Efficiency/BI factor

To evaluate the eco-efficiency, the most commonly used to evaluate the cement efficiency is the binder intensity (b_i) [101]. The b_i relates the embodied energy [102] for a unit volume of concrete is based on the final concrete mix design and a given unitary characteristic (typically MPa). It has

been well determined that the concrete in-efficiency lies in the realm of the conventional concretes [11,101,103], where-by, at lower strengths, the efficiency drops significantly (increased b_i). Even strategic mix design methods [104] promote strengths above 50 MPa with low b_i ($\sim 5 \text{ kg}\cdot\text{m}^{-3}\cdot\text{MPa}^{-1}$), with conventional strengths and high comparative b_i for 40 MPa mixtures ($b_i > 10 \text{ kg}\cdot\text{m}^{-3}\cdot\text{MPa}^{-1}$). To define eco-efficiency on a moving scale, the outer bounds of 20 and 40 MPa typically have b_i of 15 and $8 \text{ kg}\cdot\text{m}^{-3}\cdot\text{MPa}^{-1}$, respectively. Works [94,105] in this regime have been accompanied by limited success, but typically employ high quantities of admixtures ($>2\%$ by mass of cement), which can offset the sustainability of a desired mixture. Furthermore, works by [62] propose a 20 – 40% quantity of optimal cement replacement by inert fillers can provide a 40% reduction to embodied energy while maintaining desired characteristics. Figure 2.9 shows the binder intensity of various mixtures, with the red line the benchmark for conventional concrete mixtures.

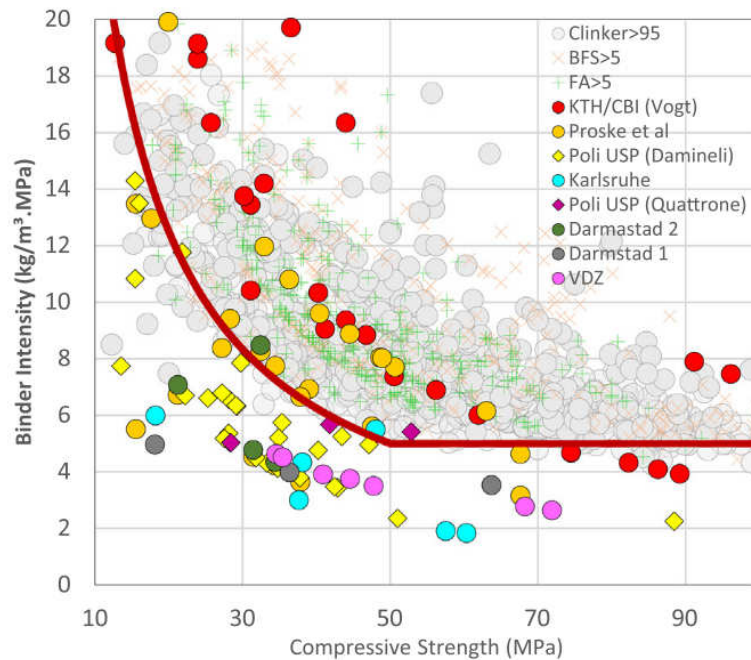


Figure 2.9: Binder intensity for worldwide mixture.

2.7.

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Chapter 3.

Investigation the Impact of Mobility Parameters on the Rheological and Hardened Behaviour of Low Cement Content Concrete Mixtures

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Abstracts

Literature demonstrates an increasing demand for eco-efficiency in concrete production worldwide. Variable outcomes in fresh and hardened states have been demonstrated when proportioning concrete mixtures using limestone fillers (LF) content and particle packing models (PPMs). To better understand highly packed system, twelve concrete mortar fraction was developed and the mobility parameters (*inter-particle separation distance* - IPS) and *maximum paste thickness* - MPT) are employed. The mixtures were developed with cement content ranging from 480 to 221 kg/m³ and filler content up to 245 kg/m³. Time dependent rheological profile and mortar slump flow, in addition to fresh pH, and batch temperature are performed in the fresh state. The compressive strength, ultrasonic pulse velocity, porosity, and surface electrical resistivity are used to assess the hardened state and microstructural characteristics. Results suggest that the MPT contributes to understanding rheological properties (i.e., flow behaviour factor, torque, and viscosity) of the mortar mixtures appraised, suggesting its use in concrete mix design would be an effective measure in supplementing PPM mix designs for eco-efficient concrete mixtures. Additionally, conventional mortar strength models do not account for a filler effect, and a novel dilution measurement IPS_{cement} is employed to appraise the physical effect of high volumes of inert limestone replacements. Then, binder intensity index was applied to confirm the eco-efficiency of the mixtures.

Keywords: Eco-efficient concrete, particle packing models, inert limestone fillers, inter particle separation distance, maximum paste thickness, rheology.

3.1. Introduction

Pressure is mounting in the construction industry to reduce its carbon footprint. Concrete production corresponds to upwards of 8% anthropogenic carbon dioxide emissions; hence, improving concrete mixture efficiency is a focus of a number of recent research programs [1,2]. Portland Cement (PC), which is one of the main concrete mixture components, is the most contributive to the embodied energy of a concrete mixture, accounting for 90% of its carbon footprint [3].

Amongst the possible solutions, two distinct practices which have shown effective are presented hereafter: a) using high volumes of supplementary cementitious materials (SCMs) [4,5] and limestone fillers (LF) [6–8] as a PC replacement, b) optimizing concrete mixtures through the use of advanced mix-design techniques (e.g., Particle Packing Models - PPM) [9,10]. While SCM use has been largely studied and applied, the increasing concrete demand outpaces the production of SCMs [7,11]. Conversely, LF has shown to be one of the most promising type of inert filler due to its proximity to concrete plants and abundancy for being a by-product of limestone aggregate production [6,8]. Use of upwards of 15% has demonstrated negligible impacts to concrete [12], however, increasing conventional mass based replacement approaches have shown variable impacts in both the fresh and hardened states. Mixtures with fine LF noted a microstructural enhancement due to the filler effect and the addition of nucleation points [13]. However, at increasing replacement levels, a mechanical dilution was also noted. The use of PPMs offers a methodology for efficient limestone replacement through the enhancement of the physical orientation of the system. However, these aforementioned packed systems generally present

challenging fresh state performance and trial-and-error experimentation is required for improving fresh properties [14–16]. Mobility parameters (e.g., Interparticle Separation Distance – IPS [17] and Maximum Paste Thickness [18] – MPT) have a good correlation to the fresh state behaviour (i.e., mixing energy and slump) of highly packed concrete mixtures containing high amount of LF [19,20], however, the investigated ranges between aforementioned studies present barriers to understanding the impact of each parameter. Further studies are required to present ideal ranges for IPS and MPT for each application (i.e., yield stress and viscosity) of eco-efficient mixtures developed using PPM and high LF.

3.2. Literature Review

A description of the important terminology is displayed in Table 1 to facilitate the flow of the text employed in this research.

Table 1: Description of acronyms used in the background of this research.

Acronym	Represents
f_c	Compressive strength
τ	Shear stress
η	Viscosity
IPS	Interparticle separation distance
IPS_{cement}	Interparticle separation distance of cement particles
MPT	Maximum paste thickness
MPT_{LARRARD}	Maximum paste thickness as defined by De Larrard
PC	Portland cement
P_{OF}	Dry porosity of system
SCM	Supplementary cementitious materials
SSA	Specific surface area
V_s	Volume of solids suspended in lubricant (water)
V_{sc}	Volume of solids suspended in lubricant (paste)
VSA	Volume surface area
w/f	Water-to-fines

3.2.1.

Eco-Efficient Concrete Mixtures and Use of Limestone Fillers

Distinct methodologies can be applied to measure the environmental impact of cement-based materials. Purnell et al. [21] investigated the relationship between mix-proportions, performance, and its contribution to CO₂ emissions and observed that the binder phase possesses the highest contribution to the environmental impact. Damireli [22] proposed the use of binder efficiency (b_i) to quantify the embodied energy [23] of cement based materials based on the amount of binder required to achieve a single unit of performance (commonly compressive strength in MPa). In this context, the conventional concrete mixtures (e.g., compressive strength < 40 MPa) have elevated binder intensities. Concrete mixtures with designed for 20 and 40 MPa have a b_i of 15 and 8 kg.m⁻³.MPa⁻¹, respectively. The reduced b_i improves a materials' ecological benefits, and a method to decrease binder content is to replace PC using LF. While worldwide use of LF represents only 8% of overall PC consumption [24] previous studies [25,26] suggest that limestone filler replacement ratios below 15% has negligible impacts to a concrete mixtures performance. Additionally, when im-properly mix-proportioned, the addition of limestone filler impact was not well understood in the fresh (e.g., slump and flowability [27,28]) and hardened states [13,29] (e.g., compressive strength, filler effect, dilution effect, nucleation sites) of cement-based mixtures. To better evaluate the limestone filler impact in the material fresh and hardened state properties, several studies [30,31] classify the limestone fillers into two categories: performance and replacement fillers. The former one is composed of fillers with particle size distribution (PSD) smaller than PC, in which improves packing density [32], enhances nucleation [13,33], and changes water demand [34]; whereas replacement fillers have PSD similar to PC, and increases cement dilution [35,36] with negligible impact to the fresh state [34]. The proper dosage of replacement and performance filler is also a factor for improving the sustainability of concrete mixtures. Using a 46, 20% (replacement

and performance limestone filler, respectively), Proske [37] produced eco-efficient cement-based materials with a b_i of $5.5 \text{ kg.m}^{-3}.\text{MPa}^{-1}$ (compressive strength of 28 MPa). After improving the hardened state with optimal performance filler content experimentally, a mechanical dilution was performed using replacement fillers to further reduce the cement content, further highlighting the need for efficient mix proportioning methods of PC replacement. Additionally, the evaluation of mechanical dilution at high replacements has previously been accounted for using the water-to-fines (e.g., water to the mass of powders ratio; w/f) [6]. Since the limestone filler are inert material, when w/f is adopted as similar values of water-to-cement ratios (w/c), the material compressive strength is negatively affected. However, this strategy increases the amount of free water in the system reducing the resistance to flow in the fresh state. This balance between fresh and hardened state is a common issue amongst existing eco-concrete mixture models [16,38,39] and enhancement of the system porosity through PPMs can be a solution to balancing both the fresh and hardened state properties.

3.2.2. Particle Packing Models

Previous studies show that eco-efficient concrete mixtures can be developed using PPM while calculating the optimum content of performance and replacement filler resulting in enhanced fresh and hardened state characteristics [16,37]. PPM are divided into two main categories: discrete and continuous. Discrete models represent distinct class sizes with a methodology for calculating the packing density [40], whereas continuous models consider an infinite number of class sizes with a similarity condition in the entire range [17]. Although both categories of PPM aim to optimize system packing density (Equation 3-1), authors have suggested that real aggregate blends are better represented by continuous models [9,16,41].

$$P_d = \frac{V_s}{V} \quad \text{Equation 3-1}$$

Where: P_d is the packing density, V and V_s are the total volume and the volume of solids, respectively.

One of the newest continuous PPM methods, the modified Andreasen model (also known as Alfred's model), was developed by Funk and Dinger [17] in 1980 as shown in Equation 3-2..

$$CPFT = \frac{D^q - D_s^q}{D_L^q - D_s^q} \quad \text{Equation 3-2}$$

Where: D is the particle size in question, $CPFT$ is the cumulative percent finer than D , D_L and D_s is the largest and smallest particle size in the system, respectively, and q is a distribution factor.

Based on computational analysis, it was calculated that Alfred model highest packing occurs at a distribution factor of 0.37 yielding a system dry porosity of 2.8% based on the Westmann and Hugill model [42]; however, packed systems are achievable between a distribution factor of 0.21 and 0.37 [17]. The use of the Alfred model are predominantly focused around the dry packing and a 30% reduction in b_i was noted in mixtures with no mechanical characteristics loss and an enhanced microstructure [9,10] when using a q -factor of 0.37. Conversely, a q -factor of 0.22 is recommended to improve concrete flowability since it results in a higher fines content and lower amount of coarse aggregates. Previous studies [43,44] attempt to define distribution factor ranges for a desired system workability, however this is usually a range of distribution factors which offer a trial and error approach. Müllera [14] also developed eco-efficient concrete model employing a 0.34 distribution factor due to negligible differences in packing density between the 0.37 to 0.34 distribution factor. Although this study is focused on Alfred model, literature shows that eco-efficient mixtures can be produced with varying packing models resulting in a b_i of $11 \text{ kg.m}^{-3}.\text{MPa}^{-1}$ (no fillers - 25 MPa) [9], and a b_i of $3.5 \text{ kg.m}^{-3}.\text{MPa}^{-1}$ (with fillers and admixtures - 43 MPa) [10]. It is important to note that both aforementioned studies noted potential difficulties in fresh state

with the reduced theoretical system porosity; however, Grazia's [10] Alfred model based on eco-efficient mixtures required considerably less admixture contents to achieve lower b_i as compared to other eco-efficient mix design methods [14,16,37]. The variance between the PPMs and their potential application [45,46] suggests a need for an additional link between PPM and rheological behaviour.

3.2.3. Mobility parameters and the fresh state properties of cementitious materials

In concentrated suspensions, particle interactions are critical in determining the material's rheology (i.e., viscosity, yield stress). Generally, the rheological behaviour [14,16] of a suspension is affected by a number of factors, including the solids volume fraction [47,48], specific surface area (SSA) [49], and PSD [50]. With the aforementioned criteria in mind, Funk [17] and Bonadia [51] developed the mobility parameters to quantify the spacing distance. These mobility parameters, especially in concentrated suspensions, may help assess the fresh state behaviour of highly packed mixtures. The mobility parameters are divided into two distinct force regimes.: The IPS [17] addresses the surface and capillary forces of particles smaller than 150 μm , (Equation 3-3) and the MPT [18,51] defines the distance of particles larger than 150 μm where gravitational forces are critical (Equation 3-3).

$$IPS = \frac{2}{VSA} \left(\frac{1}{V_s} - \frac{1}{1 - P_{of}} \right) \quad \text{Equation 3-3}$$

Where: VSA is the volume surface area of the fines fraction which is measured with BET ($\text{m}^2 \cdot \text{g}^{-1}$), V_s represents the solid volume fraction, and P_{of} represents the dry predicted porosity based on the Westmann ad Hugill Algorithm [42].

$$MPT = \frac{2}{VSA_c} \left(\frac{1}{V_{s,c}} - \frac{1}{1 - P_{of,c}} \right) \quad \text{Equation 3-4}$$

Where: the VSA_c refers to the volume surface area of the coarse fraction ($PSD > 150\mu m$), $V_{s,c}$ which is the solid volume fraction considering the fluid the paste phase, and $P_{of,c}$ represents the dry predicted porosity based on the Westmann ad Hugill Algorithm [42].

The IPS is governed by surface and capillary forces, whereas the coarser aggregate particles (MPT) are governed by gravitational forces [18]. Previous studies observed a good correlation between the mobility parameters, slump [19,52,53], and mixing energy [20,54]. Rebmann [20] used ranges of IPS (0.11 and 0.16 μm) and MPT (4 and 10 μm) to relate mixing torque. Grazia used ranges of IPS (0.36 to 0.81 μm) and MPT (0.26 and 1.58 μm) comparing the increasing of mobility parameters to increased mixing energy. The implementation of the mobility parameters has shown to be effective in appraising limited aspects of a concrete mixture's workability; however, to the best of the authors knowledge mobility parameters ranges that target application (i.e., yield stress and viscosity) have not been well defined.

3.2.4. Mobility Parameters and the hardened state properties of cementitious materials

Hardened concrete can be considered a bi-phase material, composed of cement paste and aggregates. When high amounts of filler are employed, a dilution measurement in both the paste phase and aggregate is required to appraise the impact to the hardened state. The $MPT_{Larrard}$ (Maximum Paste Thickness as defined and calculated by Larrard [55]) considers this approach and assesses the spacing between two intermediary platens (e.g., aggregates). Innocentini [56] noted that the IPS was able to appraise the permeability, and range of MPT (i.e., 55-115 μm) investigated offered little additional impedance. Using a range of IPS of 0.27 to 0.90 μm , Rengifo [35] observed a correlation between particle separation distances of cementitious grains and hardened state, addressing the cement-filler blends. (calculation of IPS_{cement} can be found in the Rengifo [35]) The

need for further investigation into the particle distance ranges and their hardened state properties is defined by the limited works that employ a conventional range for their use.

3.3. Scope of the Work

As stated in Section 3.2, further studies are required to appraise the range and ability of mobility parameters to assess the rheology of eco-efficient cementitious materials. In this context, this research will use PPMs and high amounts of limestone filler to produce eco-efficient cement-based materials. A total of twelve concrete mixtures were developed through Alfred model and four distinct levels of cement content (i.e., 324, 250, 200 and 150 kg/m³). This study is divided into two phases: 1) optimization of physical packing without and with limestone fillers at constant w/c and 2) comparison between mixtures employing decreasing cement contents (i.e., 250, 200 and 150 kg/m³) at a constant workability (i.e., varying admixture for 200mm slump flow) and varying mobility parameters: IPS (0.51, 0.46, 0.42 ±0.1µm) and MPT (0.37, 0.34, 0.32 ±0.1µm). It is worth noting that main goal of this research is to further understand the mobility parameters on the fresh state performance of cement-based materials: therefore, to reduce the variables this study is targeting the mortar fraction of the concrete mixtures presented above. The fresh state was appraised using a slump flow test and a rheological profile (i.e., yield stress and viscosity). Furthermore, the hardened state was evaluated using the compressive strength, Archimedes porosity, electrical resistivity, and pulse velocity. Finally, a new equation was proposed to predict the compressive strength of eco-efficient mortar mixtures.

3.4. Materials and Methods

3.4.1. Materials Characterization

Two inert carbonate-based fillers were used as replacement for a GU type cement. The PSD of the two fillers (ASTM 1797 Type A) of varying fineness and cement (CSA A3000 Type GU) were obtained using laser diffraction data from Hydro 2000S. To assess the cement based mixtures' fraction of particles < 4750 μm , a natural fine aggregate with maximum diameter of 4.75 mm was selected and classified as per ASTM C33 [57]. The particle size distribution of the materials is shown in Figure 3.1. The SSA of the cement, carbonate fillers and sand fraction were assessed using the Brunauer-Emmett-Teller method (BET) and physically adsorbed N_2 . Table 3.2 present the PSD and physical characterization (i.e., specific gravity, SSA, and VSA), respectively, of the materials used. To improve the fresh state of mixtures, two distinct water reducing admixtures were used: a) lignosulfonic acid salt based mid range water reducer (MR), and b) plasticizing polycarboxylate based superplasticizer (SP). The combination of the two admixtures were used to improve homogeneity without an excessively dosing the mixtures [35,58,59].

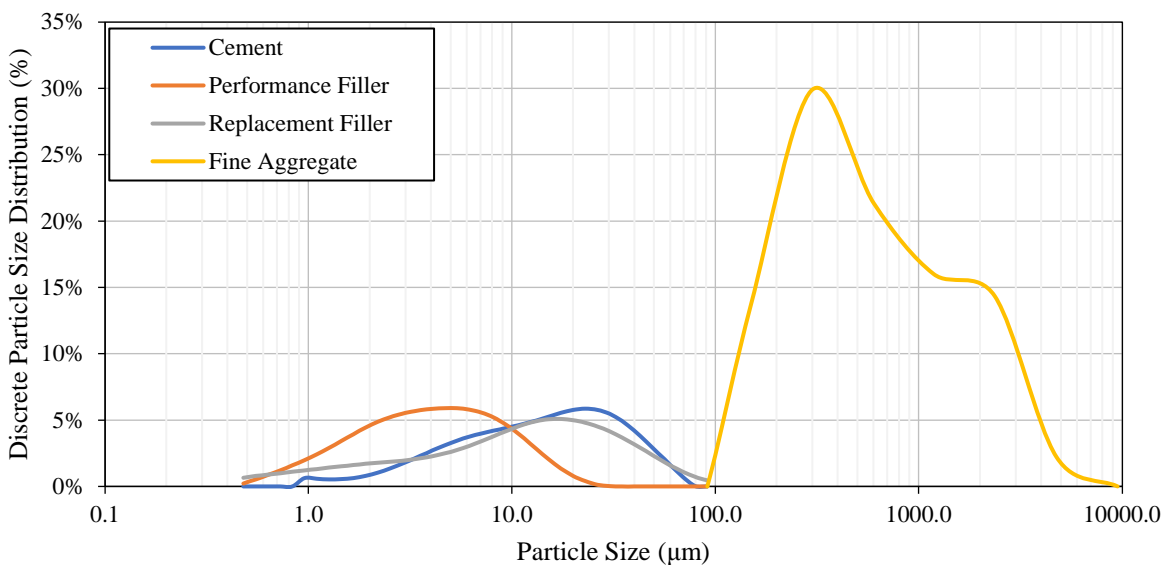


Figure 3.1: Particle size distribution of mortar components.

Table 3.2: Material characterization data

Material	Specific Gravity (g/cm ³)	SSA (m ² /g)	VSA (m ² /cm ³)
Cement	3.17	1.00	3.17
Replacement filler	2.66	0.90	2.39
Performance filler	2.6	3.70	9.62
Fine aggregate	2.74	0.92	2.52

3.4.2. Mix Design Procedure

Although a q-factor of 0.37 yields lowest theoretical system porosity (2.8%), previous studies found fresh state issues could be overcome by employing two q factors [10,60]. In this context, a total of twelve concrete mixtures were designed using Alfred model with 2 distinct distributions factors ($q=0.34$ for PSD < 150 μm and $q=0.31$ for PSD > 150 μm). The resultant systems yield a dry porosity of $3.0 \pm 0.1\%$ according to the Westman and Hugill model [42].

Additionally, the twelve concrete mixtures were further divided into two phases. Phase 1 evaluated the impact of optimal cement replacement considered to be eco-efficient (i.e., 324 kg/m³ replaced with limestone filler to 250 kg/m³ of PC) with constant w/c (i.e., 0.60, 0.56, 0.52). The three w/c represents a range of conventional concrete mixture strength (25, to 30 MPa). It is worth noting that the optimum performance filler content of 13% was determined using a method of least squares to achieve the designed q-factor (0.34) curve, whereas the replacement filler was used to obtain the cement contents mentioned above. In the second phase, the cement content was further replaced by the replacement limestone filler to achieve the desired eco-efficiency (i.e., 250, 200 and 150 kg/m³) with constant free water contents (148, 137 and 129 kg/m³). The free water contents selected additionally represent the varying mobility parameters based on previous studies [9,10,35]; IPS (0.51, 0.46, 0.42 $\pm 0.1\mu\text{m}$) and MPT (0.37, 0.34, 0.32 $\pm 0.1\mu\text{m}$).

As per conventional mix-design methodologies, the air content of the concrete mixtures was maintained at 2% for all mixtures and admixture contents were added based on the total mass of fines (i.e., cement and fillers). As mentioned before, to eliminate a single variable (i.e., coarse particles > 4750 μm), the volumetric ratios of the material fraction being investigated was maintained. The final mixture designs for the mortar fractions are shown in Table 3.3. It is worth noting that the mixtures were named using the following convention: cement content relative (i.e., 324, 250, 200, 150 kg/m^3), free water content (i.e., 148, 137 and 129 kg/m^3 represented by H, M, L, respectively), and w/c. For example, the mixture 320-0.60H contains 320 kg/m^3 of cement, a w/c of 0.60 and a relatively high IPS and MPT.

Table 3.3: Mix design for the eco-efficient concrete mixtures being evaluated.

	Mix Name	Cement kg/m^3	Filler – P kg/m^3	Filler – R kg/m^3	Sand kg/m^3	Water kg/m^3	w/c	MR %	SP %
Phase 1	320 -0.60H	463	-	-	1,501	278	0.60	-	-
	324 -0.56M	471	-	-	1,529	264	0.56	0.08	0.08
	328 -0.52L	481	-	-	1,559	250	0.52	0.20	0.15
1 & 2	250 -0.60H	370	60	46	1,615	224	0.60	0.20	0.50
	250 -0.56M	373	61	51	1,647	209	0.56	0.40	0.60
	250 -0.52L	375	62	55	1,673	197	0.52	0.90	1.00
Phase 2	200 -0.74H	297	60	109	1,623	220	0.74	0.30	0.50
	200 -0.69M	299	61	115	1,656	205	0.69	0.80	0.40
	200 -0.64L	300	62	119	1,681	193	0.64	1.00	1.00
	150 -0.97H	222	60	172	1,639	214	0.97	0.30	0.50
	150 -0.89M	223	61	178	1,671	199	0.89	0.60	0.70
	150 -0.84L	224	62	182	1,695	188	0.84	1.00	1.00

Note: Filler - P and Filler - R refer to performance and replacement limestone fillers,

respectively.

3.4.3. Fabrication and testing methods

Twenty litres of mortar were fabricated for each mixture tested. Limestone was mixed with PC in advance and added to the sand before adding water to the mixture. First, the fresh state tests were performed then, twelve 100 x 200 mm cylinders were fabricated for each mixture to appraise the hardened state behaviour [61]. After 24 hours of fabrication, the cylinders were demoulded, and specimens moist cured with relative humidity of 95% \pm 5% and temperature of 22°C \pm 2°C until testing.

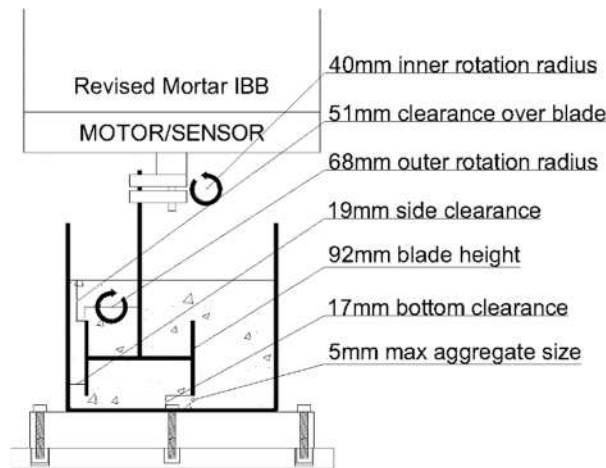
3.4.4. Fresh state assessment

All concrete ingredients were mixed in a pan mixer. The fresh mixture temperature (\pm 0.1°C) and the pH were assessed at the end of a 10- minute mixing period for each mortar mixture using litmus strips (\pm 0.5 pH). For this study, the fresh state properties of the samples are appraised using two methods (i.e., slump flow and a rheology). The slump flow was measured using a mortar slump cone (ASTM C1810 [62], 50 mm upper diameter, 100 mm bottom diameter and 150 mm height). The added mixture volumes were rodded to remove voids and promote homogeneity of samples. The conical sample mould was slowly elevated with a constant speed over 5 seconds, and the final diameter was measured with the aid of a circular measuring template. Additionally, the rheological appraisal (i.e., yield stress and viscosity) was performed in a rotation speed controlled IBB planetary rheometer with two rotation radii (i.e., inner rotation radius of 40 mm, outer rotation 68 mm radius) [63–65] and an H-impeller with a 132 mm diameter and 92 mm height. A mortar bowl with 233 mm height and 262 mm diameter (Figure 3.2) was with the width of evaluated mortar flow comparable to that of concrete [63]. It is worth noting that although IBB output values (i.e., G – torque in N.m and H - viscosity in N.m.s) are not presented in fundamental units, previous

studies [63,66,67] have noted that they correlate linearly to the fundamental units (e.g., τ - shear stress in Pa and η - viscosity in Pa.s).

In addition to the yield stress, the rheological profile data was evaluated with a two-cycle process to evaluate the material's viscosity [68]. First, an increase in shear-rate up to approximately 0.7 s^{-1} , followed by a decrease period at the same stepwise, (Figure 3.2b). The resulting curves represent the comparative change in shear stress with respect to shear rate and the evaluation of viscosity is performed. The evaluated mixtures were in a similar condition during the second descending cycle and the rheology (i.e., yield stress and viscosity) was appraised of this ramp [69,70].

a)



b)

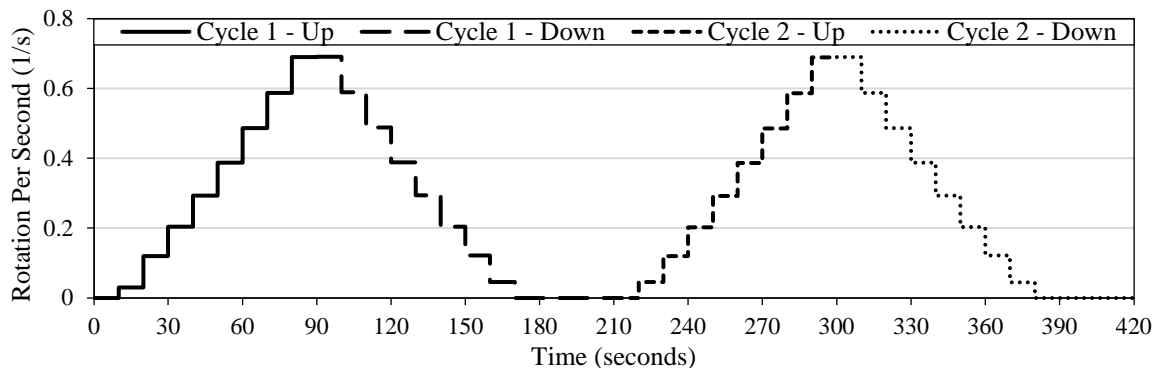


Figure 3.2: a) revised Mortar IBB Rheometer dimensions and b) Rheometer 2-cycle testing shear ramp profile.

After the initial consistency and rheology was assessed, a time-dependent evaluation was performed. The yield stress (slump flow) was appraised again at 15, 30, 60, 90 and 120 minutes and the Equation 3-5 was used to compare the slump loss in a relative fashion. Additionally, the rheology of the mixtures (i.e., yield stress and viscosity from rheometer) were subjected to the same tests after 15 and 30 minutes.

$$\text{Slump Loss} = \frac{(D_l - d_t)}{(D_l - b)} \% \quad \text{Equation 3-5}$$

Where: D_l is the initial mortar slump flow, d_t is the mortar slump flow measure at time t , and b is the base diameter of the cone (100 mm).

3.4.5. Hardened State Evaluation

The surface electrical resistivity and the ultrasonic pulse velocity (UPV) were tested on three cylinders at 28 days, whereas the compressive strength of these cylinders was gathered at 7, 14 and 28 days as per ASTM C39 [71]. The surface electrical resistivity (ER) was measured using a device based on the Wenner probe as per AASHTO T358-15 [72]. Four probes located in a straight line (and equally spaced) apply a current from the outer probes to the mortar sample surface and the potential drop is measured by the interior probes.

The UPV was measured as per ASTM C597 [73]. The Equation 3-6 relates the speed of the pulse to through the hardened mortar sample to dynamic modulus of elasticity (E).

$$E = \left(\frac{t}{L}\right)^2 \rho * \frac{(1 + \mu)(1 - 2\mu)}{(1 - \mu)} \quad \text{Equation 3-6}$$

Where: t is the time for a constant wavelength to traverse the length of the cylinder, L is the length of the cylinder, ρ is the density of the concrete, and μ is the dynamic Poisson's ratio (0.2 mm/mm).

The apparent porosity (AP) was obtained using Archimedes method [74] at 28-days. At each age, a cylinder (100 mm diameter x 200 mm height) was cut into three sections. The sections were dried at 60°C until a constant mass (m_d). The samples were then submerged (in water) in a vacuum

chamber. After 24 hrs, the samples were removed from the vacuum chamber and the immersed mass (m_i) and the wet mass (m_w) were measured. Equation 3-7 was used to calculate the apparent porosity of each mixture.

$$AP (\%) = \left(\frac{m_w - m_i}{m_w - m_d} \right) * 100\% \quad \text{Equation 3-7}$$

3.5. Results

3.5.1. Slump, slump loss, pH and fresh density

Table 3.4 shows the results for the pH, temperature, fresh density, and air content. As temperature may affect most of the fresh state properties, the batch temperature was measured and was within $22.0 \pm 2^\circ\text{C}$ for all mixtures appraised, regardless of the cement content selected. Moreover, one may notice that most mixtures (9 out of 12) presented a pH of 12.5. Only 328-0.52L displayed a 0.5 increase of pH and the two mixtures with lowest cement content and w/c (150-0.97H and 150-0.84M) yielded a pH of 12. Mixtures with a 38% reduction of cement content, yielded similar alkalinity. Regarding the fresh density, a small difference was seen between the all the groups which had on average achieved 2292 kg/m^3 and standard deviation of 27 kg/m^3 .

Additionally, Table 3.4 presents the IPS and MPT calculated for the 12 cement-based mixtures appraised. The ratio of materials in the fines (PSD < 150 μm) remains constant, therefore the IPS does not change when compared to the full range of particles in the mixture. However, the relative volume of the coarse particles (4750 μm to 19000 μm) removed results in an varied paste thickness (i.e., the measured Maximum Paste Thickness evaluated fraction). The MPT shown in Table 3.4 corresponds to the evaluated mixtures in this study. As previously mentioned, the initial mortar slump flow of all mixtures was maintained at $200 \pm 15\text{mm}$. Moreover, the higher the mobility parameters (MPT and IPS), the lower the quantity of admixtures required for the target slump. For example, 320-0.60H did not require any admixture, whereas 324-0.56M and 328-0.52L required

0.16% and 0.35%, respectively. Although G2 has the same w/c of G1, on average 1.0% more admixture was required to achieve the target slump due to the lower mobility parameters. However, Phase 2 mixtures (G2, G3, G4) required a similar dosage mobility parameter grouping (0.8%, 1.2% and 2% for the respectively H, M, L) to achieve the target slump flow.

Table 3.4: Fresh state properties of the various mixtures.

Mix Name	pH	Fresh Density (kg/m ³)	Batch Temp (°C)	MR (%)	SP (%)	IPS (µm)	MPT (µm)	Mortar Slump Flow (mm)
320 -0.60H	12.5	2262	22.1	-	-	0.92	0.54	208
324 -0.56M	12.5	2263	21.7	0.08	0.08	0.85	0.48	185
328 -0.52L	13.0	2260	23.2	0.20	0.15	0.79	0.45	195
250 -0.60H	12.5	2292	20.5	0.20	0.50	0.54	0.40	195
250 -0.56M	12.5	2317	20.8	0.40	0.60	0.49	0.38	187
250 -0.52L	12.5	2320	21.2	0.90	1.00	0.45	0.36	197
200 -0.74H	12.5	2286	20.9	0.30	0.50	0.51	0.40	190
200 -0.69M	12.5	2319	20.7	0.80	0.40	0.46	0.37	197
200 -0.64L	12.5	2330	22.5	1.00	1.00	0.42	0.35	190
150 -0.97H	12.5	2258	23.7	0.30	0.50	0.49	0.38	192
150 -0.89M	12.0	2283	20.8	0.60	0.70	0.44	0.36	198
150 -0.84L	12.0	2317	21.7	1.00	1.00	0.40	0.34	185

Figure 3.3a and b present the slump loss of Phase 1 (G1 and G2) and Phase 2 (G2, G3, and G4) mixtures, respectively.

It is worth noting that G2 results were repeated in Figure 3.3a and b to facilitate the visual comparison between group with same w/c and w/f, respectively. From Figure 3.3a, one can see that G1 had lower slump loss than G2 after 15 minutes. Additionally, 320-0.60H and 324-0.56M only achieved 100% slump loss after 120 minutes, whereas 328-0.52L and all G2 mixtures achieved 100% slump loss after 60 minutes. When comparing mixtures with lower cement content, Figure 3.3b shows that all mixtures lost 100% consistency by 60 minutes. However, 250-0.56M and 150-0.84L, had 100% slump loss by 15 minutes. Moreover, mixtures with higher w/f presented less slump flow loss over time. However, at the 30-minute, mixtures with middle w/f (250-0.56M, 200-0.69M, 150-0.89M) displayed the highest slump flow loss (average 93%), while mixtures with high and low MPs presented an average slump loss of 64% and 84%, respectively. Alternatively,

the decreasing cement contents (250, 200, 150 kg/m³) did not directly impact the consistency loss at 30 minutes as the losses presented less than 20% variability amongst the cement contents.

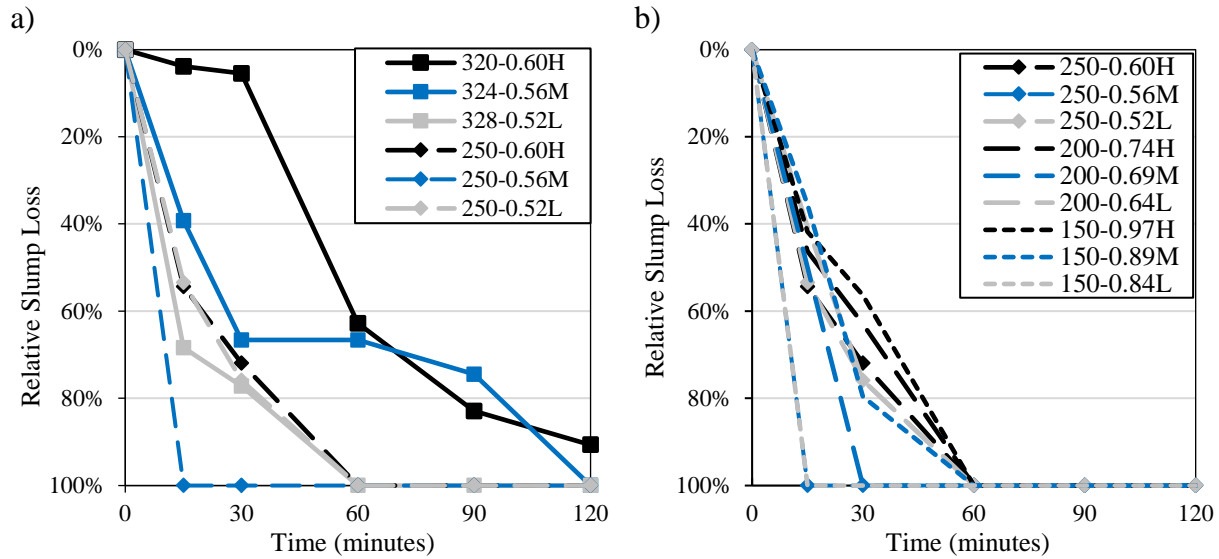


Figure 3.3: Slump Loss in a) Phase 1 mixtures and b) Phase 2 mixtures.

3.5.2. Rheological Behaviour

The raw data from the second descending cycles are presented for Phase 1 and Phase 2 in Figure 3.4a and Figure 3.4b, respectively. Mixtures without limestone fillers (cement content 320 kg/m³) presented with a linear relationship between the rotation rate and the torque. Non-linear shear rate behaviour (e.g., decreasing shear stress at higher shear rates) was apparent with the increasing eco-efficiency (i.e., reduced cement content from 250 to 150 kg/m³) as demonstrated in the Figure 3.4b. To facilitate the comparison of the mixtures Figure 3.4c, d, presents the torque values at low and high shear rates for all mortar mixtures are presented. As previously mentioned, the initial slump flow was kept constant for all mixtures, which resulted in a similar yield stress for all mixtures ranging from 1.3 N.m to 2.4 N.m (Figure 3.4c). However, in Figure 3.4d, one may notice that the mixtures presented different final torque measured at higher shear rate regime ($\sim 0.7 \text{ s}^{-1}$). Although same w/c was selected, mixtures with 324 kg/m³ cement content had a lower variability of final torque (ranging from 3.8 to 7.4 N.m) than mixtures with 250 kg/m³ cement, which varied

from 9.1 to 17.5 N.m. In Phase 2 (mixtures with same free water content and varying admixtures), the final torques increased as a function of the free water decrease (i.e., H, M, L). Expect, 150-0.84M, which is developed with middle range free water, presented similar torque (19.4 N.m) to 250-0.52L (low water) and 200-0.64L (low water). Moreover, mixtures with higher cement content (250 kg/m³) yielded lower final torque than (200 kg/m³) and (150 kg/m³), except for mixture 250-0.56M (15.2 N.m) compared to 200-0.69M (13.1 N.m).

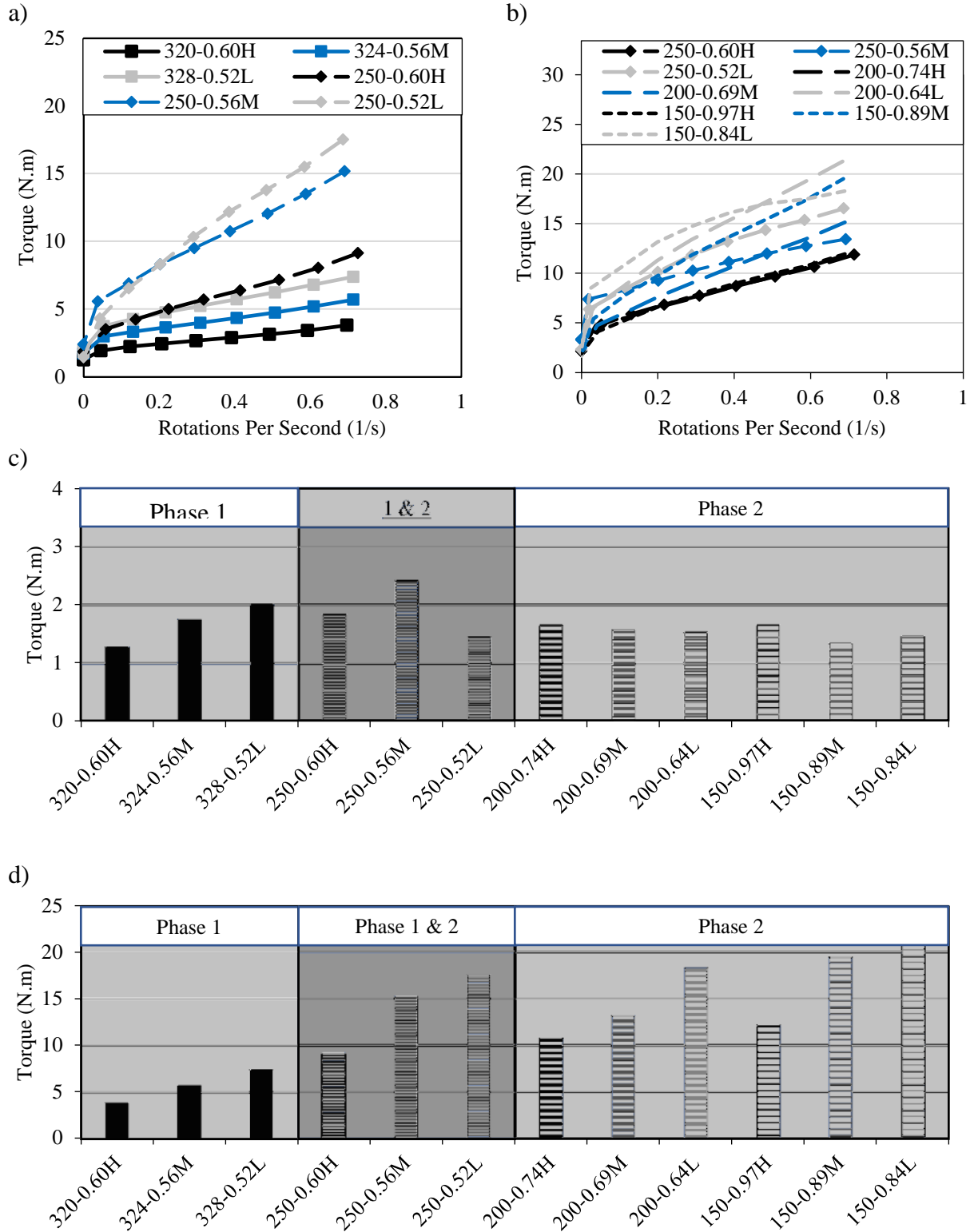


Figure 3.4: Raw rheometer data for a) Mixtures from phase 1, b) eco-efficient mixtures from phase 2, c) initial torque (0 s^{-1}) and d) high shear rate torque (0.7 s^{-1}) for Phase 1 and Phase 2 mixtures.

The initial torque and final torque measured at 0,15, and 30 minutes is presented Figure 3.5. One may note that mixtures with no limestone replacement had a marginal increase (on average 0.3 N.m) in the initial torque when compared from 0 to 30 minutes test. Although mixtures with 250 kg/m³ of cement were developed with same w/c, 250-.0.56M and 250-0.60H had a significant initial torque increase after 30 minutes (3.6 and 3.0 N.m, respectively). In Phase 2, mixtures with the highest cement content (250 kg/m³) represented the largest initial torque increase over 15 and 30 minutes. Although a clear increase trend in the initial torque is seen in Figure 3.5a, at higher shear rates (0.7 s⁻¹) Figure 3.5b shows a marginal change after 30 minutes. Similar to trends observed in the initial torque, mixtures without replaced limestone (cement content of 320 kg/m³) presented a slight increase of 0.5 N.m at high shear rates (0.7 s⁻¹). Nevertheless, when comparing the final torque after 30 minutes of mixtures with same w/c, mixtures with 250 kg/m³ resulted in more than twice the torque of those without any limestone filler. In Phase 2, eco-efficient mixtures (G2, G3, and G4) appears to not follow a clear trend. However, analyzing mixtures with same cement content, the lower the free water (i.e., H, M and L) the lower the final torque, except 150-0.89M at 30 minutes test.

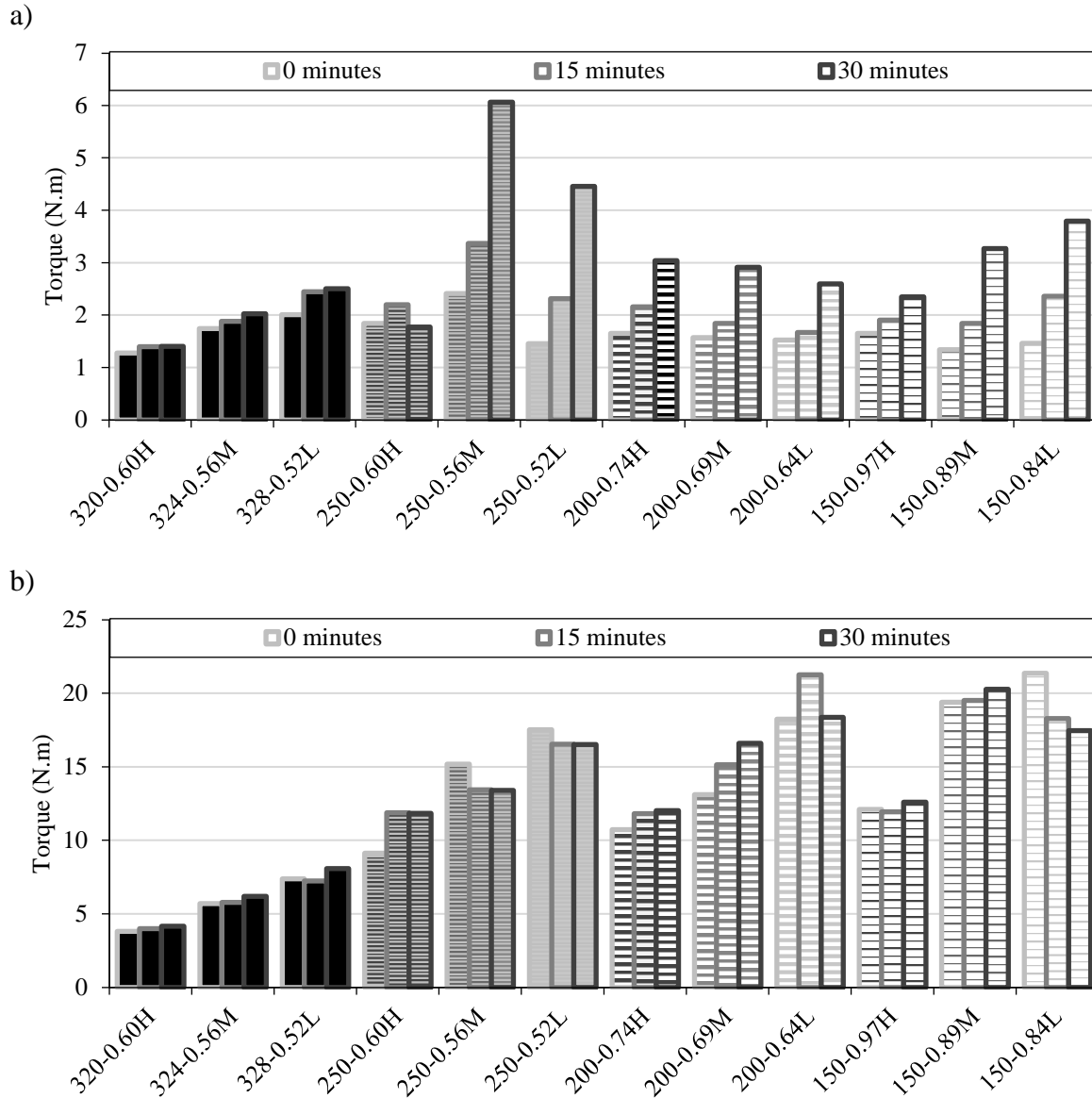


Figure 3.5: Time dependent rheological data for shear rates corresponding to a) 0 s^{-1} and b) 0.7 s^{-1}

1.

3.5.3. Compressive Strength

The compressive strength of the mortar mixtures appraised is presented in Figure 3.6. In general, all mixtures yielded 82% (SD 6%) and 91% (SD 3%) of final compressive strength after 7, 14 days, respectively). After 28 days, mixtures containing 22% less cement content, same w/c, and $\sim 105 \text{ kg/m}^3$ of limestone filler (i.e., mixtures with 320 to 250 kg/m^3), showed the promising ability

of producing eco-efficient mixtures since it resulted on average 12% higher compressive strength. The physical enhancement is further exemplified by the comparison of 328-0.52L and 250-0.56m, which resulted in similar 28-day compressive strength (~40 MPa) even though the w/c increased from 0.52 to 0.56 and the cement content decreased from 328 to 250 kg/m³. Regarding mixtures with cement content of 200 and 150 kg/m³, the 28-day compressive strength ranged from 27.9 to 37.0 MPa and from 13.4 to 24.1 MPa, as expected it was significantly lower than G1 and G2 results due to the increased w/c (from 0.74 to 0.64 and from 0.97 to 0.84, respectively). Moreover, the eco-efficiency potential of Phase 2 mixtures was evident as 250-0.6H and 200-0.64L yielded similar compressive strengths (~37 MPa) with a 16% decrease of cement content and increase of w/c by 0.04.

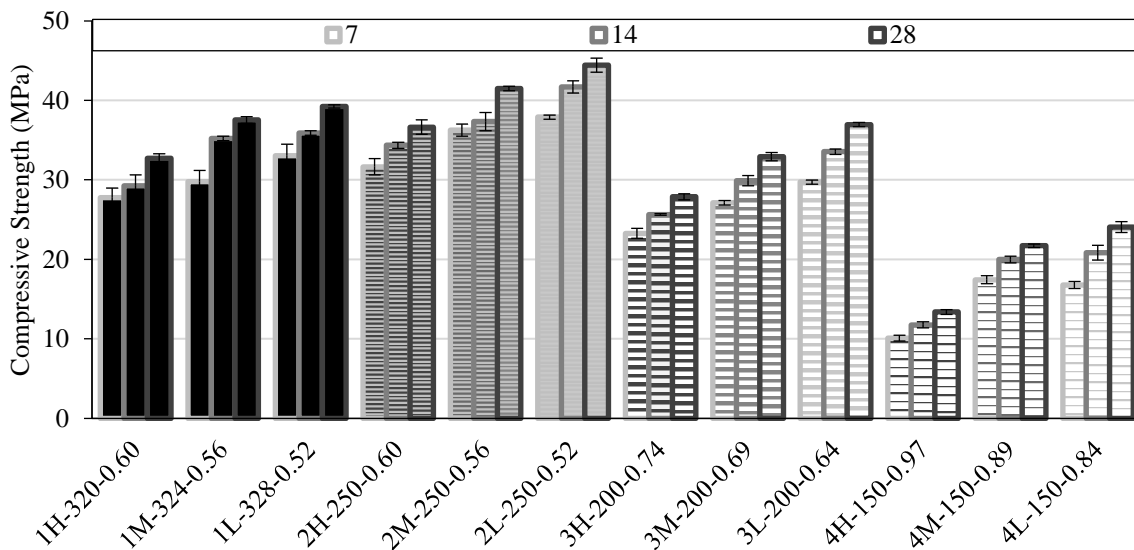


Figure 3.6: Compressive strength over time for all mixtures.

3.5.4. Physical properties

Figure 3.7a presents the capillary porosity and surface ER of evaluated mixtures. Since porosity is direct proportional to the paste microstructural quality, similar trends between the porosity and the ER were observed, where the lower the porosity the higher the mixture ER. For instance, in G1,

328-0.52L yielded porosity and ER of 10.5% and 5.1 k Ω .cm, respectively, while 320-0.60H achieved 9.2% and 7.8 k Ω .cm, respectively. Proving the efficiency of the eco-friendly mixtures, 250-0.52M and 250-0.60H achieved on average 18% lower porosity and 14.5% higher ER than G1 with same w/c due to their enhanced microstructure. The only exception was found on the comparison between 328-0.52L and 250-0.52L, in which the latter one presented a slightly lower porosity (reduction of 2.0%) and surface ER (decrease of 0.9 k Ω .cm). In Phase 2, as expected due to the high w/c on mixtures with low cement content, the porosity increased, and the ER decreased as a function of the w/c.

Moreover, Figure 3.7b shows the dynamic modulus of elasticity (MoE). Similarly to ER, UPV results from Phase 1 (cement contents of 320 and 250 kg/m³) follow the same trend where the lower the porosity the higher the UPV. Mixtures with the same w/c (i.e., 0.60, 0.56, 0.52) presented similar MoE, ranging between 35, 37 and 38 GPa, respectively. Moreover, regardless the cement content, eco-efficient mixtures (G2, G3, and G4) achieved similar MoE of 37.5 GPa with standard deviation of 2.37 GPa. Furthermore, unlike the ER and porosity, when comparing mixtures with same free water (i.e., H, M and L), the samples yielded MoE of 34.9, 38.0, and 39.6 GPa, respectively. Moreover, from Figure 3.7b, one may notice that the MoE of mixtures in each distinct range of free water (i.e., H, M and L) appears to increase (34.9, 38.0 and 39.6 GPa, respectively with a COV less than 0.2%) independent of the microstructure (w/c). Therefore, when mix-proportioning eco-efficient mixtures with high filler content, the MoE has a direct relationship to w/f instead of w/c, where the higher the w/f the lower the MoE.

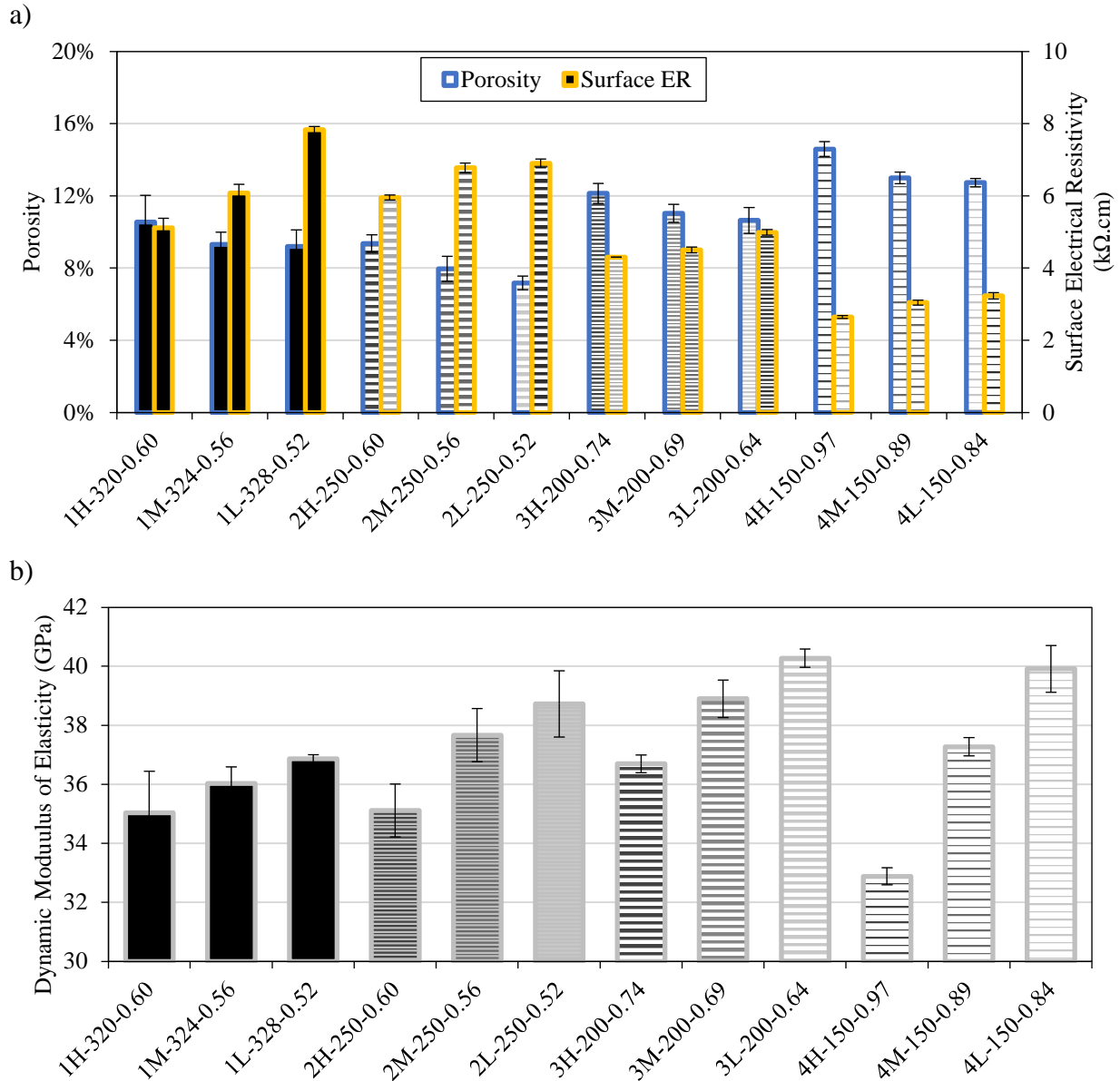


Figure 3.7: a) 28-day capillary porosity and surface electrical resistivity and b) 28-day dynamic modulus of elasticity.

3.6. Discussion

3.6.1. Rheological models for describing the mixtures' behaviour

Cement-based materials can be classified as Bingham model [75] (Equation 3-8), where there is a linear relationship between shear stress and shear rate [76]. However, previous studies [27,76–78] show that eco-efficient cement-based materials developed with PPM and high volume of limestone fillers are frequently classified as non-linear shear behaviour, in which are better represented by

Modified Bingham (Equation 3-9) [79] and/or Herschel-Bulkley model (Equation 3-10) [75]. It is worth highlighting that the IBB rheometer outputs are not in fundamental units; hence, for comparison purpose of this paper τ , τ_0 , and $\dot{\gamma}$ are presented in torque, initial torque, and rotation units, respectively.

Table 3.5: Compared rheological models.

Name	Equation	Equation Reference
Bingham	$\tau = \tau_0 + k_B \dot{\gamma}$	Equation 3-8
Modified Bingham	$\tau = \tau_0 + \mu_p \dot{\gamma} + c \dot{\gamma}^2$	Equation 3-9
Herschel Bulkley	$\tau = \tau_0 + k_{HB} \dot{\gamma}^n$	Equation 3-10

Where: τ is the shear stress, τ_0 is the yield stress, k_B is the viscosity constant of Bingham and $\dot{\gamma}$ is the shear-rate, μ_p is the modified Bingham viscosity, c is the modified Bingham constant, k_{HB} is the viscosity constant of Herschel-Bulkley and n is flow behaviour factor, which is $n < 1$ for suspensions presenting shear thinning behaviour and $n > 1$ for shear thickening ones [77].

Table 3.5a and b present the three rheological models compared to cement contents of 320 and 250 kg/m³ experimental data, respectively. It worth noting that similar trends were observed for cement contents of 200 and 150 kg/m³; hence, their graphs are not presented here. As one can see, Herschel Bulkley model is the one that better represents the rheological behaviour of eco-efficient mixtures developed with PPM. The rheological behaviour of twelve mixtures appraised at 0 minutes presented average minimum square error (MSE) of 1.86, 0.40 and 0.29 for Bingham, Modified Bingham, and Herschel Bulkley, respectively. As expected, Bingham model presents the higher MSE, as the mixtures presenting a non-linear shear-stress shear rate trend. Although the two models able to predict non-linear behaviour achieved lower MSE, when analyzing individual mixture, the Herschel Bulkley (HB) MSE was lower than the Modified Bingham ones. G1 mixtures presented lower MSE of 0.1 and a linearity highlighted by the flow behaviour factor ($n = 1$). Mixtures with decreasing cement content had on average MSE of 0.35. Moreover, cement

contents of 250, 200 and 150 kg/m³ showed increasing non-linearity as the flow behaviour factor (n from Equation 3-10) was 0.92, 0.89, and 0.64, respectively. Therefore, the increase of the limestone content results in a general rise in shear thinning behaviour. Moreover, the analysis show that HB model better represents rheological behaviour of the studied mixtures at 0, 15 and 30 minutes.

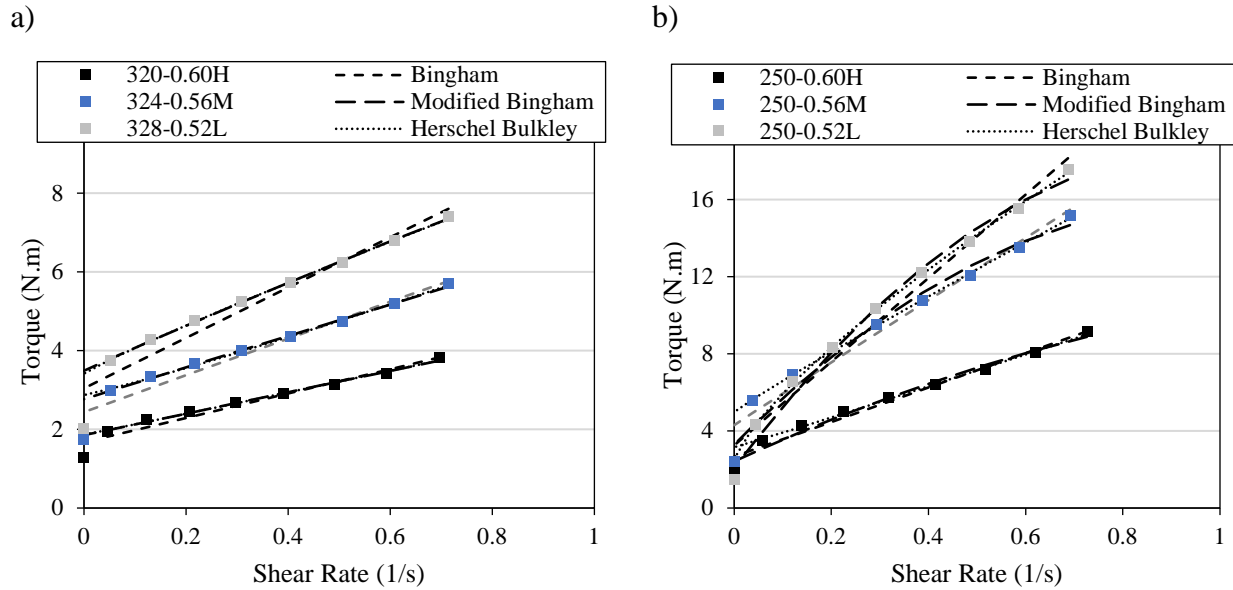


Figure 3.8: Rheological models comparison (Bingham, MB and HB) in a) Group 1 and b) Group 2 mixtures.

The real viscosity profile (Figure 3.8) was calculated through the derivative of HB model at 0 minutes, as it was concluded to be the model that better represents the analyzed data. The viscosity profile shows the importance to appraise the rheological behaviour of mixtures to analyze their viscosity at appropriate shear-rate. G1 mixtures present approximately the same viscosity regardless of the shear-rate applied; however, mixtures presenting lower w/f (gray ones) had a higher viscosity at 0.1 s⁻¹ (low shear-rate) than at 0.7 s⁻¹ (high shear-rate). At 0.7 s⁻¹, mixtures with 320 kg/m³ yielded an average viscosity of 4.0 N.m.s , while mixtures with same w/c and lower cement content (250 kg/m³) yielded a viscosity more than twice higher. Analyzing Figure 3.9b, it is clear that mixtures with same free water presents similar viscosity at 0.7 s⁻¹ being 8.8, 14.8 and

17.6 N.m.s for H, M and L, respectively. Mixture 150-0.89M was an exception as it presented viscosity similar to mixtures with lower w/f. Therefore, one may conclude that 150-0.89M achieved a threshold value of 51.8% of filler in the mixture, as it started to impact the viscosity. Similar results were observed by [34,80–82], where the viscosity increased when 20% or more of filler is added.

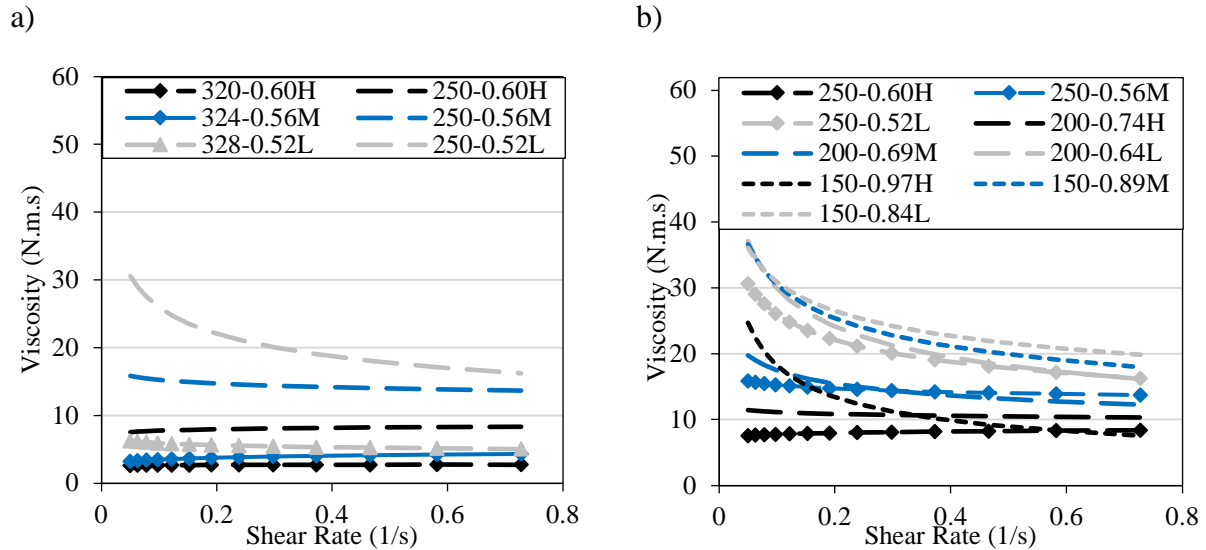


Figure 3.9: Real viscosity of non-Newtonian mixtures calculated through Herschel-Bulkley model, where a) Phase 1 and b) Phase 2 mixtures are presented.

3.6.2. Analyzing the rheological behaviour through mobility parameters

A correlation between the increasing HB flow behaviour factor (n , denoting the linear dependency on the shear rate) was observed with the mobility parameters (MPT and IPS), regardless of the cement content (Figure 3.10a). It is worth noting that 150-0.97H (red triangle in Figure 3.10), which has MPT of $0.35 \mu\text{m}$, may be considered as an outlier to the trend. Without it, the linear relationship between flow behaviour factor and mobility parameters presents a R^2 of 0.83 and MSE of 0.27. The shear-thinning behaviour was also observed by Yahia [76] and Varhen [82] in cement-

based materials, when a w/f above 0.33 is selected, which agrees with this study where the w/f ranged from 0.40 to 0.47.

Figure 3.10b shows the relationship between mobility parameters and initial and final torque at 0.1 and 0.7 s⁻¹, respectively. Regardless the w/c and w/f, all mixtures appraised have a strong correlation (R² of 92) with IPS and MPT at high shear-rate (0.7 s⁻¹). A linear behaviour was found for yield stress (torque at shear-rate of 0.1 s⁻¹), which is expected as the slump flow of all mixtures were kept constant.

Figure 3.10c shows the true viscosity at the 0.1 and 0.7 s⁻¹ as a function of MPT. Mixtures in low and high (0.1 and 0.7 s⁻¹) shear-rate regimes demonstrated a notable correlation to MPT with a R² of 0.83 and 0.92, respectively. It should also be noted that these behaviours were largely independent of the w/f. Although Menezes [19] correlates mobility parameters with slump results, the current study is in agreement with Rebmann [54], which predicted the final torque and maximum apparent viscosity using mobility parameters. Additionally, the influence of the filler content (i.e., percentage and type) is captured by the mobility parameters as the five aforementioned rheological behaviours (flow behaviour parameter, initial and final torque, and initial and final viscosity) are proportional to the mobility parameters.

It worth noting that the admixtures has a predominant impact on the surface force regime explained by IPS [83]; and the present study maintained slump flow constant (similar yield stress). Therefore, at low shear-rate regimes, the collision force regime of the fine aggregates explained by MPT would govern. Additionally, [84,85] studied a high range of solids content (i.e. percentage of cement, filler, and aggregates to the total volume) and it was concluded that above a critical concentration (65%), mixtures are governed by direct frictional forces (MPT) instead of the hydrodynamic force regime (IPS), agreeing with the current study as the solids content is between

77% and 81%. Moreover, Daminieli [86] used distinct amounts of admixtures to obtain maximum dispersion for a given IPS and it was concluded that since admixtures are not accounted in the IPS, the mixtures viscosity did not present correlation with IPS. It agrees with the present study, where admixtures were employed to maintain a constant dispersion (slump flow), which leads again to the understanding that initial viscosity of mortar mixtures would relate to the MPT instead of IPS.

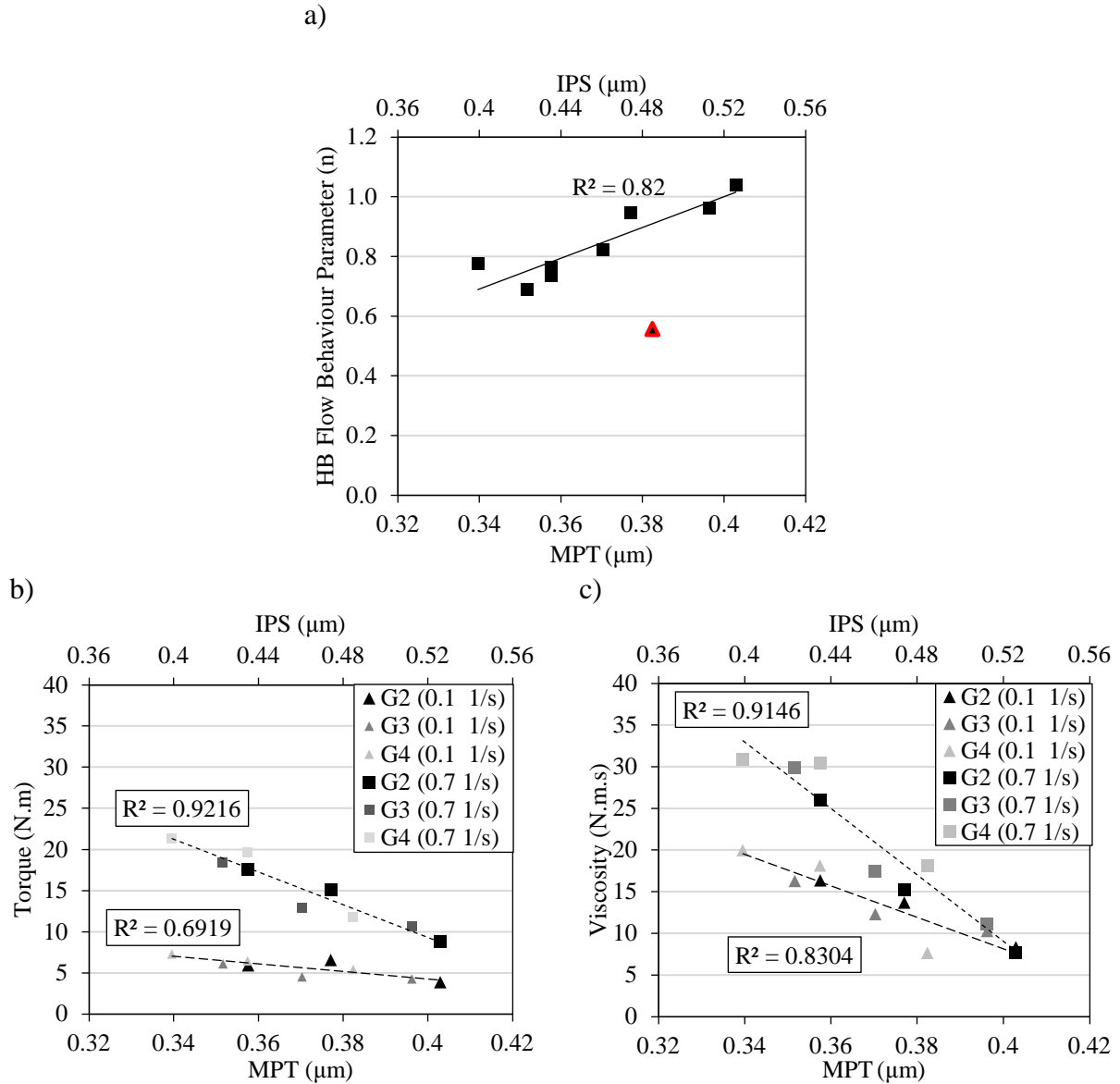


Figure 3.10: Correlation between MPT of sustainable mixtures and a) flow behaviour factor from Herschel Bulkley model, b) initial torque (at 0.1 s^{-1}) and final torque (at 0.7 s^{-1}), and c) initial viscosity (at 0.1 s^{-1}) and final viscosity (at 0.7 s^{-1}).

3.6.3. Compressive strength and binder intensity

The hardened strength of cement-based materials is traditionally defined by Abrams law, which relates the space available for hydrates and impacts the porosity and microstructure of the material [87–89]. Additionally, the compressive strength is inversely linked to the porosity (i.e., higher strength generally having lower porosity). Although this research is focused on the workability

condition, the optimized PPM's particulate spacing (i.e., spacing between cement grains, and hydrated product distances) develops of the spacing concepts for hardened state [55,90], although its focus is on the fresh state. The w/f concept (employed as a workability condition descriptor as discussed in Section 3.4.2) has been mentioned as a possible method to evaluate the reduced spacing for hydrate formation by John [6], and the observed relationship in the second phase (i.e., the phase with fillers) does not show a link between the w/f and compressive strength or porosity. This may be due to the selection process of research used to support their hypothesis. Figure 3.11a demonstrates no relationship between the compressive strength and solely the w/f in this research data set. The w/c ratio traditionally observed provided much better relationship to the compressive strength, although there was a noted variation between the mixtures with and without limestone fillers. Figure 3.12b shows the relationship between the w/c and the compressive strength of the mortars. Although w/c well predicts pure cement and sustainable mixtures separately, the compressive strength of high limestone filler replacement sustainable cement-based mixtures is not accurately addressed.

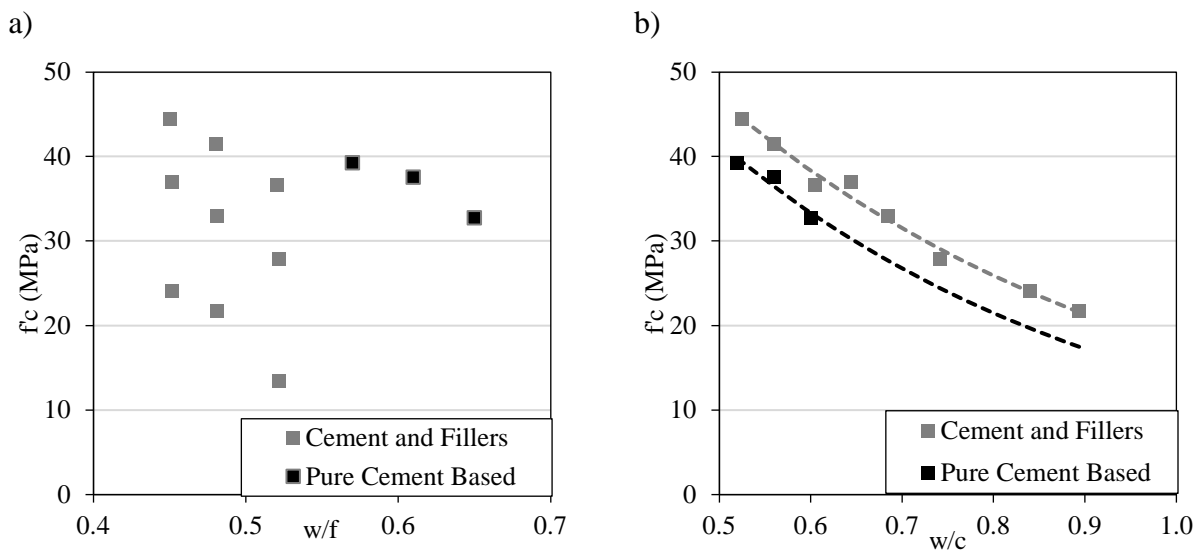
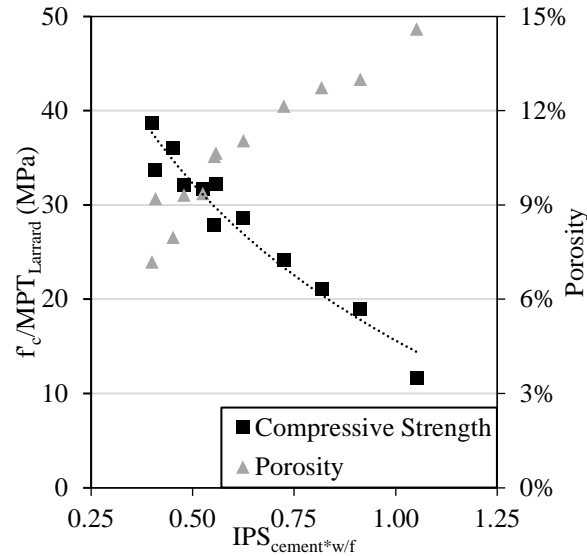


Figure 3.11: Compressive strength vs. a) w/f and b) w/c compared between Phases.

Traditional mortar strength laws does not account for inert filler effects (e.g., dilution effect, nucleation effect, and packing effect) and the inclusion of varying types of fillers (i.e., performance and replacement) is not addressed in the dilution model of Cyr [89]. Novel research into w/c suggests that available cement particulate distance [91] combined with decreased porosity [35] through filler packing may explain the increased mechanical capacity. In this context, an alternative method used to predict compressive strength of PPM mixtures developed with high limestone filler content is proposed by [35], where the compressive strength has an exponential relationship to $IPS_{\text{cement}^*w/f}$. Similarly to IPS, IPS_{cement} appraises the distance between particles [92], but in this case only cement particles are considered solids of investigation. The limestone filler effectively acts to both increase the spacing (dilution) and fill the pores (filler) while not generating C-S-H to improve compressive strength. Furthermore, when the impacts of the coarse spacing based on Larrard's hardened state parameter [55] are combined there is an improvement in the relationship in the hardened state. Figure 3.12b shows the aforementioned models (i.e., IPS_{cement} and MPT_{Larrard}).



$$\frac{f'_c}{MPT_{Larrard}} = \frac{68.51}{4.14 IPS_{cement} * \frac{w}{f}}$$

$$R^2 = 0.94$$

Figure 3.12: Combined dilution model employing IPS_{cement} and $MPT_{Larrard}$.

As previously mentioned, the binder intensity (b_i) factor can be used to appraise eco-efficiency of materials. Figure 3.13 shows the relationship between b_i and compressive strength achieved per mixture. Moreover, exponential lines were presented to highlight the cement content used for each group. The mixtures with 373 kg/m^3 cement content achieved b_i on average of $9.1 \text{ kg.m}^{-3}.\text{MPa}^{-1}$ (STD 0.86). These mixtures were classified as more sustainable than the pure cement mixtures in which b_i was on average $13 \text{ kg.m}^{-3}.\text{MPa}^{-1}$ (STD 0.94). Moreover, mixtures developed with 300 kg/m^3 had a b_i ranged from 5.4 to 7.2 for compressive strength between 37.0 and 27.9 MPa. Therefore, 200-0.69M and 200-0.64L achieved similar compressive strength than control mixtures (320-0.60H and 324-0.56M, respectively) with a b_i 36% lower, highlighting the ability of producing sustainable mixtures with the presented mix-design method. However, G4 mixtures may have reached the filler percentage limit, as their b_i is similar or higher than 200-0.74H, but the compressive strength is significantly lower. Although this work presents study of conventional mortar strength ($< 45 \text{ MPa}$), previous studies [93] were also able to produce sustainable mortar

with difference PPM approach to focus on high strength materials (>45 MPa). Moreover, previous studies [94] used on average 606 kg/m³ of cement to produce mortar with compressive strength between 25-45MPa [94], highlighting the importance of the mix-design presented in this study.

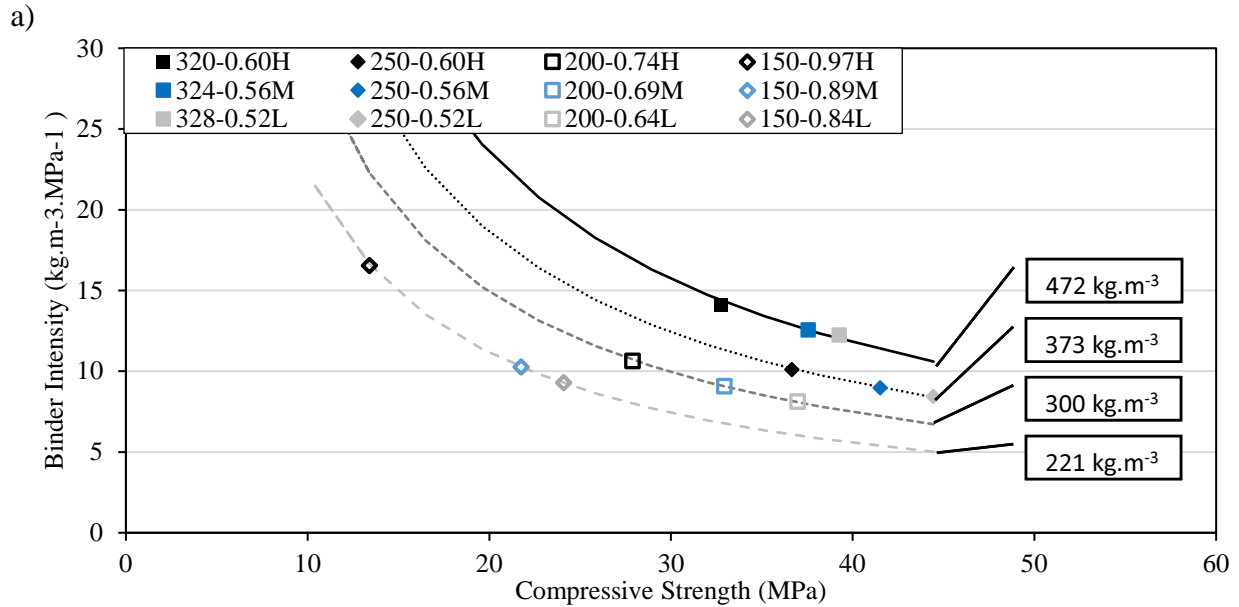


Figure 3.13 : Sustainability appraisal of mortar mixtures.

3.7. Conclusion

The current research aimed to appraise the feasibility of using mobility parameters to predict the fresh state of mortar mixtures designed using PPMs containing high limestone fillers content. The main findings of this research are presented hereafter:

- Replacing cement content by limestone filler enhanced the mortar hardened state properties when same w/c was selected.
- Five rheological parameters (i.e., flow behaviour parameter, torque at low and high shear rates, and viscosity at low and high shear rates) relationship of eco-efficient mixtures could be appraised using mobility parameters.

- MPT directly correlates to the low shear rate mixture viscosity of highly packed mortar systems with similar initial consistency, regardless of the cement content.
- Further cementitious replacement (up to 48%) was well predicted through a combined use of a dilution measurement (IPS_{cement}) and w/f as compared to Abrams law.
- Potential for eco-efficiency was noted with reductions of cement content upwards of 22% yielding improved mechanical and microstructural performance.

3.8.

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4.1. Conclusions

Eco-efficiency of concrete is lacking in conventional concrete mixtures with mechanical strength between 20-40 MPa. While representing most of the concrete supplied, this area of research has limited focus due to its inherent inefficiency and preference of increased strength in research. The use of particle packing models to enhance the packing, combined with effective dilution using inert limestone fillers has produced eco-efficient concretes with limited applicability due to its high resistance to flow. Optimized mixtures with the techniques required a better understanding without requirements for excess physical experimentation for wider spread application. Methods used in slurry pumping, combined with optimal use of relatively abundant waste by-products, was appraised in the fresh state using mobility parameters in the paste phase (inter-particle separation – IPS) and aggregate phase (maximum paste thickness - MPT). The combination of the two parameters are evaluated in the mortar phase to assess the concrete rheology in a step wise fashion similar to previous highly experimental works with promising results (UHPC). In this research, the ability for mobility parameters to assess the rheology of concentrated concrete mortar fraction of increasing eco-efficiency was appraised. Using 12 mixtures, and a time dependent rheological analysis 5 rheological descriptors were correlated; 1) the flow behaviour, 2) high shear rate shear stress; 3) low shear rate shear stress; 4) high shear rate viscosity; and 5) low shear rate viscosity.

- Five rheological descriptors were assessed based on mobility parameters and a strong correlation was observed.

- Independent of cement content, and water to solids in the fines, the mobility parameters provided an improved correlation to the rheological descriptions.
- Cement contents of 250, 200 and 150 kg.m⁻³ were employed to assess the increasing eco-efficiency and were able to produce concrete mortar fractions within a range of 36-45, 27-37 and 13 –24 MPa, respectively. The hardened state was assessed using a dilution measurement which accounts for the hydrate forming space available in the system.
- The eco-efficiency of the mortar fraction was between 10.3 and 5.4 kg.m⁻³.MPa⁻¹ for 21 and 37 MPa. This is well below the 15 and 8 kg.m⁻³.MPa⁻¹ apparent in typical concrete mixtures.
- The aforementioned mixtures employed up to 48% cement replacement with inert materials and were successfully able to achieve desired compressive strength that is well defined by a dilution parameter.

4.2. Future recommendations

A major goal of this research was to increase the body of knowledge in eco-efficient cement-based materials research for various applications. Although this work brings new insight to the field of mobility parameters, further investigation and correlation is required for wider use.

- Investigation into the concrete phase would be the logical next step to evaluate the contribution of successive phases
- Durability related parameters would be important, especially in considering the freeze-thaw exposure conditions in Canadian climates
- This study focuses on the fresh state of inert SCM's, extension to reactive SCM's and their successive contribution to the time dependent rheology would be necessary

- Development of a formal performance-based mix design methodology that incorporates sustainability concepts
- Site development with concrete producers to evaluate the feasibility of the proposed in a real-world application would be beneficial to the development of the mix design.

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