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Manuscript title: From composition to the microstructure and durability of limestone ternary blended cements: A Systematic review

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Abstract

Limestone ternary cements have attracted significant research and commercial attention recently, for technical and environmental reasons. Standardization of these cements is imminent under BS EN197-5. Presently, detailed understanding of the hydration and microstructure evolution of limestone ternary cements from different alumina-rich supplementary cementitious materials (SCMs) exists in the scientific literature; improved reaction kinetics and additional phase assemblages refine the pore structure. However, understanding of the performance of these cements under exposure conditions is less prevalent. In this contribution, we review these data in a way that allows stakeholders to appreciate the capabilities of the different compositions and their performance. We focus our discussion on critically examining the interplay between the cement composition and the microstructure on durability. It is demonstrated that limestone ternary cements offer a pathway for reducing the embodied CO₂ of concrete without compromising their performance. The resistance to chloride ingress, sulphate attack and ASR are significantly improved in a manner similar to binary cements. Carbonation and freeze-thaw resistance is generally lower than OPC but adequate air entrainment can offer improvement in freeze-thaw resistance. The challenge to widespread adoption of these cements is evidence of durability under field conditions. To this end, we recommend large-scale field trialling of these cements and understanding of the role of combined exposures on durability and mechanical properties.

Keywords: Durability; low carbon cement; limestone; ternary cement; microstructure; coupled exposure

Introduction

Climate-change poses a significant threat to our current way of life. As a result, there is increasing pressure to reduce global greenhouse gas emissions and hence limit global temperature rise. Amongst the principal contributors to global warming is the emission of carbon dioxide (CO₂), of which the concrete industry is a considerable emitter. Globally, the demand for concrete is second only to potable water, with demand predicted to rise (Allwood et al., 2012, IEA, 2017) with growing industrialisation in low- and middle-income countries. The production of Portland cement, the commonest binder in concrete, stands at an estimated 4.1 billion tonnes per year (USGS, 2020). With production of 1 tonne of Portland cement giving rise to emissions of 0.87 tonnes of CO₂, of which 0.53 tonnes is due to calcination of limestone (Damtoft et al., 2008). Global cement production is responsible for 5-8% of man-made greenhouse gas emissions. Therefore, despite major strides in improving plant efficiency and in the use of alternative fuels, one of the major challenges confronting the cement industry is meeting the increasing demand for cement-based infrastructure while striving to reduce its CO₂ footprint.

Lowering the clinker factor in cements ranks highly amongst embodied CO₂ mitigation strategies in the cement and concrete industry (IEA, 2017, Scrivener et al., 2018b). This involves partial replacement with SCMs, reducing the clinker content and hence the CO₂ associated with clinker production, whilst valorising industrial wastes that would otherwise end up in landfills. Indeed, the World Business Council for Sustainable Development (WBCSD) estimates that lowering the average clinker factor to 0.6 could save ~35% of direct process CO₂ emissions by 2050. Both ground granulated blast furnace slag (GGBS) and pulverised fuel ashes (PFA) have found extensive industrial use, as SCMs for reducing the clinker factor. However, whilst cement production has more than doubled over the last two decades as evident from Figure 1, production of PFA and GGBS globally have plateaued, and currently represents about 30% of annual cement production. Furthermore, not all of these industrial by-products are suitable as SCMs, limiting GGBS and PFA usage as SCMs to under 10% of the demand for cement. A possible alternative as a low-cost, globally abundant SCM is low-grade calcined clays (Scrivener et al., 2018a).

Finely ground, uncalcined limestone has become a popular constituent in modern cements in a drive to further reduce the clinker factor, without additional demand for conventional SCMs (Lothenbach et al., 2008, Lothenbach et al., 2011, Scrivener et al., 2018b, Tennis et al., 2011). Up to 5% limestone may be used as a fraction of the minor additional constituent in cements. Meanwhile, Portland limestone composites (CEM II) may contain up to 35% ground limestone. Over the past two decades, a raft of scientific papers have been published, exploiting the interactions between aluminates and carbonates to formulate limestone ternary blended cements as low carbon alternatives to Portland cement. A new European norm, expected to be published in 2021 (BS EN 197-5) is dedicated to ternary cements with and without limestone. Whereas the reaction mechanisms and associated engineering properties of limestone containing ternary cements are broadly understood (Dhandapani et al., 2021, Lothenbach and Zajac, 2019, Wang et al., 2018), durability of these cements has attracted significantly less attention (Juenger et al., 2019).

In this contribution, our objective is to review durability of ternary cements containing more than 5% limestone powder as SCMs. The paper is structured around the microstructural parameters affecting durability and performance in aggressive exposure environments e.g. carbonation, chloride ingress, sulphate attack, alkali-silica reactions and freeze-thaw induced

damage as well as combined aggressive exposures. For each exposure, an overview of the controlling degradation mechanism precedes recount and synthesis of the published data. Gaps in the existing literature are also highlighted.

2. Overview of limestone ternary cements

2.1. Composition, hydration, pore solution and phase assemblages

GGBS, PFA and calcined clays (including metakaolin), the most common SCMs for limestone ternary cement formulations, comprise predominantly crystalline and glassy silicates (40 - 60%) and aluminates (5 - 40%). The bulk composition of SCMs influence the ultimate phase assemblages within the hardened cement, but the rate of dissolution is a function of the amorphous glassy phase, pH and temperature (Lothenbach et al., 2011, Oelkers, 2001). GGBS and calcined high purity clays can contain over 90% glassy phase (Fernandez et al., 2011, Hollanders et al., 2016) but much lower amorphous contents are seen in fly ashes (Matsunaga et al., 2002, Chancey et al., 2010, Moreno et al., 2005). SCM hydration is mostly limited to the amorphous glassy phase except in calcareous fly ashes, where reactive crystalline components e.g. belite and calcium aluminate phases may exist (Chancey et al., 2010, Moreno et al., 2005).

In limestone ternary cements, the aluminosilicate phase reacts slowly, with limited limestone dissolution (Arora et al., 2016, De Weerd et al., 2011a, Zhu et al., 2021). However, a combination of the filler effect, increased effective water content, and space for hydrate growth enhances clinker hydration, with the extent being greater in the presence of limestone powders than with inert fillers (Adu-Amankwah et al., 2017, Avet and Scrivener, 2018, De Weerd et al., 2011b). The degree of SCM hydration varies with the physical and mineralogical composition. Typical 28d degrees of hydration are 20-40% for GGBS (Adu-Amankwah et al., 2017, Hoshino et al., 2006); 7 - 22% for fly ash (De Weerd et al., 2011a) and 9 - 35% for calcined clay (Antoni et al., 2012, Avet and Scrivener, 2018). Thus, a significant volume of the SCMs and limestone remain unreacted, even after 180d (Berodier and Scrivener, 2015, Avet and Scrivener, 2018, Zajac et al., 2020)-

Pore solution compositions of limestone ternary cements have been reported for different alumina-silicate materials (Adu-Amankwah et al., 2017, De Weerd et al., 2011a, Fernández et al., 2018, Nguyen et al., 2018, Sui et al., 2019). These vary with mix composition, w/b ratio, degree of hydration and phase assemblage. The data reviewed herein considers samples with 0.4 - 0.5 w/b and after 28d hydration. The trends indicate slightly lower pore solution pH than complementary binary mixes (De Weerd et al., 2011a, Fernández et al., 2018, Nguyen et al., 2018). Figure 2 compares the aluminium and alkali pore solution concentrations in binary and corresponding limestone ternary cements where reported in the same study. The nature of the SCM strongly influences the aluminium concentration in the pore solution, with calcined clay mixes consistently showing elevated aluminium concentrations (Nguyen et al., 2018, Shi et al., 2017). Limestone addition reduces the aluminium concentrations in the pore solution. Meanwhile, higher alkali concentrations were observed in fly ash mixes, decreasing with time and limestone substitution (De Weerd et al., 2011a). Similar trends were seen in limestone-GGBS ternary cements (Adu-Amankwah et al., 2017, Sui et al., 2019) but with a much smaller pH reduction than in fly ash systems. The slag's higher calcium content, reflected in the C-S-H Ca/Si ratio and alkali-uptake into hydrates, to maintain charge balance in low-Ca systems, explains the pH trends.

The hydration products of limestone ternary cements are broadly similar to those of CEM II binary cements, but with significantly higher carboaluminate contents (Antoni et al., 2012, Arora et al., 2016, De Weerd et al., 2011a). This in turn stabilizes ettringite (Lothenbach et al., 2008, De Weerd et al., 2011a, Zajac et al., 2014) with the effect being distinct in cements formulated with more reactive aluminosilicates, e.g. calcined clay and slag (Antoni et al., 2012, Avet and Scrivener, 2018). Silicates in the SCMs form additional C-S-H but with lower Ca/Si ratios and greater Al incorporation. The C-S-H Ca/Si ratios in limestone blends are slightly increased, mainly due to an increased degree of clinker hydration. Consequently, increasing the limestone content at the expense of reactive SCM would reduce the C-S-H content. Meanwhile, portlandite levels depend on the clinker content but consumption largely depends on the SCM composition.

For example, more C-S-H but less portlandite was calculated in a limestone-metakaolin or fly ash ternary mix compared to an equivalent slag mix (Lothenbach and Zajac, 2019). Meanwhile, aluminium from the SCM is partly incorporated into the C-S-H with a higher fraction of carboaluminate formed at the expense of mono-sulphoaluminates (Lothenbach et al., 2008, Matschei et al., 2007).

In GGBS-containing cements, an alumina-rich, double-layered hydroxide assemblage, hydrotalcite is formed in addition to the extra low Ca/Si C-S-H (Whittaker et al., 2014, Fernández et al., 2018). However, in calcined clay systems, strätlingite is observed (Lothenbach and Zajac, 2019, Antoni et al., 2012, Avet and Scrivener, 2018). Reactions between dissolved alumina and limestone lead to the initial formation of hemi-carboaluminate, transforming to mono-carboaluminate as more limestone dissolve. Meanwhile, the ettringite/carboaluminate balance, as well as the amount of reactive carbonates, varies with the sulphate/aluminate ratio (see Figure 3) (Matschei et al., 2007). Higher ratios stabilize AFt and monosulphoaluminate since dissolution of calcite is retarded. Conversely, an increasing carbonate/aluminium ratio stabilizes carboaluminate, but with implications on mechanical and possibly the transport properties due to differences in the molar volumes of AFt and AFm (Ferreiro et al., 2017, Matschei et al., 2007). The accelerating effect of limestone on clinker hydration can further modify the AFt/AFm interaction, due to adsorption of sulphates onto the C-S-H. Under- and over-sulphation both retard aluminosilicate reactions due to modifications of pore solution (Adu-Amankwah et al., 2018a). Moreover, ettringite precipitated prior to reaction of the aluminosilicate significantly impacts on pore solution composition and microstructure, and on the subsequent aluminosilicate reaction, as also reported for C₃S/C₃A systems (Zunino and Scrivener, 2020).

2.2. Pore structure and transport properties

Modification of hydration kinetics and phase assemblages in limestone ternary cements are reflected in the pore structure, so affecting transport properties. Additional hydration products densify the structure, reducing porosity over time. This however relies on aluminosilicate hydration. For example, greater capillary pore volume and larger critical diameters were reported in limestone-fly ash blends compared to OPC, even after hydrating for 6 months (Pipilikaki and Katsioti, 2009). Similar observations were made elsewhere (De Weerd et al., 2011a) but the capillary pore volume reduced significantly after 90 days as more of the fly ash reacted. Meanwhile, decreasing micro-capillary pores were reported in fly ash-limestone blends, only after 7 days (Kim et al., 2015). It is noteworthy that the latter study contained 80% clinker content as opposed to <60% in the preceding studies. In blends with more reactive SCMs e.g. slag and calcined clay, refinement of capillary pores is observed at clinker contents of 50% and below (Figure 4). Lower critical pore sizes, and hence threshold radii,

have been reported at 28 days in slag cements compared to CEM I (Zajac et al., 2018, Ramezaniapour and Hooton, 2014) whilst significant refinement was already evident after 3 days in LC3 systems (Avet et al., 2019a, Dhandapani and Santhanam, 2017). However, one must recognize that these pore refinements do not necessarily lead to lower total porosity. Indeed, up to 10% increase in total porosity was determined in slag and LC3 blends with 50% clinker factor, for which the derivative plots are shown in Figure 4. Increasing gel porosity (i.e. < 10 nm) in ternary cements (Figure 4) arose from the additional hydrates formed from the reactive aluminosilicates, which filled the inter-particle/hydrate pore spaces and made the pore ranges finer. Refinement of the critical pore sizes (i.e. the peak of the derivative plot which denotes the pore size at which maximum intrusion occurred) increased the gel pore volume. Reactivity of the aluminosilicate influenced densification significantly, with further improvements achievable also from increased curing time. Detailed discussion of the pore structure evolution mechanisms in these cements are reported elsewhere (Berodier and Scrivener, 2015, Dhandapani and Santhanam, 2017, Krishnan et al., 2019, Adu-Amankwah et al., 2017). Increasing the limestone to aluminosilicate ratio did not change the gel pore volume significantly, but the critical pore size increased due to dilution arising from limited reaction of limestone. One must however note that the gel pores are mostly disconnected and hence don't impact negatively on transport properties, while refinement of capillary pores reduces water, gas, and ion migration.

Lower sorptivity coefficients and ion conductivities were reported in limestone-natural pozzolan ternary blends in the RCPT test (Ghirci et al., 2007). These were comparable to those observed for binary OPC-natural pozzolans but better than for OPC. Similar observations were made by Celik *et al.* who proposed ~50% clinker substitution threshold in limestone-aluminosilicate blends (Celik et al., 2014). Resistance to chloride conductivity, sorptivity and oxygen permeability was significantly improved in ternary blends of CEM II A-L with fly ash or slag compared to Portland limestone cement concrete samples (Githachuri and Alexander, 2013). While chloride migration and sorptivity data for blended cements tend to be consistently better than OPC concrete, incorporation of more than 10% limestone was slightly detrimental compared to a binary blends (Wu et al., 2016). Similarly, LC3 systems show improved sorptivity, chloride migration, and oxygen permeability coefficient compared to equivalent OPC (Antoni et al., 2012, Dhandapani et al., 2018, Scrivener et al., 2018a). The effect of different aluminosilicate sources on the transport properties has also been considered in the literature. Based on 28-day test data with ~10% limestone, metakaolin and slag tended to show better performance than fly ash in relation to chloride migration, sorptivity and oxygen permeability (Githachuri and Alexander, 2013, Aguayo et al., 2014). This is likely due to them being more reactive and therefore showing a higher degree of hydration.

The tortuosity factor and fractal dimension of pore tortuosity, indicators of the convolutedness of the pore network are increasingly used to characterise diffusivity of matter in hydrated cements (Dhandapani and Santhanam, 2017, Alderete et al., 2019, Georget et al., 2020). These increase with hydration time and reactive SCMs which reduce connectivity of the pore network, being proportional to total porosity and the matrix formation factor. Alderete *et al.* (Alderete et al., 2019) showed that more than 10% limestone additions lowered apparent tortuosity whilst the reverse was true for natural pozzolans and slag. Similar conclusions were noted by He *et al.* (He et al., 2019) who examined Portland-limestone mixtures at 50 – 80 % limestone contents and Zeng *et al.* (Zeng et al., 2013) who studied GGBS pastes and mortar samples. An inverse relationship between chloride diffusivity coefficient and the fractal dimension of the pore tortuosity was reported in (Li et al., 2018).

Coarser limestone or increasing its dosage made the concrete more permeable to chloride ions. Limited tortuosity and fractal dimensions data in limestone ternary cements exist in the literature. Villagrán-Zaccardi *et al.* (Villagrán-Zaccardi *et al.*, 2021) investigated mortar samples with variable slag or limestone contents and their combination. At 40% SCM dosage, the limestone-slag ternary mortars had comparable surface fractal dimension (~2.3) to the binary cement. At 20% OPC substitution, Yang *et al.* (Yang *et al.*, 2017) found nearly a doubling of the geometric tortuosity in limestone-metakaolin ternary cement (10.2) compared to neat cement concretes (5.95). Raising the limestone to metakaolin ratio from 1:1 to 2.5:1 caused a reduction in tortuosity (8.47) but this was still better than the OPC concrete and sensitive to the w/c ratio. Dhandapani and Santhanam (Dhandapani and Santhanam, 2020) reported significantly higher electrical tortuosity in LC3 concrete compared to binary fly ash and neat cement concrete. This increased with the strength of concrete and curing age. The concept of migration tortuosity was introduced in Yang *et al.* (Yang *et al.*, 2017) with similar trends as the geometric tortuosity and both depended more on the alumino-silicate content but decreased with the limestone dosage. Whilst tortuosity and fractal dimensions are invaluable characteristics of the pore structure, extensive research is needed to elucidate scale and maturity dependency as well as compositional sensitivity to different SCMs in limestone ternary cements.

3. Durability of limestone ternary blended cements and concrete

The pore solution composition, phase assemblages and permeability all influence the durability of cementitious materials. As discussed above, these differ in limestone ternary cements compared to OPC and binary cements. This section therefore reviews the literature on durability of limestone ternary cements against common deterioration processes. For each process, performance is explained by considering the pore solution chemistry, phase assemblage and pore structure.

3.1 Carbonation resistance

Carbonation in cementitious materials is a physico-chemical mechanism involving the diffusion of atmospheric CO₂ into concrete pores, dissolution in pore water and subsequent reaction with calcium-bearing phase assemblages. The subsequent reduction in pore solution alkalinity causes de-passivation of reinforcement and ultimately leads to its corrosion. The principal calcium-bearing phases involved in carbonation are portlandite (CH), calcium silicate hydrate (C-S-H) and ettringite. In all instances, calcite or its polymorphs form alongside alumina-silica gel or gypsum, depending on the carbonating phase (Auroy *et al.*, 2018, Morandea *et al.*, 2014, Morandea *et al.*, 2015) and the CO₂ concentration to which the paste is exposed (Auroy *et al.*, 2018).

The extent of carbonation is governed externally by the duration of exposure, the ambient relative humidity and the CO₂ concentration (Castellote *et al.*, 2009, Leemann and Moro, 2016). However, two intrinsic features of the cement paste affect the extent of carbonation, namely: the pore structure governing CO₂ ingress into the matrix, and the CO₂ binding capacity of the hydrated cement paste (Šavija and Luković, 2016, Shi *et al.*, 2016). Both of these features are modified in limestone ternary cements.

The higher the reactive CaO content of the cement, the greater the buffering capacity against carbonation (Leemann and Moro, 2016). With or without limestone additions, various studies have shown lower CO₂ binding capacities in blended cements than in OPC due to reduced portlandite availability. This, in-turn, reduces the carbonation resistance (Morandea *et al.*, 2015, Shah and Bishnoi, 2018b, Lauch *et al.*, 2016). In accelerated carbonation studies of ternary limestone-slag and limestone-fly ash blends, carbonation resistance was proportional

to the clinker content (Lauch et al., 2016, Khan et al., 2020), with the limestone-slag mix slightly outperforming the corresponding limestone-fly ash blend. However, both performed less well than the reference OPC. This was attributed to clinker replacement in the blended mixes with more residual calcium hydroxide present in the slag-limestone mix than fly ash-limestone mix (Lothenbach and Zajac, 2019) giving a greater CO₂ binding capacity. These findings have been corroborated elsewhere (Bostancı et al., 2016, Shah and Bishnoi, 2018b). Concrete formulated with binary (i.e. OPC with slag or fly ash) and LC3 ternary cement, showed an increased carbonation coefficient with decreasing clinker replacement (**Figure 5**)(Shah and Bishnoi, 2018b, Lin et al., 2021). The blended cements were particularly sensitive to the high CO₂ concentrations used in accelerated tests. Similarly, while all mixes performed worse when the w/b ratio was raised from 0.3 to 0.45, at equivalent clinker content and w/b ratio, the LC3 blends carbonated more than binary OPC-slag and ternary OPC-Slag-PFA mixes. However, greater capillary porosity did not necessarily increase susceptibility to carbonation. For example, the OPC and 60% kaolinite LC3 samples had comparable capillary porosities, but the latter's carbonation coefficient was an order of magnitude higher. At the same time, the 80% kaolinite LC3 concrete, despite being more reactive and hence having a lower capillary porosity, was more susceptible to carbonation than the reference OPC (**Figure 5**). This highlights the importance of CO₂ binding capacity and the nature of hydrated phase assemblages in carbonation resistance. As shown in Figure 4, ternary mixes, and particularly LC3 ones, have more refined porosities and would be expected to offer improved resistance against CO₂ ingress. However, the portlandite content is an influential parameter (Scrivener et al., 2018a). The lower reactive calcium contents of the cements mean that portlandite is consumed upon hydration, leaving other calcium-bearing phases more prone to carbonation.

However, reduced portlandite (CH) contents in composite cements is not solely responsible for lower carbonation resistance. Shi *et al.* showed that carbonation of CH may have little impact on pH in OPC-metakaolin-limestone ternary blends since the C-S-H still had a high Ca/Si ratio (Shi et al., 2016). C-S-H plays an active role in the carbonation of ternary blended cements. C-S-H carbonation is a complex decalcification-polymerization process leading to the formation of amorphous silica gels and calcium carbonate (Black et al., 2007, Morandau et al., 2014). The nature of the resultant carbonate is influenced by many factors, including CO₂ concentration (Castellote et al., 2009, Morandau et al., 2015). All three calcium carbonate polymorphs - vaterite, aragonite and calcite were observed upon natural carbonation of a limestone ternary blend, with only calcite formed upon accelerated carbonation (Goñi et al., 2002). Whilst aragonite was the predominant polymorph precipitated during accelerated carbonation of a metakaolin-limestone ternary blend at 3% CO₂ (Antoni, 2013), calcite was dominant upon natural carbonation. The formation of calcite at higher relative humidities has been reported upon exposure of portlandite to CO₂. This is due to conversion of other polymorphs to calcite during natural carbonation, due to exposure at high relative humidity (Dubina et al., 2013) and may well explain the differences between accelerated and natural carbonation, assuming that field-exposed concrete specimens will, at some point, be exposed to relative humidities greater than 80%.

As discussed in section 2.2, the pore structure plays a critical role in defining transport properties, and therefore carbonation behaviour. Pore refinement, as seen with binary composite cements, can greatly reduce permeability, and as discussed already, the capillary porosity is further refined in mature ternary blends. Furthermore, smaller pores remain saturated at lower relative humidity. Since the rate of CO₂ diffusion through water is many

orders of magnitude less than through air, saturated pores significantly reduce the rate of carbonation (Medjigbodo et al., 2018).

However, not only does the initial pore structure influence carbonation, the process of carbonation itself alters the pore structure (Figure 6 a). Coarsening of pore structures and an increase in porosity due to carbonation of C-S-H is widely reported for limestone ternary cements (Sulapha et al., 2003, Gruyaert et al., 2013, Shi et al., 2016). Increased porosity was reported upon natural carbonation of an OPC-metakaolin-limestone ternary cement (Medjigbodo et al., 2018), explained by the higher C-S-H content from the pozzolanic reaction. Furthermore, the effect might be exacerbated by the slightly higher Ca/Si ratio of the C-S-H formed in the presence of limestone as discussed in Section 2.1. C-S-H decalcification causes carbonation shrinkage; increasing the porosity and coarsening the pore structure (Borges et al., 2010, Auroy et al., 2015, Šavija and Luković, 2016). However, these observations should be treated with caution, since coarsening of LC3 and other ternary cements was much more significant upon accelerated carbonation than under natural conditions (Shah and Bishnoi, 2018a). The threshold pore diameter, defined as the inflexion point on the cumulative curve, above which the intruded volume sharply increases was coarsened in all samples after carbonation including the neat cement and limestone ternary blends (Figure 6 b) as reported elsewhere (Shi et al., 2016).

The above indicates that limestone ternary cements are more susceptible to carbonation compared to OPC but slightly more than corresponding binary cements. At equivalent clinker factor, blends containing fly ash tend to carbonate more with the carbonation depth increasing with the limestone content and w/c ratio due to a combination of matrix pH reduction and higher porosity. Lower gas permeability in these cements (Dhandapani et al., 2018, Githachuri and Alexander, 2013) implies matrix pH is more critical and hence, the clinker factor must be optimized accordingly. More importantly, post carbonation performance of these cements needs to be assessed to evaluate the risk to carbonation-induced corrosion. This should take into account the inherent pore refinement, CO₂ binding, and the role of the coarsened pores. Although portlandite and the C-S-H make the bulk of the phase assemblages in these cements with their carbonation mechanisms well reported (Black et al., 2007, Morandau et al., 2014, Shi et al., 2016). However, stability of the additionally formed carboaluminate phases need examining.

3.2 Resistance to chloride ingress and corrosion

Chloride ions near the embedded steel reinforcement in concrete depassivate the steel surface, leading to corrosion. Susceptibility of a given concrete to chloride ingress depends on two main factors – transport of water or air-borne chloride ions and the nature of chloride ions in the concrete (i.e. bound or free). Sorptivity and ionic diffusivity are the most important transport parameters as far as chloride resistance is concerned. As reviewed earlier, water absorption capacity and sorptivity of limestone ternary cement concrete are within the range of binary blends but consistently better than OPC at equivalent water to cement ratios (Celik et al., 2014, Dhandapani et al., 2018, Ghirci et al., 2007, Githachuri and Alexander, 2013, Courard and Michel, 2014).

The non-steady state migration test indirectly measures resistance to ionic transport in concrete. The migration coefficient (D_{nssm}) in limestone ternary cements depends on the SCM and replacement level (Aguayo et al., 2014, Githachuri and Alexander, 2013). At 20% replacement with fly ash and limestone (1:1), the chloride migration coefficient is comparable to that of OPC, whereas 20% replacement with metakaolin and limestone (1:1) leads to its halving, reducing further with time (Aguayo et al., 2014). However, replacing more than 35% of OPC led to coefficients similar to, or higher than the reference OPC. Wu *et*

al. showed that, at equivalent paste volume, the chloride migration coefficient in limestone-GGBS ternary blends was greater than in complementary binary mixes, but significantly lower than OPC or a corresponding PC-limestone concrete (Wu et al., 2016). These were corroborated in further studies (Proske et al., 2018). Similarly, LC3 (Dhandapani et al., 2018, Antoni et al., 2012) and limestone natural pozzolan blends (Celik et al., 2014, Ghirci et al., 2007) all show significantly lower chloride migration coefficients compared to OPC. Chloride migration coefficients extracted from the literature on ternary blends containing ~30% aluminosilicate and 15 – 20% limestone are compared to OPC for specimens containing 0.35 – 0.5 w/c ratios and cured for 56 days or more in Figure 7. The trends are in agreement with the rapid chloride migration data in (Aguayo et al., 2014, Ghirci et al., 2007) for specimens cured for 56 days or longer. Although limited data have been published on the electrical conductance, the trends indicate that the charge admittance through the limestone-ternary blends were low to moderate according to ASTM C1202 ratings (Dhandapani et al., 2018, Aguayo et al., 2014, Ghirci et al., 2007).

In addition to transport properties, the nature of chlorides, i.e. bound or free, is also an important parameter defining corrosion resistance. Sotiriadis *et al.* measured bound and free chloride concentrations in limestone ternary cement concrete formulated with natural pozzolans, fly ash, GGBS or metakaolin and exposed to chloride solutions for up to 180d (Sotiriadis et al., 2019). The total chloride concentrations were comparable in all specimens except that containing fly ash, where the total chloride content was notably lower. More chlorides were bound in the ternary cements compared to the baseline Portland limestone cements, with the limestone-metakaolin mix showing the greatest binding capacity (Wang et al., 2019b). Meanwhile, chloride binding capacities of cement pastes made from ternary blends of limestone with silica fume, GGBS or fly ash showed that silica fume blends bound significantly less chloride (Ipavec et al., 2013). In samples cured for 100 days, fly ash was more effective than GGBS; highlighting the important role of dissolved alumina in chloride binding (Thomas et al., 2012, Shi et al., 2017, Wang et al., 2019b).

However, it is worth noting that limestone-bearing cements show reduced chloride binding capacity compared to corresponding binary mixes, Figure 8. Aluminium uptake into carboaluminate reduces Al concentrations in pore solutions (see Figure 2) impeding Friedel's salt formation. This appears to be further worsened by reduced calcium availability. However, Shi *et al.* showed that increasing chloride concentrations may destabilize monocarboaluminate (in the ternary limestone-metakaolin blend) or stratlingite (in the OPC-metakaolin mix), rather promoting Friedel's salt formation (Shi et al., 2017). Instability of the hydroxyl or carbonate bearing AFm at higher chloride concentrations in the pore solution was attributed to demand for calcium to sustain Friedel's salt precipitation. Machner *et al.* (Machner et al., 2018) noted enhanced chloride binding in ternary dolomitic limestone-metakaolin blends. The additionally formed hydrotalcite, from the reaction of dolomite, was the main factor underpinning the enhanced binding capacity compared to limestone. These suggest that a combination of pore refinement and phase assemblages in limestone ternary blends reduce chloride ingress and enhance binding capacity.

Studies of rebar corrosion in limestone ternary cement systems have shown a reduction in the threshold chloride concentration to initiate corrosion proportional to the clinker factor (Pillai et al., 2019, Li et al., 2020). Meanwhile, half-cell and linear polarization data showed increased corrosion probability in limestone-GGBS blends than in OPC (Alonso et al., 2019). Similarly, half-cell corrosion potentials have been shown to be highest in fly ash blends, with all ternary cements showing greater susceptibility than reference Portland limestone cement

(Sotiriadis et al., 2019). However, once corrosion had initiated, the propagation stage of corrosion in LC3 systems is comparable to OPC (Nguyen and Castel, 2020).

The literature demonstrates that partial substitution of clinker for alumina-rich SCMs enhances chloride binding due to binding by alumina and calcium into Friedel's salt. Chloride binding capacity increased in the order of fly ash, slag and metakaolin and curing time higher w/c ratios and limestone dosage relative to the SCM further increased chloride ingress. The addition of limestone reduces alumina in the pore solution by dilution as well as by uptake into carboaluminate. This seems to lower the chloride-binding capacity compared to binary cements. Notwithstanding, significant refinement of the pore network in composite cements including limestone ternary cements reduces diffusivity (Ramezani pour and Hooton, 2014, Maraghechi et al., 2019, Dhandapani et al., 2018), thus improve resistance to chloride ingress, extending the time to corrosion initiation. It is important to elucidate stability of carboaluminate and the additionally formed hydrates in chloride rich environment and the impact on performance. Further research is needed to clarify rebar corrosion risk in limestone ternary cement concrete particularly assessment of the corrosion initiation stage taking into account the dense microstructures, binding capacity and realistic exposure regimes.

3.3 Resistance to sulfate attack and thaumasite formation

Sulfate attack in concrete arises either from external or internal sources of sulfate ions e.g. soil, seawater, groundwater and binder composition (Whittaker and Black, 2015, Boubekeur et al., 2019). Sulfate ions react with the cement hydration products causing delayed formation of ettringite. This induces expansive forces in the small pores due to crystallization pressure (Kunther et al., 2013, Hossack and Thomas, 2015). These microscopic changes lead to macroscopic expansion, softening, cracking and eventually strength loss (Boubekeur et al., 2019, Irassar, 2009). To minimise damage due to sulfate attack, a denser microstructure (Lee et al., 2005, Monteiro and Kurtis, 2003), dilution of the Al_2O_3 in the system (Cao et al., 1997), increased consumption of portlandite (Belie et al., 1997) and formation of more stable hydration products are required (Bellmann and Stark, 2008).

Alumina rich SCMs, including those in limestone ternary cements, improve resistance to sulfate attack (Shi et al., 2019) but, the level of protection is proportional to the SCM content (Ramezani pour and Hooton, 2012, Hossack and Thomas, 2015, Boubekeur et al., 2019, Wu et al., 2020) and the sulfate environment (Saca and Georgescu, 2014). In the presence of SCMs, the pozzolanic reaction leads to additional C-S-H. This increases the solid volume of hydrates and densifies the microstructure, as discussed in Section 2. But, no correlation has been found between sulfate attack and the pore structure distribution as measured by MIP from several studies of SCMs including limestone ternary blends (Shi et al., 2019, Bellmann and Stark, 2008). However, low portlandite levels may explain the excellent sulfate resistance of calcined clay-limestone ternary blends (Shi et al., 2019). Here, the pozzolanic reaction lowers calcium levels and formation of gypsum and ettringite is suppressed. Limestone stabilises hemi- and monocarboaluminate, thereby restraining ettringite formation from monosulphate (Lothenbach et al., 2008, Irassar, 2009, Irassar et al., 2000). Significant pore refinement in limestone ternary cements also offer plausible explanation for the reduced penetration of sulfate ions.

One concern regarding limestone incorporation into blended cement is thaumasite form of sulfate attack. This may cause decomposition of calcium silicate hydrates under wet conditions and low temperatures (Irassar, 2009, Crammond, 2003, Ramezani pour and Hooton, 2012, Mulenga et al., 2003, Shi et al., 2012), ultimately leading to structural failure.

While thaumasite attack is often considered a low-temperature phenomenon, it has occasionally been observed at above room temperatures and lower relative humidity (de Rojas et al., 2009). A combination of factors lead to thaumasite attack in concrete. At least 10-30% carbonate ion source is suggested as a pre-requisite (Hobbs, 2003, Crammond, 2003). Despite this, thaumasite attack in limestone blended cement is subject to debate, as some studies have found thaumasite in samples without limestone (Mulenga et al., 2003, Torres et al., 2006). Here, atmospheric carbonation of calcium bearing hydrates supplied the carbonate ions, and thus exonerates carbonate from limestone as the only cause of thaumasite deterioration (Collett et al., 2004).

Both ettringite and gypsum are precursors to thaumasite formation, and their presence during the early stages of exposure may ultimately lead to thaumasite formation (Hossack and Thomas, 2015). Conversely, a study on metakaolin-limestone ternary blends exposed for over 2 years found almost no thaumasite (Shi et al., 2019). However, it must be emphasized that the samples here were cured for 90 days before exposure to sodium sulfate solution. It was presumed that metakaolin hydration led to portlandite consumption, thus reducing the availability of calcium ions to form secondary ettringite and gypsum. Similarly, Portland limestone cement (PLC) blends containing both slag and fly ash showed minimal expansion compared to PLC blended with only one aluminosilicate (Mirvalad and Nokken, 2015). The overall increase in the cement substitution and the combined influence of slag and PFA in refining the pore network were assigned to the improved resistance.

In summary, sulfate resistance at ambient and low temperature (and hence thaumasite form of sulfate attack) in limestone ternary cements do not deviate significantly from those of binary cements from the same SCM. Indeed the improved resistance are derived from the aluminosilicate SCM. Consequently, the SCM/limestone ratio should be maximized. Meanwhile, effect of external sulfates on stability of the additionally formed phase assemblages and precipitation of new ones must be elucidated.

3.4 Freeze-thaw resistance

Critically saturated concrete may deteriorate due to cycles of freezing and thawing. This may manifest as surface scaling, internal structural damage or a combination of both. Scaling is perceived as the coupled effect of de-alkalination of the surface concrete through chloride interactions (which renders the microstructure porous) and ingress of the solution in contact with concrete (Stark and Ludwig, 1997, Valenza and Scherer, 2006). Meanwhile, internal structural damage is observed in concrete structures that are in contact with water and with or without de-icing agents (Fagerlund, 1997, Deja, 2003). For both scaling and internal damage, adequate air entrainment and lower w/c ratios can be sufficient to mitigate freeze-thaw damage.

SCM additions exceeding 30% and without air entrainment significantly increase susceptibility to surface scaling due to de-icing salts (Çopuroğlu et al., 2006, Deja, 2003, Stark and Ludwig, 1997, Bilodeau and Malhotra, 1997, Rønning, 2001, Sun et al., 1999, Giergiczny et al., 2009, Stark et al., 1997, Chidiac and Panesar, 2008, Bleszynski et al., 2002). Among the reasons for lower scaling resistance are: slower rate of hydration compared to Portland cement; carbonation of the surface layer resulting in the formation of metastable calcium carbonates which may be soluble in sodium chlorides (Stark and Ludwig, 1997); carbonation induced permeable cover-crete (Wowra, 2002); and modification of the air-void system (Bilodeau and Malhotra, 1997, Deja, 2003). These effects may be more critical in early age testing and particularly in laboratory tests where the degree of hydration of the SCM may be still low and exposure conditions may be more aggressive. Meanwhile,

limestone additions exceeding 15% also reduce freeze-thaw resistance (Dhir et al., 2007, Tennis et al., 2011, Palm et al., 2016, Thomas et al., 2010) due to clinker dilution. However, in slag or limestone binary blends, comparisons are often made to Portland cement without changing w/c ratios and hence fail to recognize the microstructural distinctiveness of these binders.

Freeze-thaw resistance of limestone ternary cement concrete has been reported sparingly (Adu-Amankwah et al., 2018b, Bleszynski et al., 2002, Espion et al., 2013, Meddah et al., 2014, Proske et al., 2018) including field trials (Thomas et al., 2010, Kuosa et al., 2014). Limestone-fly ash concrete has been compared at 50% clinker substitution to binary and ternary mixes comprising OPC, PFA, metakaolin and slag (Meddah et al., 2014, Lauch and Dieryck, 2016). The limestone ternary blend performed worse than the blends comprising two SCMs or their binary counterparts, with performance reducing with limestone content. At equivalent replacement and w/c ratio, slag blends were more resistant to scaling than PFA (Lauch and Dieryck, 2016) but the disparity was smaller in older specimens. Hooton *et al.* (Hooton et al., 2010) reported scaling resistance in limestone-slag ternary cements containing 30% slag with 7 or ~ 11% limestone. The scaled mass was higher in the ternary cement compared to OPC but all mixes were generally within the 1 kg/m² limit for exposure class XF1. Adu-Amankwah *et al.* studied limestone-slag ternary cement concretes at 0.5 w/c ratio and without air entrainment. Internal damage and scaling resistance are shown in Figure 9 (Adu-Amankwah et al., 2018b). In the limestone ternary cements, the relative dynamic modulus fell below the 80% failure criterion before the 28th cycle, occurring sooner in the ternary cements. Raising the limestone content to 20% accelerated the damage. The trends in surface scaling were consistent with the relative dynamic modulus, increasing with limestone content, but the scaled matter after 56 cycles only exceeded the 1kg/m² threshold in the mix containing 20% limestone. These findings agree with studies into surface scaling and internal damage in ternary cement with 50% clinker and 20% limestone (Proske et al., 2018). This study then found that reducing the w/b ratio to 0.4 marginally improved internal damage, suggesting critical demand for entraining agents in these cements to offset internal damage. Prolonged curing (90 days) did not prevent scaling greater than >1kg/m² in limestone ternary cement concrete (Espion et al., 2013). Air entrained concrete however showed profound resistance to scaling and internal damage following short-term curing. However, scaling resistance decreased with the SCM/limestone loading, as also noticed in field data (Kuosu et al., 2014, Thomas et al., 2010).

The published data on freeze-thaw resistance of LC3 and natural pozzolans is limited (Avet et al., 2019b, Ramezaniapour et al., 2013). Even at 80% clinker factor, a limestone-tuff ternary mix without air entrainment showed considerable scaling (Ramezaniapour et al., 2013). But, this mix outperformed OPC once air entrained. Low surface scaling in LC3 concrete has been reported (Avet et al., 2019b). The mixes showed low capillary suction, indicating potential pore densification by the SCM, and consequently delaying the time to critical saturation. However, it is important to note that freeze-thaw resistance of clay-bearing composite cements depends on the clay quality (Trümer and Ludwig, 2018). Kaolinitic clay mixes consistently outperform corresponding illitic and montmorillonitic clays with respect to carbonation, chloride diffusivity and freeze-thaw resistance. This suggests that pore refinement arising from the more reactive clay was the controlling parameter.

Indeed, Figure 4 showed significant refinement of the capillary pore network whilst gel porosity rather increased in the limestone ternary cements. Ironically, PC concrete, having a larger capillary porosity tends to resist both scaling and internal damage better than composite cements. During freeze-thaw cycles, capillary pores act as freezing centres whilst

water in gel-pores remains unfreezable (Setzer, 2001, Fagerlund, 1997). Crystal precipitation in confined pores as well as the phase assemblages modify crystallization pressure (Flatt and Scherer, 2008) and could explain the lower freeze-thaw resistance in limestone ternary blends. The literature highlight reactivity of the SCM and w/c ratio as influential factors whilst air entrainment is required for freeze-thaw exposures. To enable this, compatibility between limestone ternary cements and air entrainment admixtures must be evaluated as well as stability of carboaluminate and the risk of thaumasite formation from internal sulfates at prolonged exposure to freezing temperatures.

3.5 Alkali-silica reactions (ASR)

Alkali silica reactions may occur in concrete containing reactive siliceous aggregates. Alkalis present in the pore solution react with silicates in the aggregates forming deleterious expansive gels that may lead to tensile cracks on the concrete surface and eventual spalling. Amongst the factors influencing ASR resistance, high alkali concentration, aggregate reactivity and the internal relative humidity are the most important (Lindgård et al., 2012). Depending on the substitution level, SCMs including fly ash, GGBS, metakaolin and natural pozzolans improve resistance to ASR (Ahmadi and Shekarchi, 2010, Lindgård et al., 2012, Shehata and Thomas, 2000), possibly due the mitigating effect of additionally dissolved alumina (Chappex and Scrivener, 2012).

Standards still stipulate threshold alkali contents for composite cements in terms of Na_2O equivalent. However, this is less relevant for ternary cements due to differences in reaction rate and the presence of other species in the pore solution, i.e. aluminium and silicon. Alkalis in the pore solutions of composite cements may emanate from both CEM I and SCMs. However, improved ASR resistance suggest that alkalis in SCMs are not as detrimental or are at least counterbalanced by other species in the pore solution (Chappex and Scrivener, 2012, Shehata and Thomas, 2000). Additionally, as stated in section 2, alkali concentrations in pore solutions, and hence the pH, tends to be consistently lower in limestone ternary mixes compared to corresponding binary and CEM I mixes (Adu-Amankwah et al., 2017, De Weerd et al., 2011b, Sui et al., 2019). This has significant implications on ASR resistance.

A handful of studies have examined ASR in limestone ternary cements (Favier and Scrivener, 2018, Turk et al., 2017). Figure 10 shows data from selected papers comparing ASR resistance of CEM I and limestone ternary cements, while Figure 11 illustrates the effects of limestone content. Ternary systems show significantly reduced ASR induced expansion compared to CEM I. Caution must however be taken in interpreting laboratory results due to variations in test methods and potential alkali exchange i.e. leaching or ingress from the test solution. Increasing OPC substitution in limestone-fly ash mixes reduced ASR expansion in ternary cements compared to binary fly ash mixes or OPC (Turk et al., 2017, Wang et al., 2019a). Meanwhile, expansion of Portland limestone mortar samples was even greater than that of OPC (Figure 11), demonstrating the importance of both an SCM and limestone for ASR mitigation and confirm the significance of aluminium ions in ASR mitigation (Lindgård et al., 2012, Chappex and Scrivener, 2012). Meanwhile, LC3 cements in 0.32M NaOH solution at 50 or 65% clinker substitution showed expansion an order of magnitude lower than CEM I, and significantly below the 0.04% expansion threshold (ASTM 1293) after 2 years (Avet et al., 2019b, Scrivener et al., 2019). The enhanced performance was due to reduced pore solution alkalinity and pH, as shown in Figure 2.

3.7 Combined aggressive exposures

While individual deterioration processes have been reviewed above, in service environments concrete is simultaneously exposed to multiple aggressive agents, often with synergistic effects, which can affect the rate of degradation. This section therefore reviews recent literature on coupled exposures.

Combined sulphate and chloride ingress:

Some authors (Ukpatha et al., 2019, Santhanam et al., 2006, Chen et al., 2016) have explored the combined effect of chloride and sulphate ions on composite cements. In the presence of sulphates, microcracking can increase chloride diffusivity (Chen et al., 2016). However, precipitation of ettringite can also alter the pore structure, reducing chloride ingress. Meanwhile, the activity of chlorides in the pore solution is reduced due to their incorporation in Friedel's salt. In addition to reductions in ionic activity due to binding, lower concentrations of sulphates and chlorides have been detected in combined solution exposures. This interaction and consequent reduction in diffusivity has been described as competitive antagonism in some recent studies. In fly ash blended cements, Chen *et al.* (Chen et al., 2020) observed chloride ingress was suppressed to a greater extent than that of sulphates but time dependency of the interaction has been suggested elsewhere (Yu et al., 2021). In slag blends however, although chloride ingress increases in combined solutions, sulfate induced expansion tends to be negligible (Chen et al., 2016, Maes and De Belie, 2014, Ukpatha et al., 2019). Similarly, limestone improves resistance to sulphate attack in combined solutions (Mavropoulou et al., 2016), the extent of which depends on temperature, limestone substitution and chloride concentration (Abdalkader et al., 2015). Ternary blends typically contain less portlandite but more carboaluminates. Consequently, the quantity of Friedel's salt and additional ettringite precipitating on exposure to the combined solution is lowered (Mavropoulou et al., 2016). At low temperature (<5°C) however, while Portland limestone cement samples show greater susceptibility to thaumasite formation when exposed to sulphates, chlorides can mitigate against this (Abdalkader et al., 2015). Sotiriadis *et al.* compared the performance of Portland limestone cements and limestone ternary cements at low temperature over 2 years' exposure to sulfates or combined chloride and sulfate solutions (Sotiriadis et al., 2013). Unlike the reference Portland limestone cement, the ternary cements remained intact in the sulphate solution. However, upon exposure to the combined solution, all of the samples eventually started to spall, but with differences depending on the SCM.

As shown in Figure 12, expansion was reduced and the onset of sample disintegration was delayed in the ternary cements, with the fly ash and metakaolin blends showing the least damage. The differences in performance were associated with SCM reactivity, as reflected in compressive strength data. Thus, a less reactive SCM is both weaker and more porous, and so more susceptible to sulphate attack.

Degradation of concrete under freeze-thaw cycles is considered by many as a physical mechanism (Fagerlund, 1997, Giergiczny et al., 2009, Bilodeau and Malhotra, 1997, Chidiac and Panesar, 2008), associated with micro-cracking and eventual spalling due to internal stresses from ice growth or salt crystals (Scherer, 1999, Valenza and Scherer, 2007). Deicing salts are routinely applied to concrete decks in winter to prevent ice build-up or accelerate melting. Consequently, the interaction between chloride ingress and freeze-thaw resistance has received considerable treatment in the literature (Bilodeau and Malhotra, 1997, Palm et al., 2016, Panesar and Ching, 2018, Sun et al., 2020, Zhang et al., 2017a). Freeze-thaw induced concrete degradation, typified by surface scaling, is amplified in the presence of deicing salts (mostly alkali-chlorides) irrespective of the cement type, with the extent of damage proportional to the number of freeze-thaw cycles (Kessler et al., 2016, Mu et al.,

2002, Zhang et al., 2017a). For limestone ternary cements, chloride penetration increased with the number of freeze-thaw cycles, particularly at high w/c ratio (Zhang et al., 2017a). However, the same study showed that air entrainment mitigated freeze-thaw damage, and consequently chloride ingress, irrespective of w/c ratio.

Successive freeze-thaw cycles should theoretically increase susceptibility to carbonation due to internal damage. Similarly, pore coarsening upon carbonation of composite cements should intensify scaling. Increased carbonation has been noted in both OPC and composite cements when concrete samples are subjected to freeze-thaw cycles prior to carbonation (Zhang et al., 2017b, Ferreira et al., 2017), and in field data (Kuosa et al., 2014), where micro-cracking can account for the reduced carbonation resistance. Conversely, carbonation may mitigate surface scaling depending on the cement type. For example, lower scaled matter was measured under freeze-thaw conditions in pre-carbonated concrete containing clinker factors exceeding 80%. At lower clinker factors (<50%), there was reduced buffering of C-S-H carbonation and hence permeability increased (Zhang et al., 2017b), leading to faster saturation.

Field performance of air entrained composite cement concrete, including limestone ternary blends, under combined exposure to carbonation, chloride ingress and freeze-thaw have been reported (Kuosa et al., 2014) after three winter seasons. At equivalent w/c ratio and air entrainment, chloride concentrations increased with SCM replacement level. However, this was mainly limited to the outer ~5mm cover, with concentrations decreasing significantly with depth. It can be deduced that chlorides moved inwards as the freezing front and potential screening effect must have restricted this to the cover region (Sun et al., 2020). Beyond the outer 5mm, chloride concentrations fell sharply to levels comparable to the reference concrete. Whilst the high chloride binding capacity of SCMs may limit increases in total chloride concentration with progressing freeze-thaw exposure, it is evident that binding capacities reduce significantly at low temperature (Panesar and Ching, 2018) and hence may pose a greater risk to reinforcement corrosion. Indeed, freeze-thaw data indicated significant internal damage in air entrained concrete, including limestone ternary cements containing <50% Portland clinker, contrary to those tested in chloride free test solutions.

4. Summary and perspectives

This paper has systematically reviewed the literature, showing relationships between the composition, microstructure and durability of limestone ternary cements. The environmental and technical drivers underpinning this generation of low carbon cements, compositional variability as well as hydration and microstructural development were initially reviewed with emphasis on phase assemblages, pore solution and pore structural differences and their associated durability. Where possible, we have highlighted the efficiency and shortfalls of different aluminosilicate materials (i.e. SCMs) and the limestone content to provide the background information for specification and importantly gaps in the literature. These are particularly important in the light of the recently published BS EN 197-5, which permits limestone ternary cements formulated from a range of commonly used SCMs.

For up to 50% OPC replacement, limestone ternary cements outperform OPC in aggressive chemical environments, with regards to chloride ingress, sulphate and ASR, due to a combination of pore structure refinement and pore solution effects. These benefits are only realised at w/c ratios below 0.5 and SCM/limestone ratios better than unity. These systems however are more susceptible to carbonation. Lowering the clinker factor and hence the reactive calcium content lowers portlandite contents. This increases the risk of carbonation of other calcium bearing phase assemblages. The post carbonation performance must be understood to dispel concerns over carbonation-induced corrosion. Published field data on

these cements is limited, as is performance data under combined aggressive exposures. Investigations into these must be accelerated as widespread adoption of these cements is expected.

Below are a summary of key questions identified from the literature that must be explored to facilitate efficient and large scale utilization of limestone ternary cements.

1. Limestone in ternary cements enhance clinker hydration and the additional hydrates refine the pore structure of ternary cements. However, refinement reaches a maximum, beyond which further hydration does not modify porosity. The underpinning mechanism is not yet understood. Further research is needed to optimize the composition-microstructure relationship to maximize the benefits of pore structure refinement.
2. Despite pore refinement and potentially lower gas permeability coefficients, limestone ternary cements are more prone to carbonation compared to equivalent OPC concrete. Additionally, the chloride threshold to initiate corrosion and propagation are lower in these cements. The severity of these anomalies, which are attributed to the lower matrix pH must be clarified, particularly in relation to carbonation induced corrosion. Further, the chloride induced corrosion risk must be assessed in a manner that takes into account the densified microstructure, binding capacity and realistic exposure conditions.
3. Durability of these cements in aggressive environment relies on reactivity of the SCM and pore densification. The role of admixtures is critical in this regard. The interaction between plasticisers and air entrainers and these cements must be clarified particularly the latter due to lower freeze-thaw resistance.
4. The additionally formed carboaluminate phase plays a greater role in stabilizing ettringite, densifying the pore structure and maintaining ionic balance of the pore solution. These could however be transformed in chloride environment and upon carbonation. Such transformation bears implications on engineering performance which must be elucidated for all chemical environments and their coupling.

In view of the above summary, it is our view that ternary cements offer an alternative to binary composite cements, offering similar performance but with a lower clinker content and/or a lower SCM content. This helps the cement industry to reduce their carbon footprint without rapidly consuming global reserves of SCMs. However, performance of these cements in acidic environment, coupled action with stress and potential interactions between different deterioration processes must be explored in order to assure their performance in service environments.

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Figure captions

Figure 1 Global production of cement, ferrous slag and coal fly ash. Data on cement production extracted from the US Geological Survey's mineral commodity summary reports from 2000 – 2020 (USGS, 2020), coal production and hence PFA from IEA World Energy Balances (IEA, 2020) and Steel production and hence GGBS from World Steel Statistics Yearbook (WorldSteel, 2010, WorldSteel, 2020). Note: fly ash was estimated based on 0.2t of fly ash generated per tonne of coal combusted (Yao et al., 2015) and ferrous slag based on 0.38t of ferrous slag produced per tonne of iron formed in a blast furnace (Das et al., 2007).

Figure 2 Pore solution compositions in ternary cements from different SCMs and their corresponding binary mixes after 28d hydration. (a) Aluminium ion concentration; (b) total sodium and potassium ion concentration. Note: Colours represent mixes for a

given cement type; trend lines show changes in ion concentration from binary to corresponding limestone ternary mixes where these are reported in the same studies. The CEM I substitution level and limestone content are indicated in the bottom rows. Pore solution data extracted from (Adu-Amankwah et al., 2017, De Weerd et al., 2011b, Fernández et al., 2018, Nguyen et al., 2018, Sui et al., 2019) with w/b ratio ranging between 0.4 – 0.5.

- Figure 3 Predicted phase assemblages of alumina-sulfate-carbonate system as may exist in ternary cement, after (Matschei, 2007)
- Figure 4 Comparison of the pore size distribution of limestone ternary blended cement pastes from (a) GGBS as a function cement composition and limestone dosage and (b) calcined clay compared to Portland cement and binary cement pastes. Data taken from (Adu-Amankwah, 2016, Avet et al., 2019a)
- Figure 5 Carbonation coefficient of concrete samples exposed to natural and accelerated carbonation at 1% or 3% CO₂ content and at 0.35 or 0.45 water to binder ratios. Data extracted from (Shah and Bishnoi, 2018b).
- Figure 6 Effect of carbonation on the (a) total porosity and (b) threshold pore diameter of ternary cements compared to unary and binary cement pastes. Data extracted from (Shah and Bishnoi, 2018a)
- Figure 7 Effect of aluminosilicate source on the non-steady state migration co-efficient (Celik et al., 2014, Dhandapani et al., 2018, Proske et al., 2018). Note: CEM CSL (i.e. GGBS-limestone ternary cement) concrete and I were made at 0.5 w/c ratio and tested after 98d. LC3 (i.e. limestone calcined clay cement) concrete from 0.45 w/c mix, tested after 90d whilst CNL (ternary natural pozzolans-limestone) and CFL (i.e. fly ash-limestone ternary cement) were measured on 1 year old concrete made with 0.35 w/c ratios.
- Figure 8 Effect of limestone on chloride binding of binary and ternary cements (Ipavec et al., 2013)
- Figure 9 Influence of limestone addition on the freeze-thaw resistance of composite cements compared to CEM I 42.5R (a) internal damage and (b) scaling of surface matter, after (Adu-Amankwah et al., 2018b). Note: C=CEM I 42.5R, CS=CEM I 52.5R+50% GGBS, CS-L=CEM I 52.5R+40% GGBS+10%L, CS-2L=CEM I 52.5R+30% GGBS+20%L
- Figure 10 Comparison between ASR resistance of CEM I and limestone ternary cements with different SCMs, data extracted from (Hooton et al., 2010, Scrivener et al., 2019)
- Figure 11 Effect of limestone of the limestone and slag content on ASR resistance, data extracted from (Hooton et al., 2010)
- Figure 12 Effect of aluminosilicate type in the limestone ternary cement on mass change caused by the combined chloride and sulphate exposure. Note the clinker factors are in bracket; N=natural pozzolans, FA=fly ash, S=GGBS and MK=metakaolin. Inserts are photographs of the specimen after 24 months in the combined solution, extracted from (Sotiriadis et al., 2013)*Coupled freeze-thaw and chemical attack on concrete:*

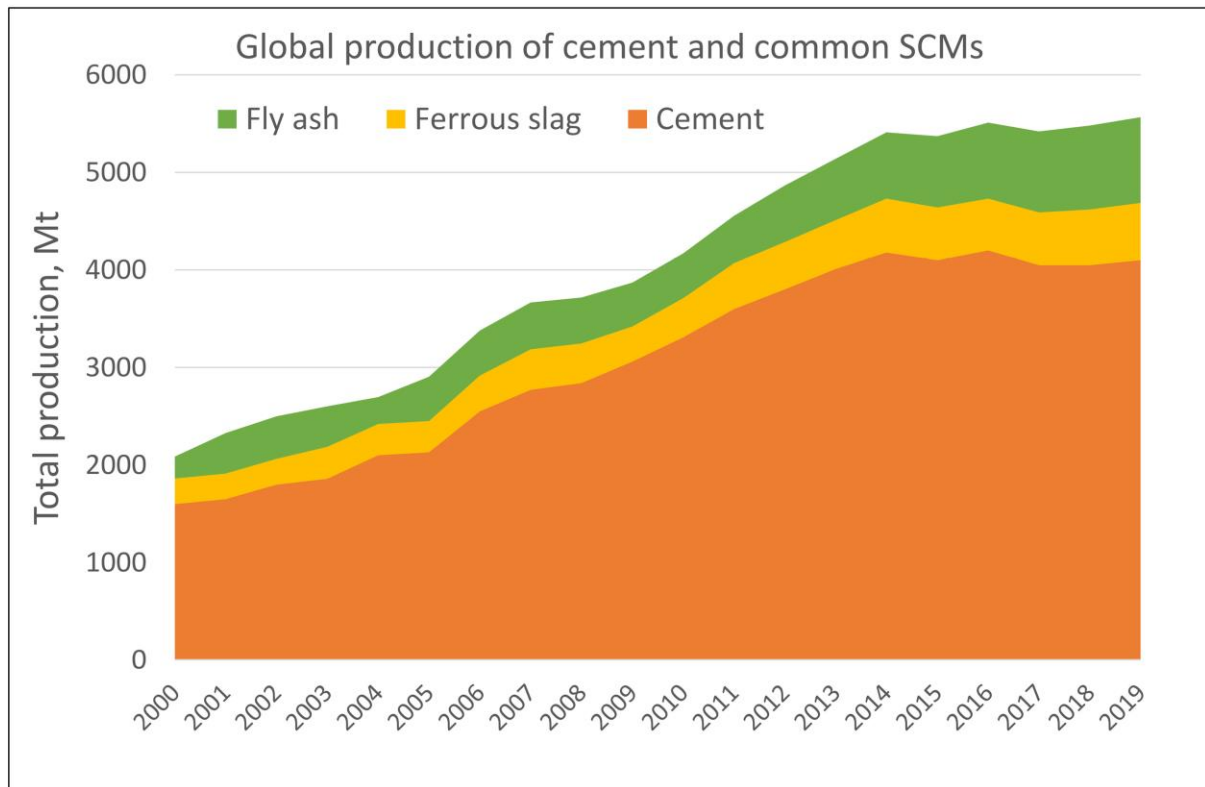


Fig 1

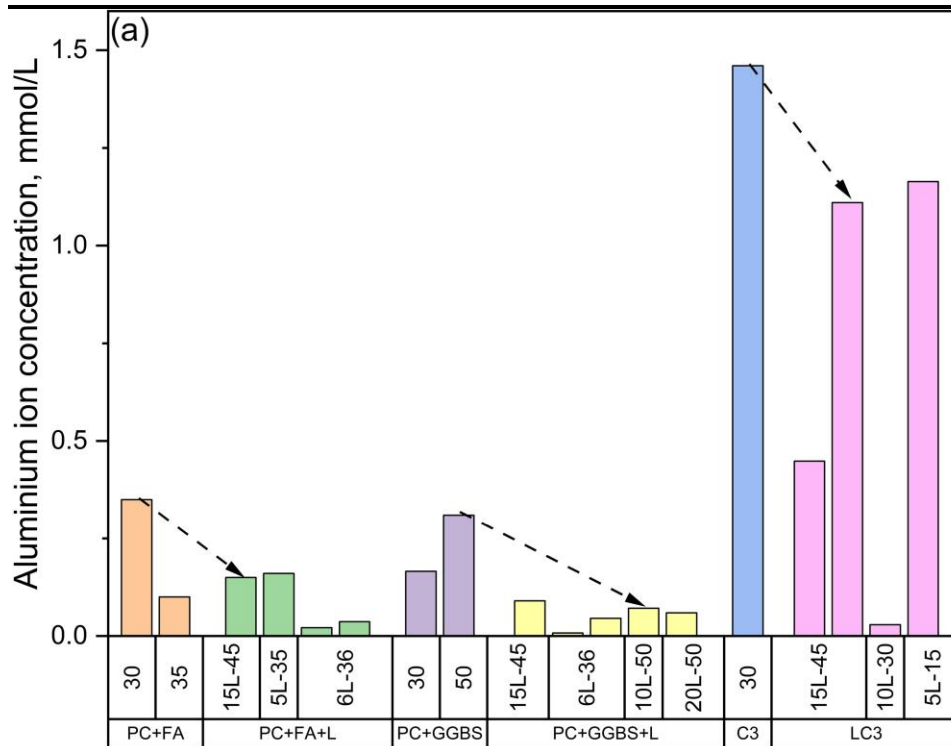


Fig 2a

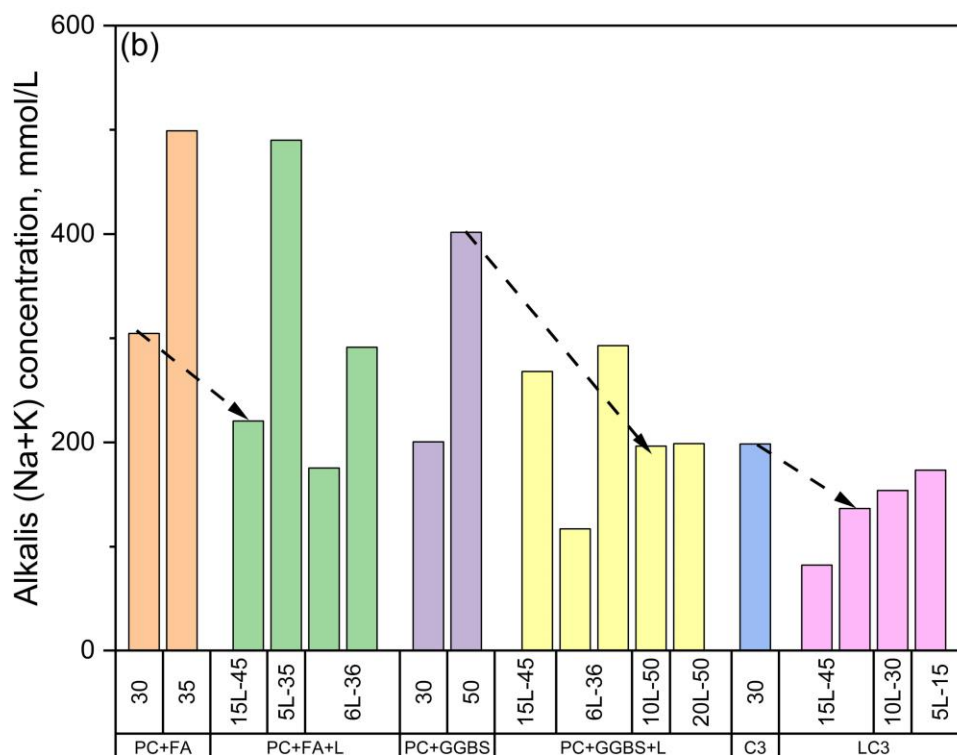


Fig 2b

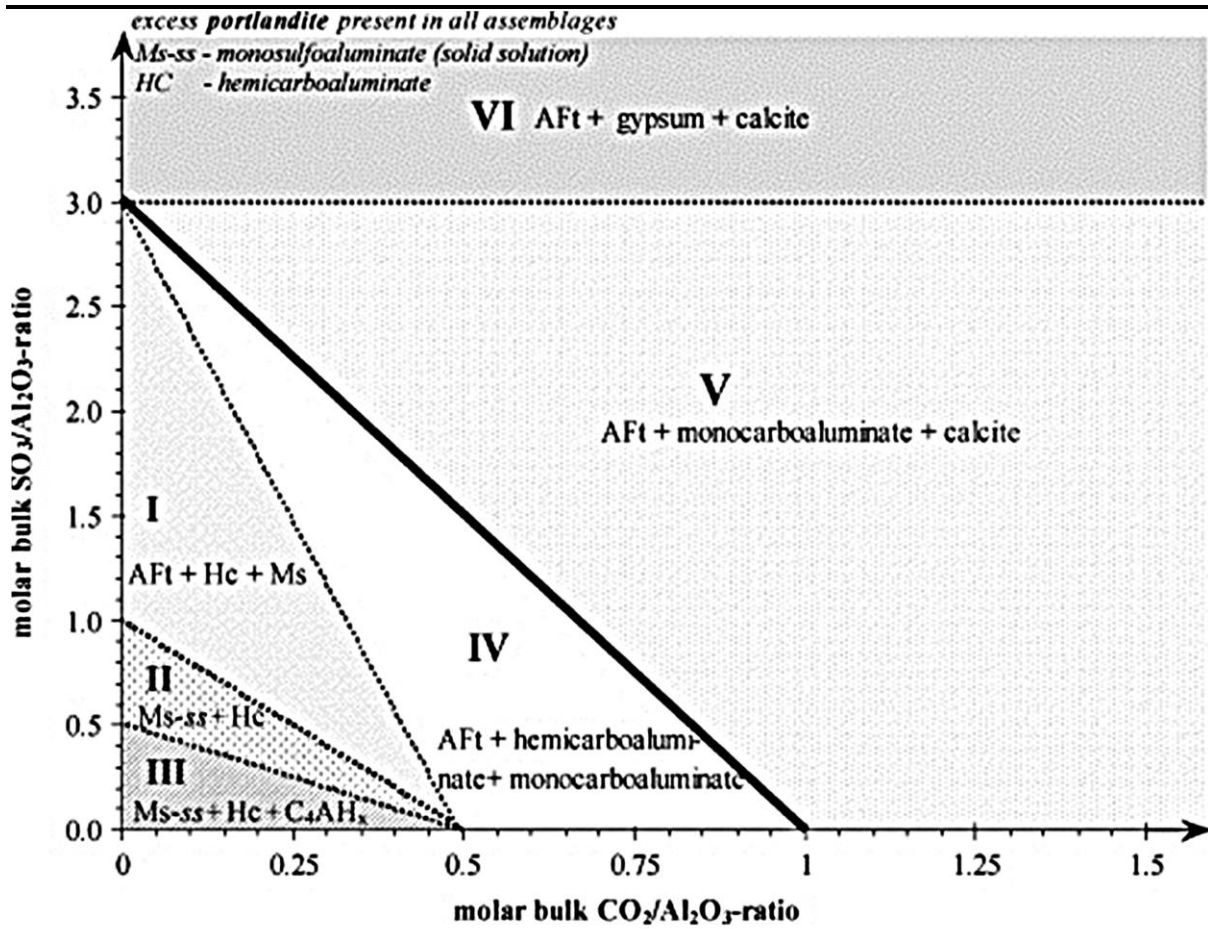


Fig 3

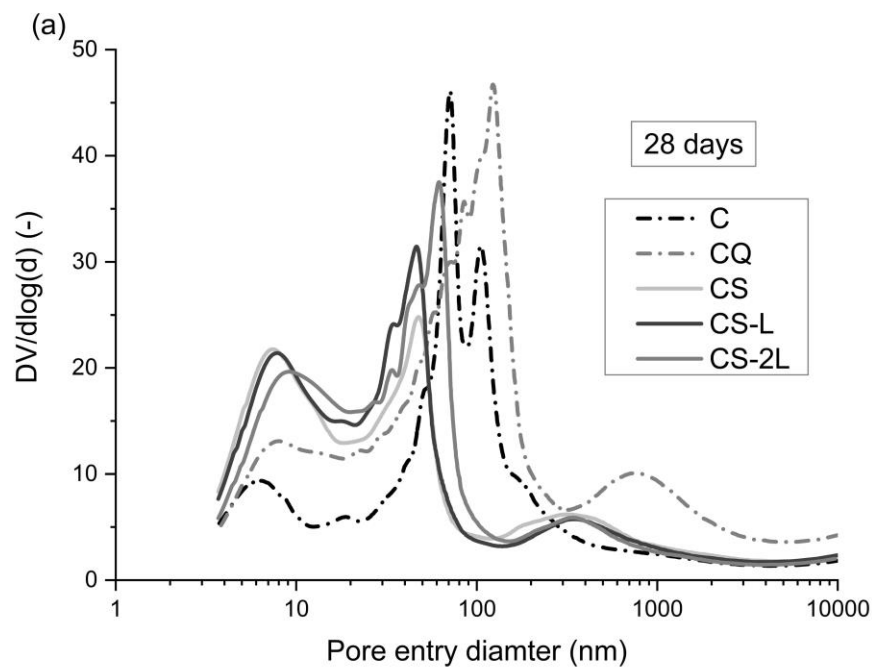


Fig 4a-rev2

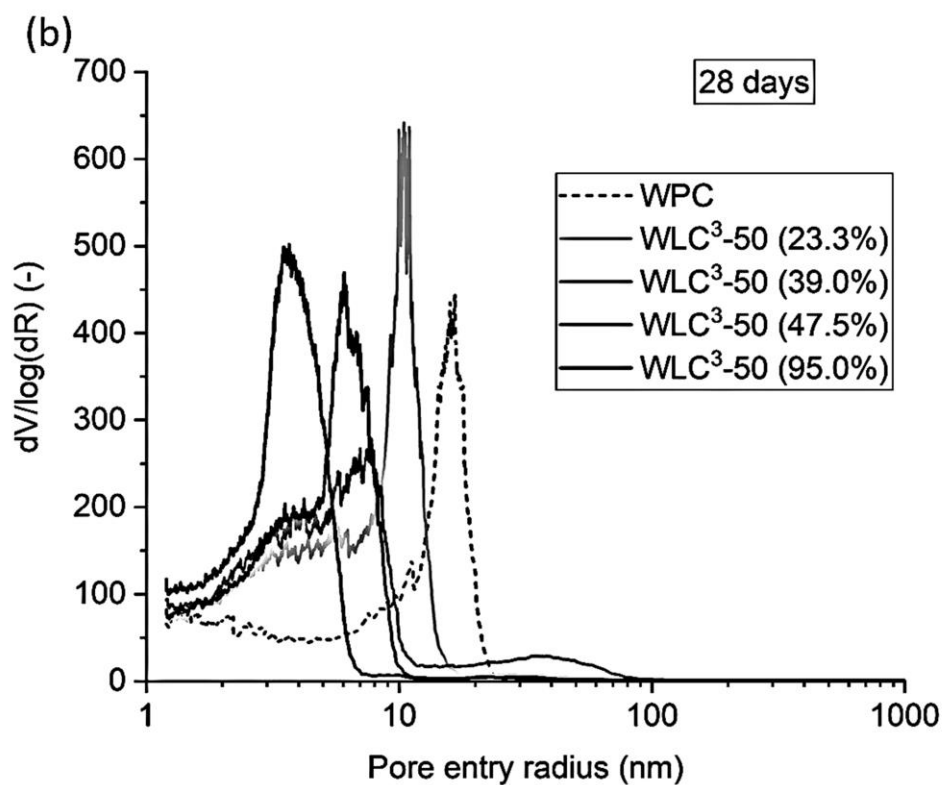


Fig 4b-rev2

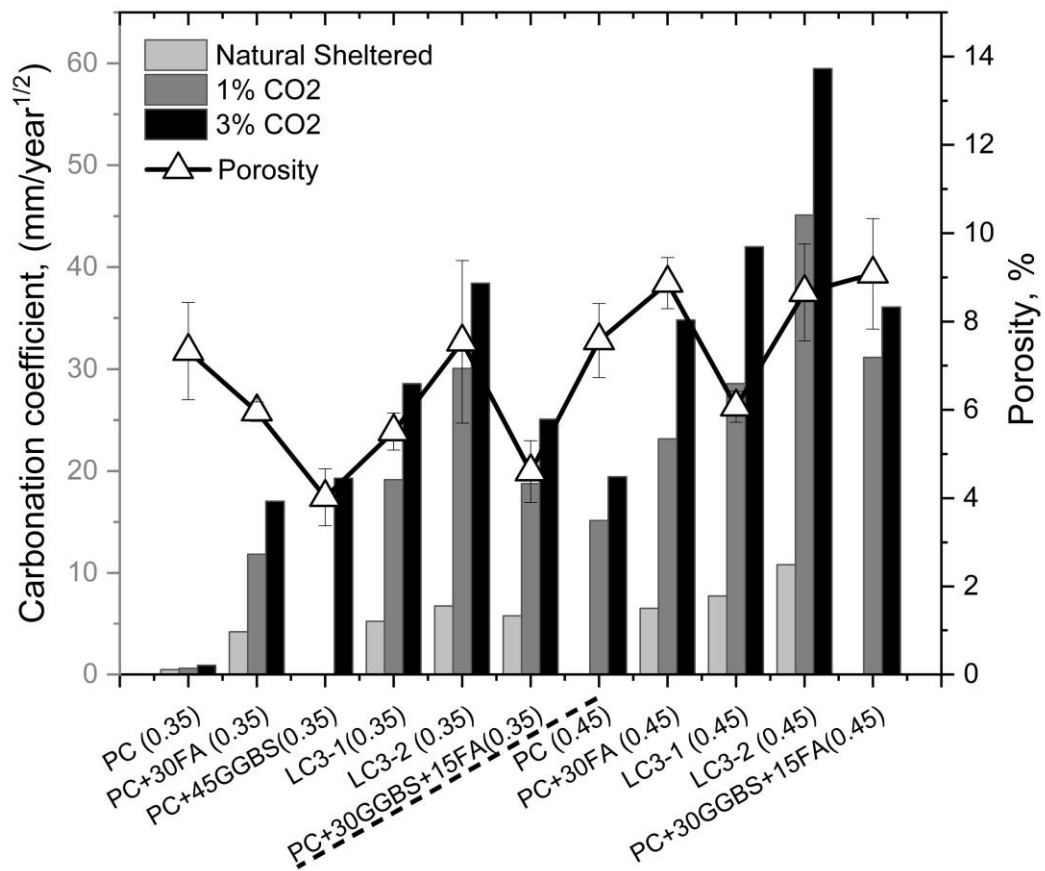


Fig 5

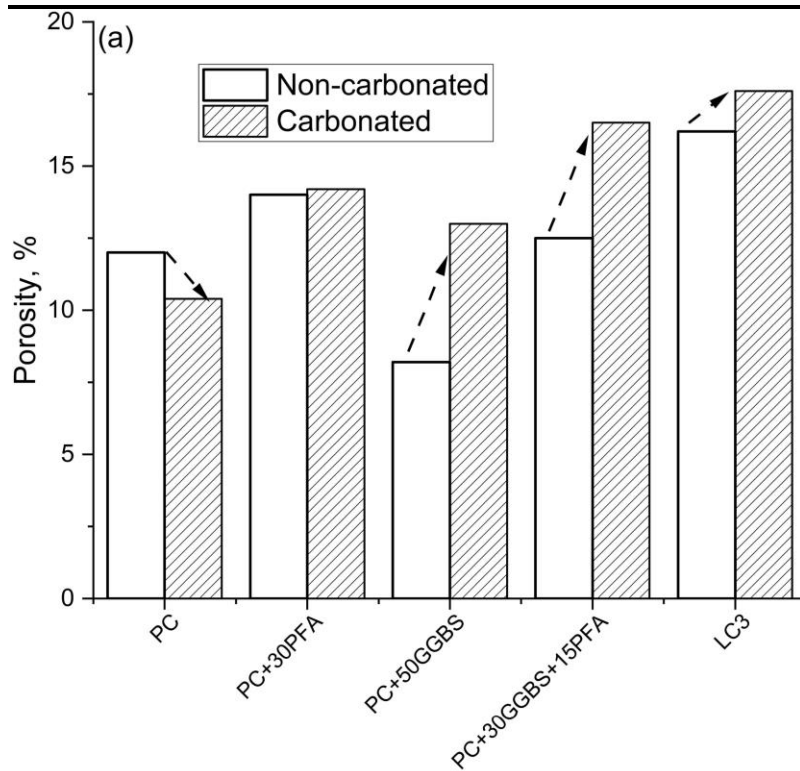


Fig 6a

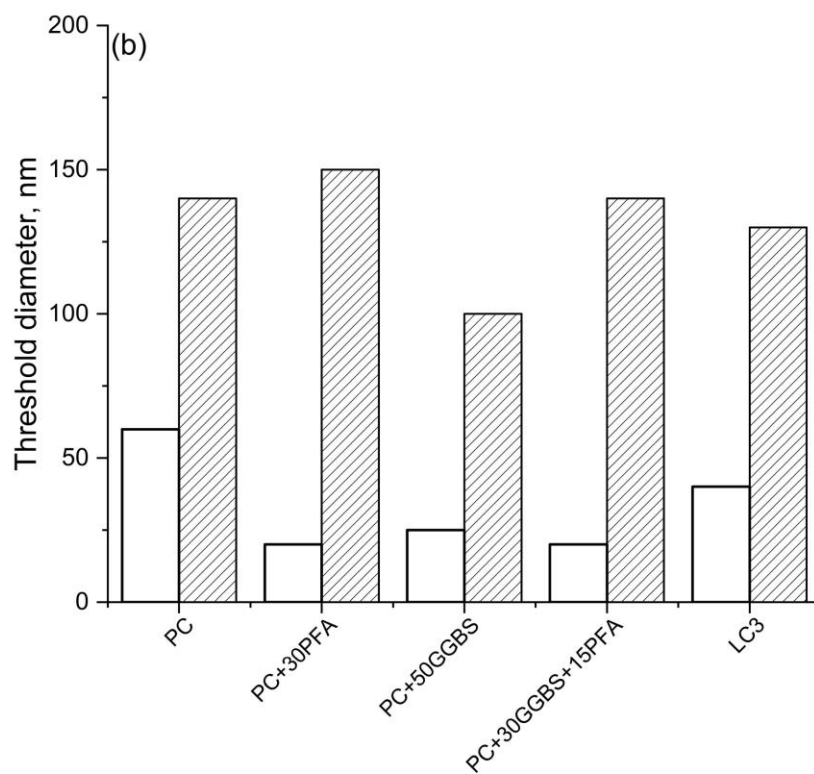


Fig 6b

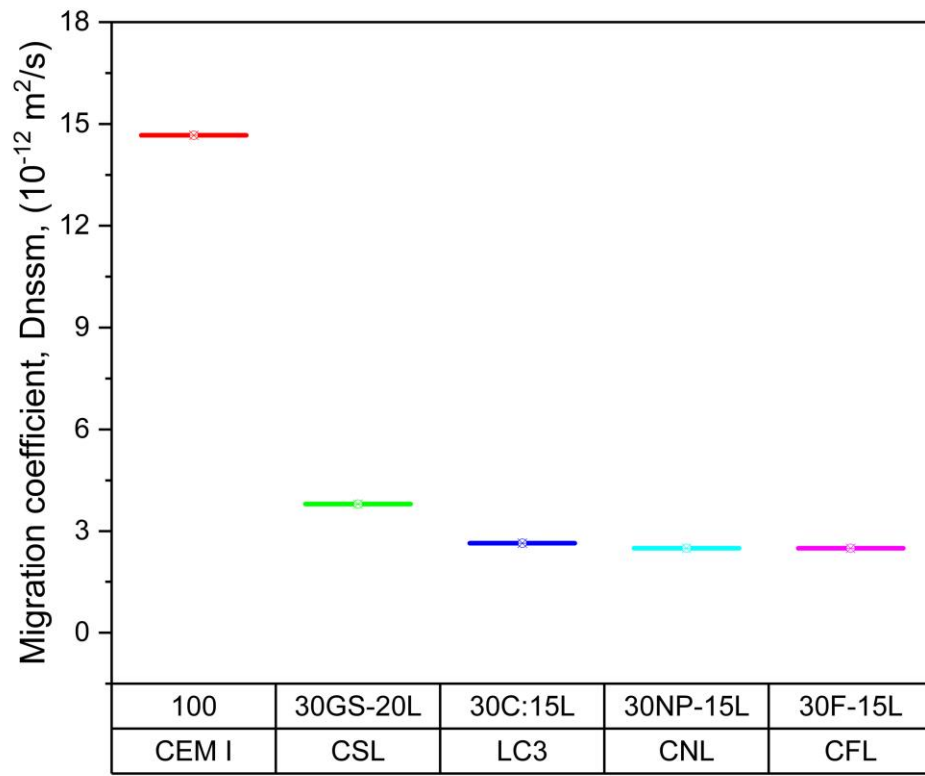


Fig7

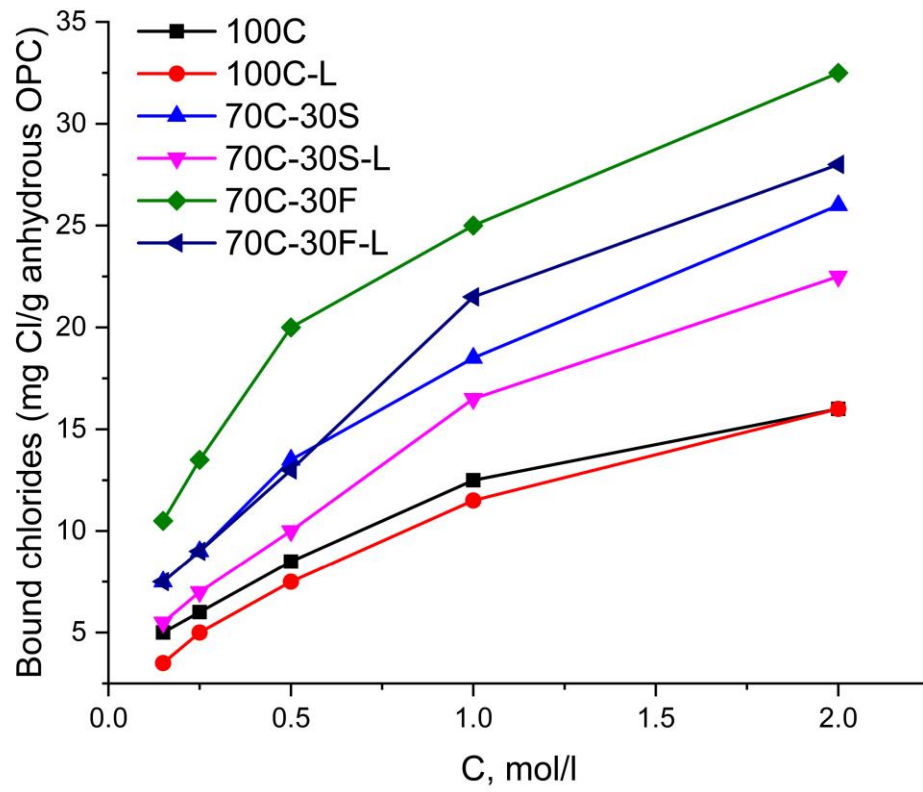


Fig8

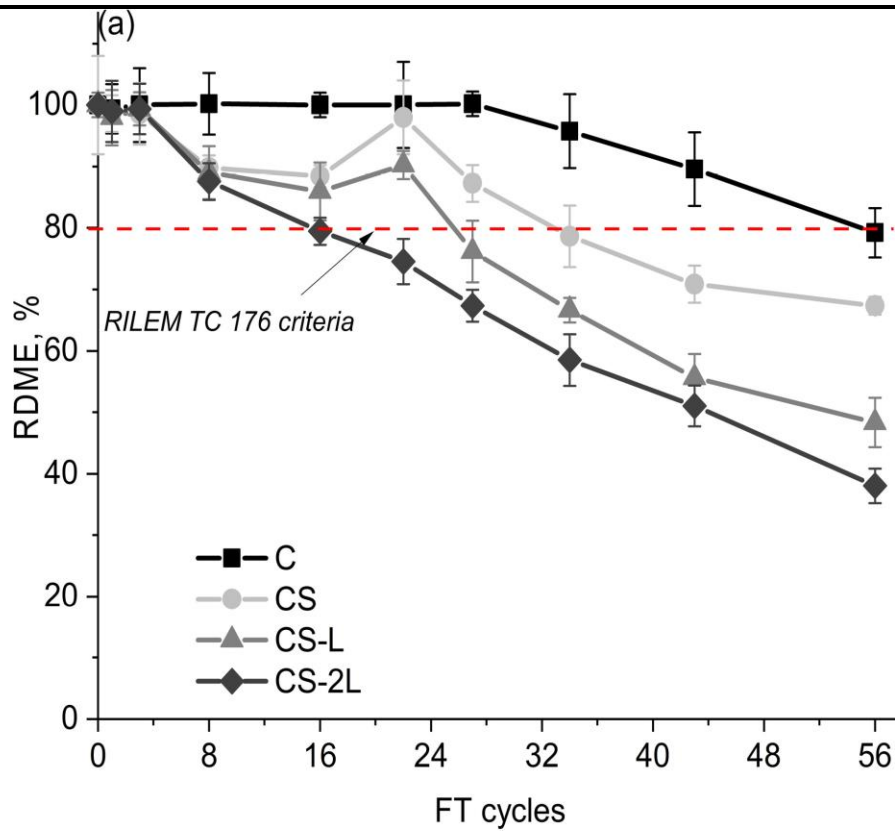


Fig9a

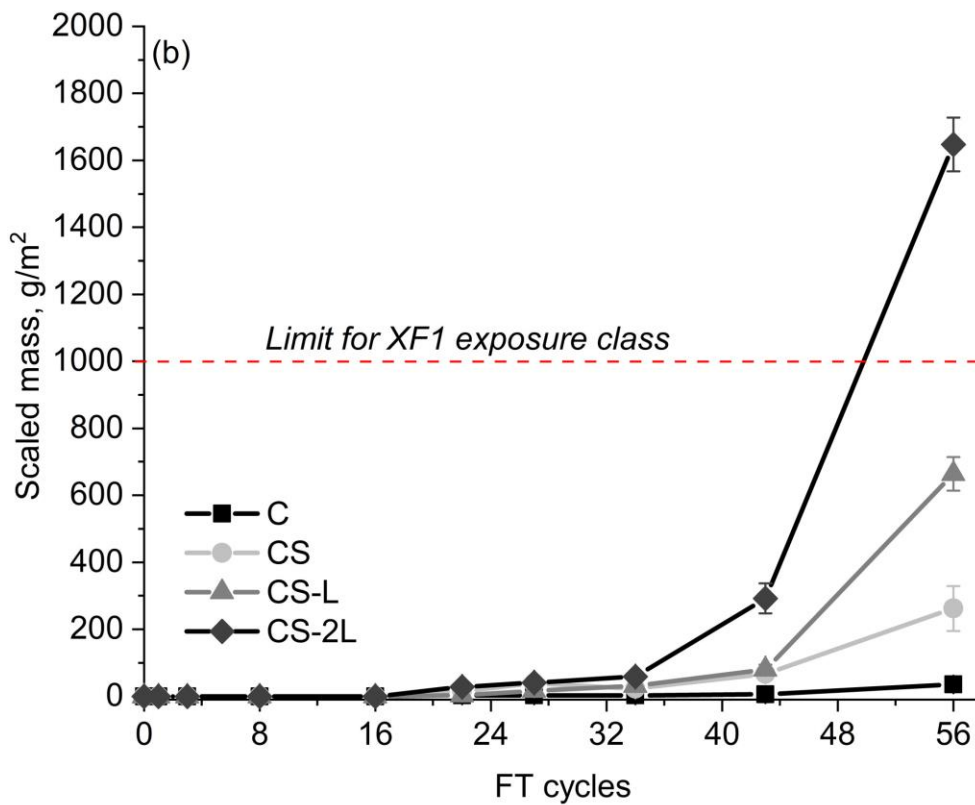


Fig9b

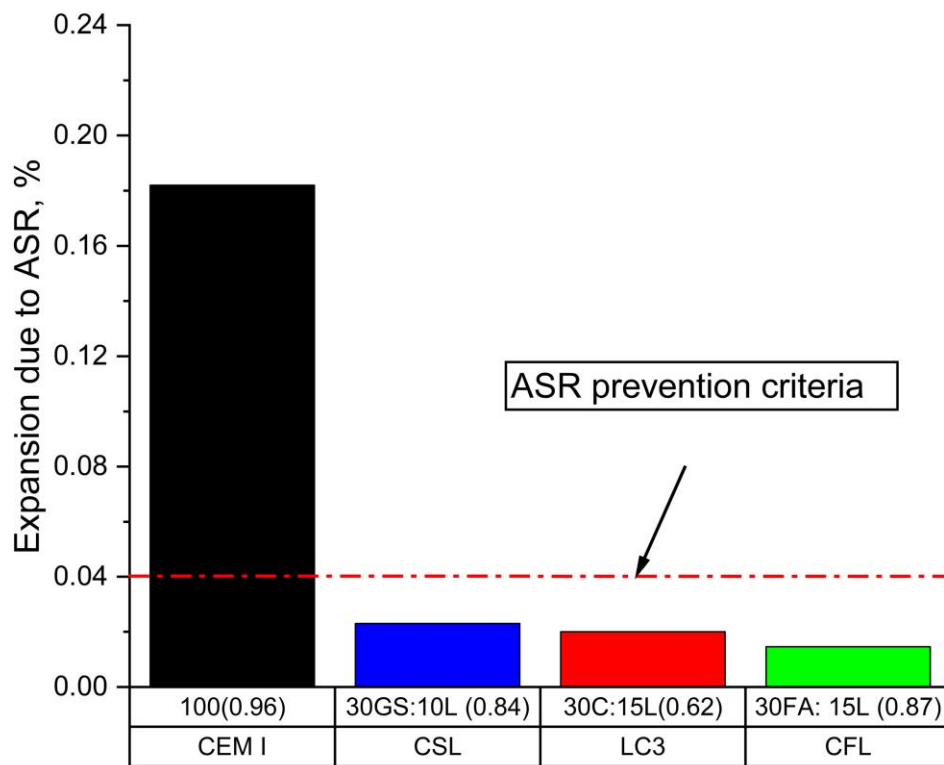


Fig10

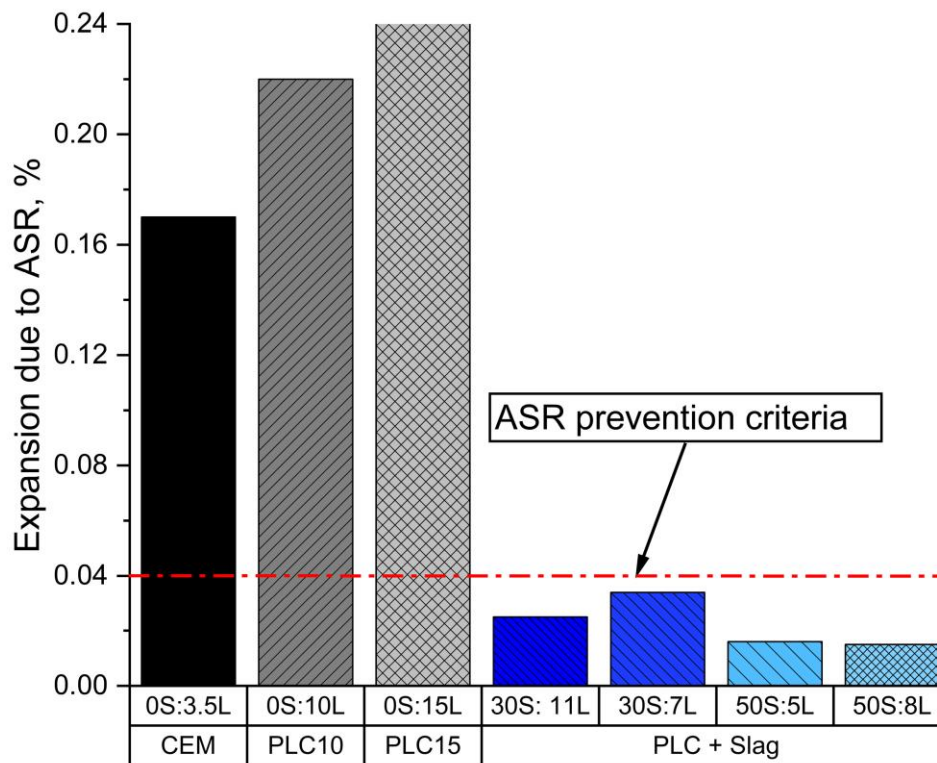


Fig11

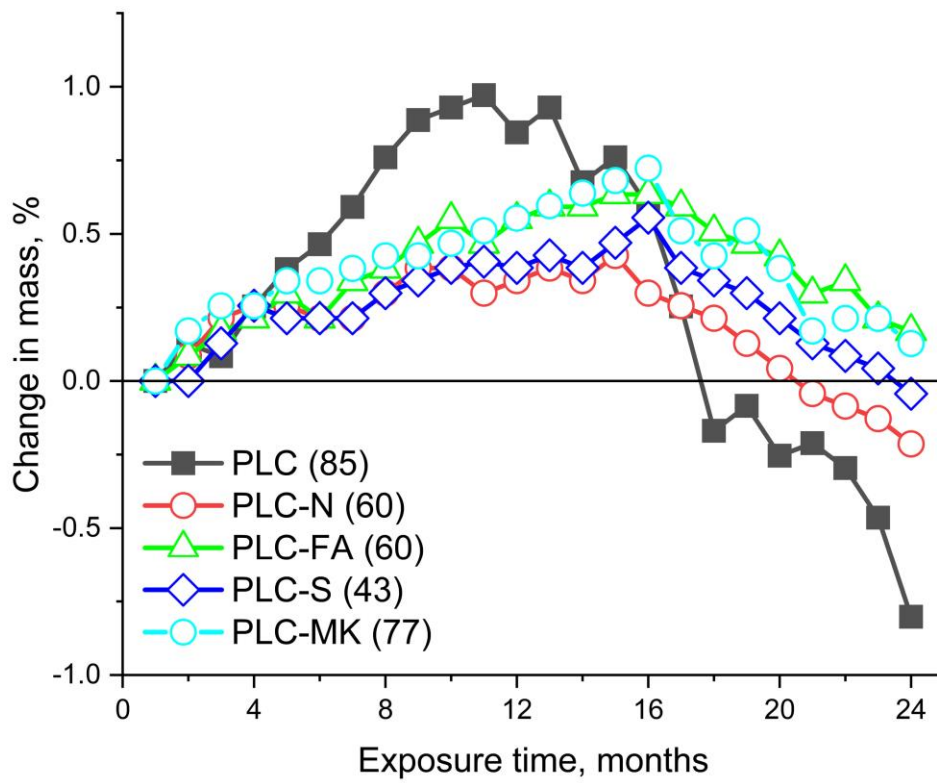


Fig12