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# Recent advances in understanding the role of supplementary cementitious materials in concrete

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### ABSTRACT

Supplementary cementitious materials (SCMs) are commonly used in concrete mixtures as a replacement of a portion of clinker in cement or as a replacement of a portion of cement in concrete. This practice is favorable to the industry, generally resulting in concrete with lower cost, lower environmental impact, higher long-term strength, and improved long-term durability. SCMs have been used in Portland cement concrete for decades and many of their effects are well-understood. Most recent research on SCMs has focused on a few areas: exploring new materials, increasing replacement amounts, developing better test methods, treating or modifying materials, and using additives (e.g. limestone or nanosilica) to improve performance. The advances in knowledge provided by research in these areas are reviewed in this paper, emphasizing the impact of the research on the field.

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### 1. Introduction

Supplementary cementitious materials (SCMs), including fly ash, ground granulated blast furnace slag, silica fume, calcined clays and natural pozzolans, are commonly blended with clinker to make portland cement or used as a replacement for a portion of portland cement in concrete. The practice of using SCMs is increasing, with the world average percent clinker in cement having decreased from 85% in 2003 to 77% in 2010, and it is projected to further decrease to 71% in the future [1]. In the U.S., SCMs are usually added to concrete rather than blended with clinker, and currently more than 60% of ready-mixed concrete uses SCMs [2].

While fly ash and ground-granulated blast furnace slag represent the majority of SCMs used, there is a shift to embrace other materials, which is driven by many factors, including supply-and-demand concerns. In 2011, 3.6 billion tons of cement were produced worldwide [3], and this is projected to rise to 5.8 billion tons by 2050 [4]. A way to meet this rising demand is to continue increasing the use of SCMs in concrete. It is understood that only part of this demand can be met through the use of fly ash and slag, since the annual global productions of these materials are approximately 1 billion tons and 360 million tons, respectively [5,6]. Therefore, the focus of much of the recent research on SCMs has been on the exploration of alternative SCMs and their performance in concrete. While itemizing newly discovered alternative SCMs is not

http://dx.doi.org/10.1016/j.cemconres.2015.03.018 0008-8846/© 2015 Elsevier Ltd. All rights reserved. the goal of this review paper, research on these materials is discussed when findings are applicable to a wider range of SCMs.

This paper summarizes the advances achieved in the past four years in our understanding of SCM use in concrete. One of the primary reasons for SCM use is to reduce the environmental impact of concrete, and recent publications on this topic are reviewed first. Identifying appropriate new materials, maximizing their use, and improving their performance can best be achieved through appropriate material characterization and tests for pozzolanicity, which are reviewed next. Correspondingly, there have been significant advances in the pre-treatment of SCMs for improved reactivity or additives to improve mixture performance, particularly at the nanoscale. The interactions of SCMs with Portland cement is addressed in terms of the impact on early hydration, fresh state properties, mechanical properties, and long-term durability. Lastly, the role of SCMs in ultra-high performance concrete, is reviewed, focusing on the impact of these materials on long-term properties.

#### 2. The role of SCMs in sustainable concrete production

While the use of SCMs in concrete in relatively small amounts (5-20% replacement of clinker) is often driven by economics and improvements in the long-term mechanical properties and durability of concrete, the impetus to replace an increasing percentage of clinker with SCMs often comes from pressure on the industry to reduce  $CO_2$  emissions from concrete production. Often these high volume clinker replacements result in losses in performance at early ages, driving research into balancing sustainability and performance and finding means of performance prediction.

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Since the manufacture of Portland cement is dramatically more energy-intensive and greenhouse gas-emitting than the production of other concrete components, a driver in the production of sustainable concrete is to minimize cement content. Most of the information on the environmental impacts of concrete components comes from life cycle analyses (LCA), which have been extended to include SCMs and admixtures to quantitatively compare them to Portland cement. However, when evaluating SCMs, careful attention needs to be paid to the classification of the materials for the purpose of allocation. For example, Van den Heede and De Belie [7] explained that fly ash and blast furnace slag are often considered to be "avoided waste," with no allocation of the power used for their production, making them attractive concrete components from an environmental perspective. A potential EU re-classification of these materials as "useful by-products" would demand allocation of a portion of the power and pollution used in their production, resulting in a much higher environmental load, exceeding that of cement. In this situation, one could adopt an economic allocation approach in lieu of a typical mass allocation in order to consider byproduct SCM use as sustainable [7]. Petek Gursel et al. [8] also recently reviewed the methodologies used in LCAs and further pinpointed inconsistencies in assumptions and analyses and how these lead to errors in accounting. They also argued that LCAs must account for the drying, grinding, and preparation of SCMs, as this energy input is not negligible.

Assuming that increased SCM content and decreased cement content make sustainable concrete, there have been several recent studies presenting optimization methods for this strategy. For example, Hooton and Bickley [9] highlighted SCM use coupled with aggregate gradation optimization, admixtures, and fillers, enabling the reduction of the Portland cement content for a typical bridge deck concrete mixture from 12 vol.% to 3 vol.% (Fig. 1). Optimization of particle size distributions of powders in concrete, including cement, SCMs, and fillers, can be used to maximize SCM content with minimal negative impact on early age properties. For example Bentz et al. [10] used this method to design blended cements with 35 vol.% fly ash having identical early and later age mechanical properties to a straight cement mixture. Zhang et al. [11] used a gap-graded powder, consisting of fillers, SCMs, and Portland cement, with the materials ground and classified to fit the desired particle size distribution. They recommended that the most efficient use of materials for optimal early and late properties, economics, and environmental impact is to have Portland cement in the 8-24 µm fraction, with fine, reactive SCMs and fillers occupying the finer fraction and coarse, less reactive SCMs occupying the coarser fraction

One of the challenges that arises from increasing the volume of SCM replacement is the prediction of mechanical properties and durability in these systems. To this end, Gruyaert et al. [12] explored the application of an "equivalent performance" metric and "k-value concept," both of

which were found to be challenging to apply to a wide range of performance metrics. This is of particular concern when attempting to replace Portland cement with high volumes of SCMs, as some standards and legislation use these concepts to limit the maximum replacement by SCMs [7]. With all of these strategies, one should not forget that the most foolproof way to design for sustainability is to design for long-term durability, as argued by Hooton and Bickley [9], not only with respect to material choices, but with respect to construction processes; one should not neglect the construction processes that lead to improved durability.

### 3. Material characterization

There is an increasing variety of SCMs being investigated, with much of the recently published literature on SCMs focusing on trial testing of new potential SCMs from waste-streams and natural sources. Some of the challenges with the introduction of so many new materials are finding methods to appropriately characterize them and recognizing the limitations of some existing methods that were developed for other materials [13]. Some of the characteristics of interest when evaluating SCMs are their physical properties, including particle size distribution and specific surface area, and their chemical properties, including oxide composition, phase composition, and amorphous content. All of these affect pozzolanic reactivity, while some also affect interaction with cement hydration and water demand.

Particle size distribution is typically measured by laser diffraction techniques, which represent an advancement over sieving and other standardized methods, but which should be approached cautiously with SCMs because of challenges relating to the agglomeration, refractive index determination, etc. [14]. Surface area is typically measured by nitrogen sorption using the Brunauer-Emmett-Teller (BET) model for analysis, which is more reliable for SCMs than the air-permeability tests standardized for Portland cement [14]. Nitrogen sorption can also be used to assess more than the specific surface area, when additional models such as the Barrett-Joyner-Hallenda (BJH) models and t-plots are used. The BJH model was used by Quercia et al. [15] to determine the pore size distribution in a nanosilica using t-plots to differentiate between external and internal surface area. This type of information is useful when trying to understand the role of internal versus external surface area on workability and reactivity. Further, the t-plot analysis can be used to examine the shape and type of pores [15], providing extensive characterization for porous SCMs.

Oxide composition is important for pozzolanicity, with high silica and alumina content generally agreed to contribute to the pozzolanic reaction. However, recent work by Walker & Pavía [16] suggests that the amorphous content outweighs the silica content as a predictor of long-term pozzolanic activity, which is not surprising since crystalline



Fig. 1. Illustration of potential reductions in Portland cement content through various methods, including SCM use [9].

silica is not generally soluble in cement pore solution. Therefore, oxide compositions should be used with caution as a performance predictor, and only in conjunction with phase composition.

It is generally agreed that amorphous phases in SCMs are more reactive than crystalline phases (with the exception of zeolites), so many studies have addressed the measurement of amorphous content in order to relate this to performance. This can be done rather simply, by looking at the size of the amorphous hump in an X-ray diffraction plot [16]. Rietveld analysis of X-ray diffraction data allows the determination of phase composition using an internal or external standard to quantify crystalline phases and the total amorphous content through subtraction. However, this method does not allow differentiation between different amorphous phases. Snellings et al. [17] applied a new method called "Partial or No Known Crystal Structure" method (PONKCS) to characterize SCMs as well as hydrated pastes. Just like the peaks of crystalline phases have unique 20 values, the humps of amorphous phases have unique  $2\theta$  values. While these phases have no known crystal structure, their 20 positions and hump shapes can be used in conjunction with Rietveld analysis to quantify the phase composition. For example, Fig. 2 (taken from [17]) shows the deconstruction of an X-ray diffractogram into constituent phases, showing the contributions of metakaolin and the glassy phases in slag to the shape of the plot. Application of this method allows much more complete characterization of SCMs, most of which are primarily amorphous, and, as Snellings et al. [17] demonstrated, enables the tracking of SCM degree of reaction in pastes.

Calcined kaolinite (metakaolin) is a commonly used SCM and other clay minerals, including illite and montmorillonite, are increasingly being examined for their pozzolanicity. In characterizing these materials, X-ray diffraction is important to understand amorphous content and crystalline impurities, but thermal analysis is also used to measure the degree of dehydroxylation and to determine optimal calcination temperatures [18–20]. Nuclear magnetic resonance (NMR), for silicon and aluminum, also provides useful information about calcined clays, allowing observation of changing coordination states through calcination, which can be related to SCM properties [18]. One dimensional mathematical modeling of the kaolinite calcination process can distinguish between the roles of conduction and convection in the calcination process, leading to the determination of the most effective calcination methods [21].

Interestingly, while metakaolin is often considered to be amorphous due to the absence of crystalline kaolinite peaks in X-ray diffractograms (Fig. 2), recent studies have investigated short-range order in this SCM. For example, Trusilewicz et al. [22] used transmission electron microscopy (TEM) to show that the original microstructure of kaolinite is reflected in the post-calcined material, with the appearance of



Fig. 2. XRD pattern decomposition of a sample composed of 50 wt.% metakaolin, 25 wt.% blast furnace slag, and 25 wt.% quartz [17].

aggregations of long, thin, somewhat irregular hexagonal sheets on the order of 150–300 nm. Correspondingly, selected area electron diffraction (SAED) results show both diffuse patterns, reflecting amorphous material, and areas of localized crystallinity across the material.

### 4. Pozzolanicity testing

One of the most important characteristics of SCMs is their pozzolanicity, or their ability to consume calcium hydroxide (portlandite, CH) and form calcium silicate hydrate (C–S–H). There are several methods in use to measure pozzolanicity, and advances in these methods are described here.

One common way to measure pozzolanicity is to measure the consumption of portlandite in SCM-containing cement pastes over time using thermal analysis methods such as thermal gravimetric analysis (TGA) and/or differential thermal analysis (DTA). When using this method, there are several precautions that should be taken that are increasingly recognized. For example, the decomposition temperature for portlandite varies depending on several factors, including alkalis in the system and grain size [23], so it is important to determine the appropriate temperature to use for each sample by examining the first derivative of the TGA mass-loss curve or DTA plot [24] or the second derivative [25]. Another point to note is that most pastes for TGA examination are dried first in order to store them for testing, so that the evaporable water is lost prior to testing. Since the evaporable water content of pastes varies with the degree of hydration (and the water-to-cement ratio if not held constant), the basis for percent mass loss calculations varies with each sample. There are several ways to avoid this problem, e.g. testing a sample that has not been dried prior to testing, accounting for the evaporable water loss [20], or using an "ignited weight" as the sample weight [26], assuming that the SCM itself does not lose significant mass at the temperature chosen. Another problem occurs if the samples are exposed to carbon dioxide during grinding, drying, storage, or testing, in which case the calcium carbonate content of the sample must be measured and accounted for [25], referencing that in the sample to that in the original cement. And finally, it should be noted that other hydration products also lose mass in the temperature range of portlandite decomposition, so that the mass lost in this range over-estimates portlandite content; this problem can be accounted for using a modified calculation proposed by Kim and Olek [25].

It is also becoming increasingly accepted that the most appropriate control specimen to use when measuring pozzolanicity is not a cement-only paste, but a paste containing a non-reactive filler of similar particle size distribution as the SCM being tested. This is to distinguish the pozzolanic reaction from so-called "filler effects" derived from increased nucleation sites for hydration products and increased space available for hydration product precipitation [27]. While many studies use quartz, some have shown that ground river gravel is also suitable [28]. In fact, due to filler effects, it is often observed that the portlandite content of a paste containing filler is higher than the control [29] and that increasing water-to-cement ratio can encourage a higher degree of pozzolanic reaction [28].

In the interest of time and cost savings over thermal analysis such as TGA or DTA, Mendoza and Tobón [30] evaluated the use of a moisture analyzer to measure C–S–H or C–A–S–H content on heating to 230 °C in lieu of portlandite content. The method showed good correlation with TGA results for lime–pozzolan pastes.

Since measuring portlandite content of cement pastes is generally done after 7–90 days or more of hydration, there are several chemical tests that are used to measure pozzolanicity, some of which are rapid assessments of reactivity in lime solutions (e.g. the Chapelle test [31]) or a cement–water solution (e.g. the Frattini test [32]). A variation on these methods includes the so-called "saturated lime test" used by Frías et al. [33,34], who combined 1 g of an SCM with 75 mL limesaturated solution, stored at 40 °C, and determined fixed lime from 1

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to 360 days. Examination of the solids allows determination of phase formation under these conditions. Another variation includes a method introduced by Sinthaworn and Nimityongskul [35], who tested a variety of methods and used electrical conductivity loss in the solution to gauge pozzolanicity. They determined that a solution made with Portland cement was the most effective, using 1.0 g pozzolan with 200 mL solution and an optimum testing temperature of 80 °C. In a similar study, Velázquez et al. [36] determined the optimal solution for using electrical conductivity to gauge pozzolanicity to be a supersaturated lime solution at 80 °C. However, it is important to note that these chemical tests may not correlate well with other indicators of pozzolanicity, particularly the commonly-used strength activity index. Tironi et al. [19] have suggested that solution tests for SCMs with high alumina contents, such as calcined clays, may overestimate their pozzolanicity. Further, these tests may be better predictors of short-term pozzolanic activity, which is correlated with surface area, than long-term pozzolanic activity [19].

Examining the kinetics of the pozzolanic reaction is also of interest, but this necessarily varies with the SCM tested. The apparent activation energy, or temperature sensitivity, was evaluated by Ninov et al. [37] for metakaolin–lime pastes, determining that the rate of the pozzolanic reaction was limited by diffusion and the rate of the chemical reaction. Similarly, Wang [26] evaluated apparent activation energy for Class C, Class F, and co-fired biomass ashes, determining a low activation energy for all, indicative of diffusion-controlled reactions.

Another means to examine pozzolanicity is to examine the degree of reaction of the SCM itself. As most SCMs are amorphous and finely divided, this is challenging. Work by Kocaba et al. [38] compared methods for monitoring degree of reaction of blast furnace slag, including selective dissolution, differential scanning calorimetry, scanning electron microscopy, chemical shrinkage and isothermal calorimetry. The most precise method was suggested to be the scanning electron microscopy with image analysis, while selective dissolution was shown to be unreliable. Later work by Yio et al. [39] confirmed the applicability of scanning electron microscopy with image analysis for measuring degree of reaction of slag.

### 5. Treatment of SCMs and additives to improve reactivity

### 5.1. Thermal activation

Clays, such as kaolinite, must be calcined before use as SCMs to increase reactivity through amorphization. The optimization of the calcination process is a subject of recent research, particularly in the context of optimizing temperature and time for calcining nonkaolinite clays, such as montmorillonite or illite, or blends of clay minerals. Fabbri et al. [40] noted that while the thermal treatment of kaolinite to produce metakaolin increases pozzolanicity, thermal treatment also decreases particle size and specific surface area through agglomeration and sintering, which can reduce pozzolanicity. Therefore, increasing the temperature higher than that necessary to dehydroxylate the metakaolin (beyond 600 °C in the work by Fabbri et al. [40]) reduces SCM reactivity because of this particle size reduction, so that the authors suggest not to calcine at temperatures higher than 750 °C. Fernandez et al. [18] calcined kaolinite, montmorillonite, and illite clays, relating dehydroxylation and amorphization to pozzolanicity, and seeing enhanced sintering or agglomeration with montmorillonite during calcination compared to the other clays. Natural zeolites also benefit from thermal treatment to enhance performance as demonstrated by Narasimhulu et al. [41] and Vigil de la Villa et al. [42], showing that calcination decreased water demand and increased strength of cementitious materials.

In addition to exploring impure clay blends as sources of SCMs, there is interest in examining kaolinite-containing waste materials as SCMs in the interest of finding sources of SCMs that are plentiful and of lower cost than pure kaolinite. For example, Frías et al. [43] examined metakaolins derived from thermally-treated paper sludge. Thermal treatment conditions for this material were similar to those used for pure kaolinite, but optimization considered the decomposition of organic material and the prevention of free lime formation from calcite as well. Thermal treatments are also applied to other waste materials to make them suitable for SCMs, as in another study by Frías et al. [34] who examined the possibility of thermally activating wastes from the extraction of slate for roofing, flooring, and paving tiles, optimizing calcination temperature and time for dehydroxylation, amorphization, and optimal pozzolanicity. Similarly, Li et al. [44] applied thermal treatments to coal gangue, a waste from coal excavation, to create a pozzolanic SCM through amorphization of kaolinite, feldspar, and mica phases.

Agricultural waste residues are also subjected to thermal treatments before use as SCMs in order to create a siliceous ash. Recent studies have examined the role of chemical treatment prior to combustion that can improve the SCM properties. For example, Gholizadeh Vayghan et al. [45] optimized the concentration of a hydrochloric acid solution used to leach metallic impurities and alkalis from rice husk, with the goal being to use a stronger acid at a lower concentration than used in prior work. They found that the optimal concentration for the acid leaching solution to maximize pozzolanicity was 0.01 N HCl, with this ash also possessing greater surface area than a non-treated ash. Similarly, Ataie and Riding [46] examined hydrothermal and thermochemical treatments rice straw ash and wheat straw ash, essentially comparing distilled water to 0.1 N HCl solution at different temperatures. They found that the higher the temperature, the more effective the acid was at removing alkalis and metals from the agricultural residues, thereby improving pozzolanicity. In another study, Ataie and Riding [47] examined the impact of the similar pretreatments on corn stover and high lignin residue, a by-product from bioethanol production, showing improved pozzolanicity for both after acid leaching.

#### 5.2. Additives

Researchers have tried inorganic additives to enhance pozzolanic reactivity of SCMs. Ghorbel and Samet [48] enriched kaolinite with iron by adding ferric nitrate solution prior to calcination in order to observe the role of iron on the formation of metakaolin and on the resulting pozzolanic performance. X-ray diffraction indicated the formation of hematite ( $Fe_2O_3$ ) and goethite (FeOOH) in the metakaolin, and compressive strength tests of pastes suggested that addition of up to of 2.7%  $Fe_2O_3$  enhances metakaolin pozzolanicity. Similarly, Taylor-Lange et al. [49,50] added zinc oxides to clays, including kaolinite, montmorillonite, and illite, before and after calcination. With metakaolin they found increases in 28-day compressive strength with zinc oxide additions, but not with calcined montmorillonite and illite. Interestingly, the combination of ZnO and calcined clays reduced the cement hydration retardation normally seen with zinc oxide additions.

### 5.3. Particle size reduction

Pozzolanic reactivity can generally be directly linked to particle size and/or specific surface area, so grinding pozzolans more finely, as was done in a study on rice husk ash by Van et al. [51], can lead to improved reactivity. Reducing particle sizes of SCMs and fillers to the nanometer scale has also been shown to enhance pozzolanic reactivity in addition to enhancing nucleation and growth of C–S–H during cement hydration. Work on nanoscale additions began with nanosilica and research continues into the effects of these materials [52–60], but work is also being extended to other nano-sized particles, including natural pozzolans and clays [61–63] and other oxides used as fillers or nucleation enhancers [64–66].

Silica fume and other finely divided SCMs and additives, particularly nanoparticles, are difficult to disperse in cementitious mixtures, leading to inefficiencies in their use, meaning that the full effect of their contributions to performance is not often realized. Rodríguez et al. [67] tackled this problem in silica fume by using high-frequency

ultrasonication to disperse silica fume in mixing water and found increased consumption of portlandite and formation of C–S–H with a longer chain length, increased substitution of silicon by aluminum, and a lower Ca:Si ratio than with densified silica fume. Kawashima et al. [66] took a similar approach with nano-calcium carbonate, improving dispersion through combined use of sonication and chemical admixtures.

### 6. Effects of SCMs on cement hydration

A review on SCMs by Lothenbach et al. [27] summarizes the role of SCMs on cement hydration well, describing, in particular, impacts on cement hydration kinetics, phase assemblage in hydrated systems, and composition of C–S–H. For example, SCMs have been observed to have so-called "filler effects" on cement hydration kinetics, which can be separated into two roles depending on the timing of the effect. SCMs (and inert fillers) with very small particle sizes can enhance hydration kinetics during the acceleratory period of hydration by acting as nucleation sites for C–S–H precipitation, as shown in Fig. 3A. It has also been observed that SCMs can extend the time of commencement of the deceleratory period of hydration by "diluting" cement content, thereby providing additional space for growth of C–S–H, as shown in Fig. 3B.

The filler effect concepts have been reinforced by researchers in recent publications, with rigorous examination by Oey et al. [68], for example. Antoni et al. [29] observed increases in portlandite content of cement pastes when an inert quartz filler was used, suggesting that the degree of hydration Portland cement can achieve is greater in the presence of fillers. Other researchers have shown formation of a layer C-S-H around SCM particles, particularly fly ash, when little of the fly ash has reacted, suggesting that the fly ash was acting as a nucleation site [69]. The filler effect can be utilized to combat some known problems associated with high volume SCM use, namely delayed setting and low early-age mechanical properties. Bentz et al. [70] demonstrated that fine limestone additions can reduce setting time in high volume fly ash mixtures, and limestone was more effective than a fine silica filler. Bentz [71] later showed that fine limestone additions can offset the temperature sensitivity of high volume fly ash mixtures, reducing setting times at low temperatures.

It is known that the use of SCMs reduces the calcium-to-silicon ratio of C–S–H and also increases the mean silica chain length [27]. The use of alumina-bearing SCMs can lead to the formation of C–A–S–H with aluminum substituting silicon in the C–S–H, primarily in the bridging sites [27]. When the amount of alumina exceeds that which can be accommodated by C–S–H, notable in high volume SCM replacements,

phases such as stratlingite may precipitate and can be intermixed with the C–S–H [27,72,73]. With regard to phase assemblages in the presence of SCMs, Antoni et al. [29] demonstrated that combining limestone with metakaolin and cement results in the formation of hemicarboaluminate and monocarboaluminate phases. Similarly, combining metakaolin and blast furnace slag [74] or fly ash [24] also results in the formation of hemicarboaluminate.

Several studies have pointed out the impact of SCMs on the hydration of C<sub>3</sub>A, noting the disruption caused from sulfates contributed by the SCM or sulfate consumption by the SCM. Dittrich et al. [75] have shown that soluble sulfates from fly ash can cause delayed setting. On the other hand, Antoni et al. [29] and Snellings et al. [76] note that metakaolin and zeolites, respectively, can alter the sulfate availability in the solution, causing the systems to be undersulfated. While most research focuses on the effect of SCMs on cement hydration, the role of the cement on SCM pozzolanicity should also be acknowledged. Work by Cyr et al. [77] has shown, for example, that the pozzolanicity of metakaolin is reduced in low-C<sub>3</sub>A cements.

### 7. Effects of SCMs on workability

Pozzolanicity is only one of the factors when selecting SCMs for use in concrete mixtures; many potential SCMs have detrimental effects on concrete workability, which may limit their application. In some cases, the water demand of a concrete mixture increases when a pozzolan is used because of small particle size, such as is the case with silica fume and nano-scale additives. In other cases, high internal porosity increases water demand through water absorption by the pozzolan, such as is the case with zeolites and some agricultural residue ashes. The latter effect can outweigh the former, as noted by Walker & Pavía [16], who saw that specific surface area had a much greater effect on water demand, measured by flow table tests, than particle size distribution for a variety of pozzolans tested. Quercia et al. [15] saw similar results when correlating physical properties of nanosilica to slump flow. Another factor contributing to water demand is agglomeration or flocculation of SCM particles, whereby large agglomerates trap water that cannot contribute to mixture fluidity; this effect was seen by Kong et al. [78] for nanosilica SCMs.

Optimization of particle size distribution in cement–SCM–filler systems is an approach that is used to design self-consolidating concrete and is also being employed to better control workability in traditional concrete containing SCMs. For example, Bentz et al. [79] measured rheological properties of cement–fly ash mixtures in a wide envelope of particle size distributions and replacement levels, finding that yield stress is related to particle density of cement and plastic viscosity is



Fig. 3. Illustration of filler effects of SCMs and fillers on cement hydration kinetics. A) SCMs and fillers with very small particle sizes can act as nucleation sites, increasing the rate of growth of C–S–H, B) SCMs and fillers can delay the onset of the deceleratory period by providing additional space for C–S–H growth [27].

related to total particle surface area and packing density. Correspondingly, Vance et al. [80] found for mixtures of cement with limestone filler, and metakaolin or fly ash that yield stress and plastic viscosity were also related to total specific surface area.

The interaction of superplasticizers and water-reducers with SCMs is an area of recent research, particularly since the increased water demand is usually managed through addition of these admixtures rather than through an increase in water-to-cement ratio. For example, it has been shown that polycarboxylate-based superplasticizers may not be as effective with natural pozzolans as with other SCMs, likely because of adsorption [81].

### 8. Effects of SCMs on strength

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SCMs are generally understood to increase concrete long-term strength through the pozzolanic reaction and decrease early-age strength due to dilution of cement. These trends are consistent for most SCMs, including fly ash, metakaolin, and agricultural residue ashes, as reviewed here.

Guneyisi et al. [82] examined high performance concretes containing metakaolin (MK; 5–15%) that exhibited higher (39–44%) 28-day strength than the control concretes (62–86 MPa). They concluded that the increase in strength is due to improvement in bond between cement paste and aggregate particles with the inclusion of MK, and increased density of the cement paste. The 28-day splitting tensile strength of concrete with MK (15%) varied between 4.39 and 5.92 MPa. Similarly, higher compressive strength of concrete containing 25% MK was also observed by Nicolas et al. [83] after 1 year of curing. Duan et al. [84] found that with addition of MK, compressive strength increased gradually and the calcium hydroxide (CH) content decreased. In another study, concrete containing MK (5–15%) exhibited only marginal increases in compressive strength at 56 and 84 days compared to 35 day strength [85].

In mortars, higher (7–21%) strength with MK (5–20%) was observed compared to control mixture at 27 °C due to the filler effect from MK that filled the interstitial spaces inside the hardened matrix thereby increasing the density and strength [86]. Interestingly, compressive strength of MK-containing mortars continuously decreased with increase in temperature; at 200, 400, 600 and 800 °C, the loss in compressive strength was 9, 15, 35 and 79%, respectively, with major strength loss occurring after 400 °C [86].

Vance et al. [87] reported compressive strength of cement pastes wherein cement replacement levels were between 0 and 20% with limestone and between 0 and 10% with Class F fly ash or metakaolin for ternary binder formulations. A ternary blend with 20% total cement replacement demonstrated the highest 1-day strength and lowest calcium hydroxide content. Thermal analysis revealed the formation of carboaluminate phases after 28 days in the limestone–metakaolin modified pastes, resulting in improved properties at early ages, while maintaining later age properties similar to that of traditional Portland cement systems. Ramezanianpour and Hooton [88] reported that mortar containing blends of limestone and MK exhibited maximum strength with 8% limestone and 10% MK. Antoni et al. [29] observed that a 15% blend (5% limestone + 10% MK) showed higher strength than the 100% portland cement reference mortar at all ages. A higher substitution rate led to a decrease in CH content. TGA and XRD analysis showed the formation of carboaluminates, stratlingite, ettringite and monosulfoaluminate as the hydration products.

While combining limestone with SCMs can increase strength, the SCMs can change limestone concrete properties. Limestone concrete has been shown to exhibit strength loss in both chloride-sulfate and sulfate solutions, whereas limestone concrete containing SCMs showed greater strength loss in chloride-sulfate solution than in sulfate solution (Fig. 4) [89]. Limestone cement concrete stored in chloride-sulfate solution achieved better compressive strength compared to those stored in sulfate solution, indicating the beneficial contribution of chlorides on inhibiting sulfate attack [89]. Further, immersion of limestone concrete containing fly ash (FA), ground-granulated blast furnace slag (GGBFS), and MK with siliceous sand in 1.8% MgSO<sub>4</sub> solution showed marginal strength loss after 6 and 12 months and a complete strength loss after 24 months. Incorporation of natural pozzolans and siliceous sand showed strength loss after 12 months and 40% in 24 months. Concretes containing FA, GGBFS and MK performed better with a 20–25% strength loss after 24 months [90].

It has been shown that off-white rice husk ash (15%) can be used as a partial replacement to cement without any adverse effect on compressive strength and with 9% increase in splitting tensile strength [91]. On the contrary, Madandoust et al. [92] reported lower compressive and splitting tensile strength at early ages whereas at later ages (90–360 days) the strengths became greater than normal concrete due to pozzolanic activity in RHA, further adding that 20% RHA is beneficial for long term strength development. In another study, partial replacement of portland cement (5–30%) by rice husk ash resulted in higher compressive strength compared to control concrete (0% RHA) at 28 and 91 days [93] due to filler effect of smaller RHA particles in concrete. Zerbino et al. [94] concluded that because natural RHA (NRHA) is coarser than grounded RHA (GRHA), its incorporation in concrete reduced the strength and stiffness at 28 days. Replacement of cement by 15% NRHA achieved 90% of the strength of concrete with 15% GRHA.

### 9. Effects of SCMs on long-term durability

#### 9.1. Initial surface absorption, water absorption, porosity, and sorptivity

The addition of 5–15% metakaolin improves the pore microstructure of concrete [84], resulting in a reduction in initial surface absorption

LMC







[85] and sorptivity [82,85]. This is attributed to the pozzolanic reaction whereby the free calcium hydroxide produced by cement hydration was consumed, resulting in dense C–S–H production. Regarding porosity, Antoni et al. [29], Nicolas et al. [83] and Ramezanianpour and Hooton [88] reported reduction in porosity with up to 10% MK content, but increased porosity above 10% MK content. Similarly, Ferraro and Nanni [91] observed reduction in water absorption and porosity of concrete containing off-white rice husk ash (OWRHA).

#### 9.2. Chloride and gas permeability, chloride diffusivity/binding/ingress

Gas permeability can be reduced 52–56% in concrete made with 15% MK [82]. Similar results were also reported by Nicolas et al. [83] wherein concrete with 25% flash calcined MK had lower gas permeability than the reference concrete. The reduction in the gas permeability is attributed to the refinement of pore structure of concrete due to incorporation of SCMs. However, Nadeem et al. [86] observed that chloride permeability in mortar containing 0–20% MK increased with an increase in temperature (27–800 °C) due to an increase in pore area and decrease in hydrated paste area fraction, which in turn causes durability loss. Internal cracking and coarsening of pore structure of concrete at high temperature may also be responsible for loss of impermeability.

Madandoust et al. [92] evaluated the influence of rice husk ash (15–25%) (RHA) on the chloride resistance of concrete and observed that higher the RHA content, the lower is the chloride penetrability, and the rate of chloride penetration decreased with depth (Fig. 5). The rapid chloride penetration test of RHA concrete revealed that the total charge passed (Coulombs) decreased with increase in: (i) moist curing time (3–7 days), (ii) RHA content as cement replacement, and (iii) testing age. Increasing RHA content reduces the electrical conductivity, which is dependent on the ionic strength of pore solution, thus reducing the total charge passed [93]. Diffusion of ionic species in concrete containing SCMs depends heavily on the amount of aqueous solution in the pore spaces. Shi et al. [98] observed improvement in porous microstructure of concrete by SCMs resulting in a lower chloride diffusion coefficient.

Saillio et al. [95] observed that non-carbonated and carbonated cement pastes and concrete containing MK bound more chlorides than cement paste samples for the same NaCl contact solution. During the carbonation process, hydrated phases such as C–S–H were more affected, and the cementitious matrix was not able to bind chlorides. This is due to lack of portlandite and modification of aluminate phases and C–S–H equilibrium phases (change of surface charge) during the carbonation process.

#### 9.3. Alkali-silica reaction

SCMs reduce or even stop the expansion due to alkali silica reaction (ASR) in concretes with reactive aggregates. Chappex and Scrivener [96] carried out accelerated expansion tests to study the effect of aluminum and silicon incorporated in C–S–H on the composition of cement paste pore solution containing SF and MK (5, 10 and 15%). Blends containing MK had equal distribution of Si/Ca in C–S–H, thus showing lower (0.3–0.5%) expansion over time. Addition of SCMs with high aluminate content in blends effectively reduced the expansion of mortars due to alkali silica reaction (ASR), which is supported by the findings of Chappex and Scrivener [97] that alumina acted directly on the reactive phases of the aggregates and adsorbed on the silica surface, thus restricting the dissolution of amorphous silica, restricting ASR.

Zerbino et al. [94] reported that the coarse nature of natural rice husk ash (NRHA) decreased the pozzolanic activity and its effectiveness for ASR control compared to ground rice husk ash (GRHA). Concrete containing GRHA with reactive coarse aggregates showed expansion below the limit of 0.040%, whereas concretes with NRHA showed significant expansions even with non-reactive aggregates.



Fig. 5. Chloride concentrations at 0–40 mm depth for different specimens after 360 days [92].

### 9.4. Sulfate attack

Sotiriadis et al. [89] observed slower deterioration in limestone cement concrete stored in chloride–sulfate solution compared to the severe deterioration observed in FA, natural pozzolan, MK and GGBFS concretes. This was attributed to the delayed sulfate induced deterioration by chlorides in limestone cement concrete. Similar results were reported by Skaropoulou et al. [90], wherein it was observed that inclusion of SCMs (FA, GGBFS and MK) improved the resistance of the limestone cement concrete to sulfate attack at low temperature, and this can be further improved by using calcareous sand instead of siliceous sand.

Ramezanianpour and Hooton [99] reported the formation of ettringite and gypsum resulting in expansion and cracking at the edges of mortar samples as well as longitudinally on the surface. This expansion of the mortar bars can be reduced by using SCMs such as nanosilica (NS), microsilica (MS), fly ash (FA) and ground granulated blast furnace slag (GGBFS) at replacement levels of 2–6% [100], or by using alkali activated slags (AAS) [101]. Ogawa et al. [102] concluded that long term sulfate resistance of the cement pastes can be improved by using blending of SCMs with a suitable amount of limestone powder and a controlled content of calcium sulfate instead of using SCMs alone.

### 9.5. Carbonation, corrosion resistance and shrinkage

A high content of flash calcined MK (25%) accelerated the depth of carbonation in low performance concrete compared to high performance concrete [83]. Ferraro and Nanni [91] reported extension in crack time (46 to 74 h) with inclusion of OWRHA (7.5 to 15%) in reinforced concrete prisms subjected to accelerated corrosion test. MK (up to 15%) reduced drying shrinkage at 7 days [82] and 60 days [103], whereas inclusion of 5% RHA showed least shrinkage at both 3 and 7 days of wet curing [93].

### 10. Use in ultra high performance concrete

Ultra high performance concrete utilizes particle packing optimization, filler effects, and the pozzolanic reaction to dramatically increase concrete strength. While traditionally SCMs and fillers such as silica fume and silica flour are used, researchers are examining the possibility of using other SCMs. For example, 28-day compressive strengths of 150 and 180 MPa were achieved with RHA mean particle sizes of 8 and 3.6 µm, respectively, in UHPC mixtures compared to a 28-day strength of 160 MPa in concrete blended with 0% RHA and 10% silica fume [104]. UHPC made with blends of limestone powder, GGBFS and SF [105], silica fume [106] and FA, LP and GGBS [107] achieved 28-day compressive strength between 100 and 150 MPa. Van et al. [51]

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concluded that moderate temperature treatment (65 °C) was sufficient to accelerate the 7 day compressive strength of RHA–GGBS–UHPC. Rong et al. [108] reported an increase in 28-day compressive strength from 75 MPa (control) to 95 MPa, with inclusion of 3% nano-silica (NS) as partial replacement of cement.

The low w/c used in UHPC mixtures results in interesting durability characteristics in addition to high strength. Recent work by Yu et al. [107] has shown that with an increase in w/c from 0.165 to 0.18, the water permeability of UHPC containing FA, LP and GGBS decreased, but from 0.18 to 0.2, permeability increased. At a low w/c (0.165), SCMs (FA, LP and GGBS) absorbed water readily, thus the water was not available for the formation of hydration products. It was concluded that 0.18 be considered as the optimal w/c for low permeability.

### 11. Conclusions

This paper reviews recently published literature on the effects of SCMs on concrete properties. Several new insights have been gained through recent research, which could have a significant impact on advancing the field. For example, a new way to quantitatively analyze X-ray diffraction patterns for materials containing amorphous phases, called "PONKCS," could lead to improved ability to quantify degree of reaction of SCMs in hydrated systems [17]. Advances in treatment methods for agricultural residue ashes [45-47] could lead to more widespread use of these materials. Improved understanding of the effects of sub-micrometer sized particles on workability, cement hydration, and mechanical property development may advance our ability to optimize particle size distributions for optimal performance, both from an engineering perspective and an environmental perspective. The use of particle additions, even on the micrometer scale, has already been shown to significantly impact strength, particularly when limestone additives are combined with alumina-bearing SCMs, resulting in increased strength through carboaluminate phase formation [29,87,88]. In symbiotic fashion, SCMs may protect limestone-concrete from suffering strength losses and deterioration after immersion in chloride-sulfate and sulfate solutions [89,90]. SCMs are known to increase carbonation in concrete, but interestingly this has been recently shown to also increase chloride ingress, since the carbonated C-S-H cannot effectively bind chlorides [95], worsening the concrete corrosion resistance, a problem that demands more investigation. In other durability concerns, our understanding of the ways that SCMs protect against ASR has been enhanced by research showing that aluminum in SCMs reduces the solubility of silica in alkaline solutions, restricting ASR expansions [96,97]. This could lead to more effective use of SCMs for ASR mitigation. In summary, in spite of the fact that SCMs have been used and researched for decades, the field is far from mature. The research on SCMs reported in the past four years has the potential to change future research directions and the optimal use of SCMs in the field.

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### References

- M. Schneider, M. Romer, M. Tschudin, H. Bolioc, Sustainable cement production present and future, Cem. Concr. Res. 41 (2011) 642–650.
- [2] S.H. Kosmatka, M.L. Wilson, Design and Control of Concrete Mixtures, 15th ed. Port. Cem. Assoc, Skokie, Illinois, 2011.
- [3] CEMBUREAU, The European Cement Association Activity Report, 2011.

- [4] K. Scrivener, Issues in sustainability in cements and concrete, Am. Ceram. Soc. Bull. 91 (2012) 47–50.
- [5] V.M. Malhotra, Reducing CO<sub>2</sub> emissions the role of fly ash and other supplementary cementitious materials, Concr. Int. 28 (2006) 42–45.
- [6] S. Reynolds, The Future of Ferrous Slag, Market Forecasts to 2020, Pira International Ltd, Leatherhead, UK, 2009.
- [7] P. Van den Heede, N. De Belie, Environmental impact and life cycle assessment (LCA) of traditional and "green" concretes: literature review and theoretical calculations, Cem. Concr. Compos. 34 (2012) 431–442, http://dx.doi.org/10.1016/ j.cemconcomp.2012.01.004.
- [8] A. Petek Gursel, E. Masanet, A. Horvath, A. Stadel, Life-cycle inventory analysis of concrete production: a critical review, Cem. Concr. Compos. 51 (2014) 38–48, http://dx.doi.org/10.1016/j.cemconcomp.2014.03.005.
- [9] R.D. Hooton, J.A. Bickley, Design for durability: the key to improving concrete sustainability, Constr. Build. Mater. 67 (2014) 422–430, http://dx.doi.org/10. 1016/j.conbuildmat.2013.12.016.
- [10] D.P. Bentz, A.S. Hansen, J.M. Guynn, Optimization of cement and fly ash particle sizes to produce sustainable concretes, Cem. Concr. Compos. 33 (2011) 824–831, http://dx.doi.org/10.1016/j.cemconcomp.2011.04.008.
- [11] T. Zhang, Q. Yu, J. Wei, P. Zhang, Efficient utilization of cementitious materials to produce sustainable blended cement, Cem. Concr. Compos. 34 (2012) 692–699, http://dx.doi.org/10.1016/j.cemconcomp.2012.02.004.
- [12] E. Gruyaert, M. Maes, N. De Belie, Performance of BFS concrete: k-value concept versus equivalent performance concept, Constr. Build. Mater. 47 (2013) 441–455, http://dx.doi.org/10.1016/j.conbuildmat.2013.05.006.
- [13] M. Juenger, J.L. Provis, J. Elsen, W. Matthes, R.D. Hooton, J. Duchesne, L. Courard, H. He, F. Michel, R. Snellings, N. De Belie, Supplementary cementitious materials for concrete: characterization needs, MRS Proc. 1488 (2012)http://dx.doi.org/10. 1557/opl.2012.1536 (imrc12-1488-7b-026).
- [14] E.C. Arvaniti, M.C.G. Juenger, S.A. Bernal, J. Duchesne, L. Courard, S. Leroy, J.L. Provis, A. Klemm, N. De Belie, Physical characterization methods for supplementary cementitious materials, Mater. Struct. (2014)http://dx.doi.org/10.1617/s11527-014-0430-4.
- [15] G. Quercia, A. Lazaro, J.W. Geus, H.J.H. Brouwers, Characterization of morphology and texture of several amorphous nano-silica particles used in concrete, Cem. Concr. Compos. 44 (2013) 77–92, http://dx.doi.org/10.1016/j.cemconcomp.2013. 05.006.
- [16] R. Walker, S. Pavía, Physical properties and reactivity of pozzolans, and their influence on the properties of lime-pozzolan pastes, Mater. Struct. 44 (2011) 1139-1150, http://dx.doi.org/10.1617/s11527-010-9689-2.
- [17] R. Snellings, A. Salze, K.L. Scrivener, Use of X-ray diffraction to quantify amorphous supplementary cementitious materials in anhydrous and hydrated blended cements, Cem. Concr. Res. 64 (2014) 89–98, http://dx.doi.org/10.1016/j.cemconres. 2014.06.011.
- [18] R. Fernandez, F. Martirena, K.L. Scrivener, The origin of the pozzolanic activity of calcined clay minerals: a comparison between kaolinite, illite and montmorillonite, Cem. Concr. Res. 41 (2011) 113–122, http://dx.doi.org/10.1016/j.cemconres.2010.09.013.
- [19] A. Tironi, M.A. Trezza, A.N. Scian, E.F. Irassar, Cement & concrete composites assessment of pozzolanic activity of different calcined clays, Cem. Concr. Compos. 37 (2013) 319–327, http://dx.doi.org/10.1016/j.cemconcomp.2013.01.002.
- [20] S.C. Taylor-Lange, E.L. Lamon, K.A. Riding, M.C.G. Juenger, Calcined Kaolinite– Bentonite Clay Blends as Supplementary Cementitious Materials, Manuscript Under Review.
- [21] A. Teklay, C. Yin, L. Rosendahl, M. Bøjer, Cement and concrete research calcination of kaolinite clay particles for cement production: a modeling study, Cem. Concr. Res. 61–62 (2014) 11–19, http://dx.doi.org/10.1016/j.cemconres.2014.04.002.
- [22] L. Trusilewicz, F. Fernández-Martínez, V. Rahhal, R. Talero, TEM and SAED characterization of metakaolin. Pozzolanic activity, J. Am. Ceram. Soc. 95 (2012) 2989–2996, http://dx.doi.org/10.1111/j.1551-2916.2012.05325.x.
- [23] L.M. Federico, S.E. Chidiac, L. Raki, Reactivity of cement mixtures containing waste glass using thermal analysis, J. Therm. Anal. Calorim. 104 (2011) 849–858, http://dx.doi.org/10.1007/s10973-011-1288-0.
- [24] K. De Weerdt, M. Ben Haha, G. Le Saout, K.O. Kjellsen, H. Justnes, B. Lothenbach, Hydration mechanisms of ternary Portland cements containing limestone powder and fly ash, Cem. Concr. Res. 41 (2011) 279–291, http://dx.doi.org/10.1016/j. cemconres.2010.11.014.
- [25] T. Kim, J. Olek, Effects of sample preparation and interpretation of thermogravimetric curves on calcium hydroxide in hydrated pastes and mortars, Transp. Res. Rec. J. Transp. Res. Board. 2290 (2012) 10–18, http://dx.doi.org/10.3141/2290-02.
- [26] S. Wang, Quantitative kinetics of pozzolanic reactions in coal/cofired biomass fly ashes and calcium hydroxide (CH) mortars, Constr. Build. Mater. 51 (2014) 364–371, http://dx.doi.org/10.1016/j.conbuildmat.2013.10.057.
- [27] B. Lothenbach, K. Scrivener, R.D. Hooton, Supplementary cementitious materials, Cem. Concr. Res. 41 (2011) 1244–1256, http://dx.doi.org/10.1016/j.cemconres. 2010.12.001.
- [28] V. Sata, J. Tangpagasit, C. Jaturapitakkul, P. Chindaprasirt, Effect of W/B ratios on pozzolanic reaction of biomass ashes in Portland cement matrix, Cem. Concr. Compos. 34 (2012) 94–100, http://dx.doi.org/10.1016/j.cemconcomp.2011.09.003.
- [29] M. Antoni, J. Rossen, F. Martirena, K. Scrivener, Cement substitution by a combination of metakaolin and limestone, Cem. Concr. Res. 42 (2012) 1579–1589, http://dx.doi.org/10.1016/j.cemconres.2012.09.006.
- [30] O. Mendoza, J.I. Tobón, An alternative thermal method for identification of pozzolanic activity in Ca(OH)<sub>2</sub>/pozzolan pastes, J. Therm. Anal. Calorim. 114 (2013) 589–596, http://dx.doi.org/10.1007/s10973-013-2973-y.
- [31] NF P 18-513, Métakaolin, addition pouzzolanique pour bétons: définitions, spécification, critères de conformité, 2010.

#### M.C.G. Juenger, R. Siddique / Cement and Concrete Research xxx (2015) xxx-xxx

- [32] EN 196-5 methods of testing cement, Pozzolanicity Test for Pozzolanic Cement2011.
- [33] M. Frías, R. Vigil de la Villa, M.I. Sánchez de Rojas, A. Juan Valdés, C. Medina, Scientific aspects of kaolinite based coal mining wastes in pozzolan/Ca(OH)<sub>2</sub> system, J. Am. Ceram. Soc. 95 (2011) 386–391.
- [34] M. Frías, R. Vigil de la Villa, R. García, M.I. Sánchez de Rojas, A. Juan Valdés, The influence of slate waste activation conditions on mineralogical changes and pozzolanic behavior, J. Am. Ceram. Soc. 96 (2013) 2276–2282, http://dx.doi.org/ 10.1111/jace.12387.
- [35] S. Sinthaworn, P. Nimityongskul, Cement & concrete composites effects of temperature and alkaline solution on electrical conductivity measurements of pozzolanic activity, Cem. Concr. Compos. 33 (2011) 622–627, http://dx.doi.org/10.1016/j. cemconcomp.2011.02.012.
- [36] S. Velázquez, J. Monzó, M. Borrachero, J. Payá, Assessment of the pozzolanic activity of a spent catalyst by conductivity measurement of aqueous suspensions with calcium hydroxide, Materials (Basel) 7 (2014) 2561–2576, http://dx.doi.org/10.3390/ ma7042561.
- [37] J. Ninov, I. Doykov, L. Dimova, B. Petrov, L. Brakalov, On the kinetics of pozzolanic reaction in metakaolin–lime–water system, J. Therm. Anal. Calorim. 105 (2011) 245–250, http://dx.doi.org/10.1007/s10973-011-1419-7.
- [38] V. Kocaba, E. Gallucci, K.L. Scrivener, Methods for determination of degree of reaction of slag in blended cement pastes, Cem. Concr. Res. 42 (2012) 511–525, http://dx.doi.org/10.1016/j.cemconres.2011.11.010.
- [39] M.H.N. Yio, J.C. Phelan, H.S. Wong, N.R. Buenfeld, Determining the slag fraction, water/binder ratio and degree of hydration in hardened cement pastes, Cem. Concr. Res. 56 (2014) 171–181, http://dx.doi.org/10.1016/j.cemconres.2013.12.002.
- [40] B. Fabbri, S. Gualtieri, C. Leonardi, Modifications induced by the thermal treatment of kaolin and determination of reactivity of metakaolin, Appl. Clay Sci. 73 (2013) 2–10, http://dx.doi.org/10.1016/j.clay.2012.09.019.
- [41] K. Narasimhulu, D. Ph, R. Gettu, K.G. Babu, Beneficiation of Natural Zeolite Through Flash Calcination for Its Use as a Mineral Admixture in Concrete, 2014. 24–33, http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000800.
- [42] R. Vigil de la Villa, R. Fernández, O. Rodríguez, R. García, E. Villar-Cociña, M. Frías, Evolution of the pozzolanic activity of a thermally treated zeolite, J. Mater. Sci. 48 (2012) 3213–3224, http://dx.doi.org/10.1007/s10853-012-7101-z.
- [43] M. Frías, R. Vigil, R. García, O. Rodríguez, S. Goñi, I. Vegas, Evolution of mineralogical phases produced during the pozzolanic reaction of different metakaolinite byproducts: influence of the activation process, Appl. Clay Sci. 56 (2012) 48–52, http://dx.doi.org/10.1016/j.clay.2011.11.022.
- [44] Y. Li, Y. Yao, X. Liu, H. Sun, W. Ni, Improvement on pozzolanic reactivity of coal gangue by integrated thermal and chemical activation, Fuel 109 (2013) 527–533, http://dx.doi.org/10.1016/j.fuel.2013.03.010.
- [45] A. Gholizadeh Vayghan, A.R. Khaloo, F. Rajabipour, The effects of a hydrochloric acid pre-treatment on the physicochemical properties and pozzolanic performance of rice husk ash, Cem. Concr. Compos. 39 (2013) 131–140, http://dx.doi. org/10.1016/j.cemconcomp.2013.03.022.
- [46] F.F. Ataie, K.A. Riding, Thermochemical Pretreatments for Agricultural Residue Ash Production for Concrete, 2013. 1703–1711, http://dx.doi.org/10.1061/(ASCE)MT.
- [47] F.F. Ataie, K.A. Riding, Use of bioethanol byproduct for supplementary cementitious material production, Constr. Build. Mater. 51 (2014) 89–96, http://dx.doi.org/10. 1016/j.conbuildmat.2013.10.092.
- [48] H. Ghorbel, B. Samet, Effect of iron on pozzolanic activity of kaolin, Constr. Build. Mater. 44 (2013) 185–191, http://dx.doi.org/10.1016/j.conbuildmat.2013.02.068.
- [49] S.C. Taylor-Lange, K.A. Riding, M.C.G. Juenger, Increasing the reactivity of metakaolin-cement blends using zinc oxide, Cem. Concr. Compos. 34 (2012) 835–847, http://dx.doi.org/10.1016/j.cemconcomp.2012.03.004.
- [50] S.C. Taylor-Lange, F. Rajabali, N.A. Holsomback, K. Riding, M.C.G. Juenger, The effect of zinc oxide additions on the performance of calcined sodium montmorillonite and illite shale supplementary cementitious materials, Cem. Concr. Compos. 53 (2014) 127–135, http://dx.doi.org/10.1016/j.cemconcomp.2014.06.008.
- [51] V.-T.-A. Van, C. Rößler, D.-D. Bui, H.-M. Ludwig, Rice husk ash as both pozzolanic admixture and internal curing agent in ultra-high performance concrete, Cem. Concr. Compos. 53 (2014) 270–278, http://dx.doi.org/10.1016/j.cemconcomp. 2014.07.015.
- [52] P.K. Hou, S. Kawashima, K.J. Wang, D.J. Corr, J.S. Qian, S.P. Shah, Effects of colloidal nanosilica on rheological and mechanical properties of fly ash-cement mortar, Cem. Concr. Compos. 35 (2013) 12–22, http://dx.doi.org/10.1016/j.cemconcomp. 2012.08.027.
- [53] B. Lothenbach, G. Le Saout, M. Ben Haha, R. Figi, E. Wieland, Hydration of a lowalkali CEM III/B–SiO<sub>2</sub> cement (LAC), Cem. Concr. Res. 42 (2012) 410–423, http://dx.doi.org/10.1016/j.cemconres.2011.11.008.
- [54] R. Yu, P. Spiesz, H.J.H. Brouwers, Effect of nano-silica on the hydration and microstructure development of ultra-high performance concrete (UHPC) with a low binder amount, Constr. Build. Mater. 65 (2014) 140–150, http://dx.doi.org/10. 1016/j.conbuildmat.2014.04.063.
- [55] G. Land, D. Stephan, The influence of nano-silica on the hydration of ordinary Portland cement, J. Mater. Sci. 47 (2011) 1011–1017, http://dx.doi.org/10.1007/ s10853-011-5881-1.
- [56] H. Madani, A. Bagheri, T. Parhizkar, The pozzolanic reactivity of monodispersed nanosilica hydrosols and their influence on the hydration characteristics of Portland cement, Cem. Concr. Res. 42 (2012) 1563–1570, http://dx.doi.org/10. 1016/j.cemconres.2012.09.004.
- [57] J.I. Tobón, J.J. Payá, M.V. Borrachero, O.J. Restrepo, Mineralogical evolution of Portland cement blended with silica nanoparticles and its effect on mechanical strength, Constr. Build. Mater. 36 (2012) 736–742, http://dx.doi.org/10.1016/j. conbuildmat.2012.06.043.

- [58] K.M. Kim, Y.S. Heo, S.P. Kang, J. Lee, Effect of sodium silicate- and ethyl silicatebased nano-silica on pore structure of cement composites, Cem. Concr. Compos. 49 (2014) 84–91. http://dx.doi.org/10.1016/i.cemconcomp.2013.12.009.
- [59] J.J. Kim, M.K. Rahman, A.a. Al-Majed, M.M. Al-Zahrani, M.M. Reda Taha, Nanosilica effects on composition and silicate polymerization in hardened cement paste cured under high temperature and pressure, Cem. Concr. Compos. 43 (2013) 78–85. http://dx.doi.org/10.1016/i.cemconcomp.2013.07.002.
- [60] I.F. Sáez del Bosque, M. Martín-Pastor, S. Martínez-Ramírez, M.T. Blanco-Varela, Effect of temperature on C<sub>3</sub>S and C<sub>3</sub>S + nanosilica hydration and C–S–H structure, J. Am. Ceram. Soc. 96 (2013) 957–965, http://dx.doi.org/10.1111/jace.12093.
- [61] A. Askarinejad, A.R. Pourkhorshidi, T. Parhizkar, Evaluation the pozzolanic reactivity of sonochemically fabricated nano natural pozzolan, Ultrason. Sonochem. 19 (2012) 119–124, http://dx.doi.org/10.1016/j.ultsonch.2011.05.005.
- [62] N. Farzadnia, A.A. Abang Ali, R. Demirboga, M.P. Anwar, Effect of halloysite nanoclay on mechanical properties, thermal behavior and microstructure of cement mortars, Cem. Concr. Res. 48 (2013) 97–104, http://dx.doi.org/10.1016/j. cemconres.2013.03.005.
- [63] M.S. Morsy, Y. Al-Salloum, T. Almusallam, H. Abbas, Effect of nano-metakaolin addition on the hydration characteristics of fly ash blended cement mortar, J. Therm. Anal. Calorim. 116 (2013) 845–852, http://dx.doi.org/10.1007/s10973-013-3512-6.
- [64] N. Farzadnia, A.A. Abang Ali, R. Demirboga, Characterization of high strength mortars with nano alumina at elevated temperatures, Cem. Concr. Res. 54 (2013) 43–54, http://dx.doi.org/10.1016/j.cemconres.2013.08.003.
- [65] A.R. Jayapalan, B.Y. Lee, K.E. Kurtis, Can nanotechnology be "green"? Comparing efficacy of nano and microparticles in cementitious materials, Cem. Concr. Compos. 36 (2013) 16–24, http://dx.doi.org/10.1016/j.cemconcomp.2012.11.002.
- [66] S. Kawashima, J.-W.T. Seo, D. Corr, M.C. Hersam, S.P. Shah, Dispersion of CaCO<sub>3</sub> nanoparticles by sonication and surfactant treatment for application in fly ashcement systems, Mater. Struct. 47 (2013) 1011–1023, http://dx.doi.org/10.1617/ s11527-013-0110-9.
- [67] E.D. Rodríguez, S.A. Bernal, J.L. Provis, J. Payá, J.M. Monzó, M.V. Borrachero, Structure of Portland Cement Pastes Blended With Sonicated Silica Fume, 2012. 1295–1304, http://dx.doi.org/10.1061/(ASCE)MT.1943-5533.0000502.
- [68] T. Oey, A. Kumar, J.W. Bullard, N. Neithalath, G. Sant, The filler effect: the influence of filler content and surface area on cementitious reaction rates, J. Am. Ceram. Soc. 96 (2013) 1978–1990, http://dx.doi.org/10.1111/jace.12264.
- [69] F. Deschner, F. Winnefeld, B. Lothenbach, S. Seufert, P. Schwesig, S. Dittrich, et al., Hydration of Portland cement with high replacement by siliceous fly ash, Cem. Concr. Res. 42 (2012) 1389–1400, http://dx.doi.org/10.1016/j.cemconres.2012.06. 009.
- [70] D.P. Bentz, T. Sato, I. De La Varga, W.J. Weiss, Fine limestone additions to regulate setting in high volume fly ash mixtures, Cem. Concr. Compos. 34 (2012) 11–17, http://dx.doi.org/10.1016/j.cemconcomp.2011.09.004.
- [71] D.P. Bentz, Activation energies of high-volume fly ash ternary blends: hydration and setting, Cem. Concr. Compos. 53 (2014) 214–223, http://dx.doi.org/10.1016/ j.cemconcomp.2014.06.018.
- [72] S. Bae, C. Meral, J.E. Oh, J. Moon, M. Kunz, P.J.M. Monteiro, Characterization of morphology and hydration products of high-volume fly ash paste by monochromatic scanning X-ray micro-diffraction (μ-SXRD), Cem. Concr. Res. 59 (2014) 155–164, http://dx.doi.org/10.1016/j.cemconres.2014.03.001.
- [73] Z. Dai, T.T. Tran, J. Skibsted, Aluminum incorporation in the C-S-H phase of white Portland cement-metakaolin blends studied by <sup>27</sup>Al and <sup>29</sup>Si MAS NMR spectroscopy, J. Am. Ceram. Soc. 97 (2014) 2662–2671, http://dx.doi.org/10.1111/jace. 13006.
- [74] M. Boháč, M. Palou, R. Novotný, J. Másilko, D. Všianský, T. Staněk, Investigation on early hydration of ternary Portland cement–blast–furnace slag–metakaolin blends, Constr. Build. Mater. 64 (2014) 333–341, http://dx.doi.org/10.1016/j.conbuildmat. 2014.04.018.
- [75] S. Dittrich, J. Neubauer, F. Goetz-Neunhoeffer, The influence of fly ash on the hydration of OPC within the first 44 h – a quantitative in situ XRD and heat flow calorimetry study, Cem. Concr. Res. 56 (2014) 129–138, http://dx.doi.org/10.1016/j. cemconres.2013.11.013.
- [76] R. Snellings, G. Mertens, R. Adriaens, J. Elsen, In situ synchrotron X-ray powder diffraction study of the early age hydration of cements blended with zeolitite and quartzite fines and water-reducing agent, Appl. Clay Sci. 72 (2013) 124–131, http://dx.doi.org/10.1016/j.clay.2012.12.002.
- [77] M. Cyr, M. Trinh, B. Husson, G. Casaux-Ginestet, Effect of cement type on metakaolin efficiency, Cem. Concr. Res. 64 (2014) 63–72, http://dx.doi.org/10. 1016/j.cemconres.2014.06.007.
- [78] D. Kong, Y. Su, X. Du, Y. Yang, S. Wei, S.P. Shah, Influence of nano-silica agglomeration on fresh properties of cement pastes, Constr. Build. Mater. 43 (2013) 557–562, http://dx.doi.org/10.1016/j.conbuildmat.2013.02.066.
- [79] D.P. Bentz, C.F. Ferraris, M.A. Galler, A.S. Hansen, J.M. Guynn, Influence of particle size distributions on yield stress and viscosity of cement–fly ash pastes, Cem. Concr. Res. 42 (2012) 404–409, http://dx.doi.org/10.1016/j.cemconres.2011.11.006.
- [80] K. Vance, A. Kumar, G. Sant, N. Neithalath, The rheological properties of ternary binders containing Portland cement, limestone, and metakaolin or fly ash, Cem. Concr. Res. 52 (2013) 196–207, http://dx.doi.org/10.1016/j.cemconres.2013.07.007.
- [81] M. Adjoudj, K. Ezziane, E. Hadj, T. Ngo, A. Kaci, Evaluation of rheological parameters of mortar containing various amounts of mineral addition with polycarboxylate superplasticizer, Constr. Build. Mater. 70 (2014) 549–559, http://dx.doi.org/10. 1016/j.conbuildmat.2014.07.111.
- [82] E. Guneyisi, M. Gesoglu, S. Karaoglu, K. Mermerdas, Strength, permeability and shrinkage cracking of silica fume and metakaolin concretes, Constr. Build. Mater. 34 (2012) 120–130.

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- [83] R.S. Nicolas, M. Cyr, G. Escadeillas, Performance-based approach to durability of concrete containing flash-calcined metakaolin as cement replacement, Constr. Build. Mater, 55 (2014) 313–322.
- [84] P. Duan, Z. Shui, W. Chen, C. Shen, Effects of metakaolin, silica fume and slag on pore structure, interfacial transition zone and compressive strength of concrete, Constr. Build. Mater. 44 (2013) 1–6.
- [85] R. Siddique, E. Kadri, Effect of metakaolin and foundry sand on the near surface characteristics of concrete, Constr. Build. Mater. 25 (2011) 3257–3266.
- [86] A. Nadeem, S.A. Memon, T.Y. Lo, Mechanical performance, durability, qualitative and quantitative analysis of microstructure of fly ash and metakaolin mortar at elevated temperatures, Constr. Build. Mater. 38 (2013) 338–347.
- [87] K. Vance, M. Aguayo, T. Oey, G. Sant, N. Neithalath, Hydration and strength development in ternary portland cement blends containing limestone and fly ash or metakaolin, Cem. Concr. Comp. 39 (2013) 93–103.
- [88] A.M. Ramezanianpour, R.D. Hooton, A study on hydration, compressive strength, and porosity of Portland-limestone cement mixes containing SCMs, Cem. Concr. Comp. 51 (2014) 1–13.
- [89] K. Sotiriadis, E. Nikolopoulou, S. Tsivilis, A. Pavlou, E. Chaniotakis, R.N. Swamy, The effect of chlorides on the thaumasite form of sulfate attack of limestone cement concrete containing mineral admixtures at low temperature, Constr. Build. Mater. 43 (2013) 156–164.
- [90] A. Skaropoulou, K. Sotiriadis, G. Kakali, S. Tsivilis, Use of mineral admixtures to improve the resistance of limestone cement concrete against thaumasite form of sulfate attack, Cem. Concr. Comp. 37 (2013) 267–275.
- [91] R.M. Ferraro, A. Nanni, Effect of off-white rice husk ash on strength, porosity, conductivity and corrosion resistance of white concrete, Constr. Build. Mater. 31 (2012) 220–225.
- [92] R. Madandoust, M.M. Ranjbar, H.A. Moghadam, S.Y. Mousavi, Mechanical properties and durability assessment of rice husk ash concrete, Biosyst. Eng. 110 (2011) 144–152.
- [93] A.L.G. Gastaldini, M.P. da Silva, F.B. Zamberlan, C.Z.M. Neto, Total shrinkage, chloride penetration, and compressive strength of concretes that contain clearcolored rice husk ash, Constr. Build. Mater. 54 (2014) 369–377.
- [94] R. Zerbino, G. Giaccio, O.R. Batic, G.C. Isaia, Alkali–silica reaction in mortars and concretes incorporating natural rice husk ash, Constr. Build. Mater. 36 (2012) 796–806.
- [95] M. Saillio, V. Baroghel-Bouny, F. Barberon, Chloride binding in sound and carbonated cementitious materials with various types of binder, Constr. Build. Mater. 68 (2014) 82–91.

- [96] T. Chappex, K.L. Scrivener, Alkali fixation of C–S–H in blended cement pastes and its relation to alkali silica reaction, Cem. Concr. Res. 42 (2012) 1049–1054.
- [97] T. Chappex, K.L. Scrivener, The influence of aluminium on the dissolution of amorphous silica and its relation to alkali silica reaction, Cem. Concr. Res. 42 (2012) 1645–1649.
- [98] X. Shi, Z. Yang, Y. Liu, D. Cross, Strength and corrosion properties of Portland cement mortar and concrete with mineral admixtures, Constr. Build. Mater. 25 (2011) 3245–3256.
- [99] A.M. Ramezanianpour, R.D. Hooton, Thaumasite sulfate attack in Portland and Portland-limestone cement mortars exposed to sulfate solution, Constr. Build. Mater. 40 (2013) 162–173.
- [100] H.N. Atahan, D. Dikme, Use of mineral admixtures for enhanced resistance against sulfate attack, Constr. Build. Mater. 25 (2011) 3450–3457.
- [101] M. Komljenovic, Z. Bašcarevic, N. Marjanovic, V. Nikolic, External sulfate attack on alkali-activated slag, Constr. Build. Mater. 49 (2013) 31–39.
- [102] S. Ogawa, T. Nozaki, K. Yamada, H. Hirao, R.D. Hooton, Improvement on sulfate resistance of blended cement with high alumina slag, Cem. Concr. Res. 42 (2012) 244–251.
- [103] K. Mermerdas, E. Guneyisi, M. Gesoglu, T. Ozturan, Experimental evaluation and modeling of drying shrinkage behavior of metakaolin and calcined kaolin blended concretes, Constr. Build. Mater. 43 (2013) 337–347.
- [104] N.V. Tuan, G. Ye, K. van Breugel, A.L.A. Fraaij, B.D. Dai, The study of using rice husk ash to produce ultra high performance concrete, Constr. Build. Mater. 25 (2011) 2030–2035.
- [105] C. Wang, C. Yang, F. Liu, C. Wan, X. Pu, Preparation of ultra-high performance concrete with common technology and materials, Cem. Concr. Comp. 34 (2012) 538–544.
- [106] T. Oertel, F. Hutter, R. Tanzer, U. Helbig, G. Sextl, Primary particle size and agglomerate size effects of amorphous silica in ultra-high performance concrete, Cem. Concr. Comp. 37 (2013) 61–67.
- [107] R. Yu, P. Spiesz, H.J.H. Brouwers, Development of an eco-friendly ultra-high performance concrete (UHPC) with efficient cement and mineral admixture uses, Cem. Concr. Comp. 55 (2015) 383–394.
- [108] Z. Rong, W. Sun, H. Xiao, G. Jiang, Effects of nano-SiO<sub>2</sub> particles on the mechanical and microstructural properties of ultra-high performance cementitious composites, Cem. Concr. Comp. 56 (2015) 25–31.