A Methodology to Extract the Component Size Distributions in Interground Composite (Limestone) Cements

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ABSTRACT

This paper compares the performance of commercial interground portland-limestone cements (PLC) to those of blended limestone systems. Limestone of four different median sizes is mixed with ordinary portland cement (OPC) to create blends in an attempt to match the particle size distribution of the PLCs. The interground systems are found to outperform the blended systems, plausibly because of the difference in size distributions of the clinker and limestone fractions between the PLCs and the blended systems. A novel methodology to extract the particle size distributions of the components in the interground systems is reported. This method, applicable for several types of multi-component powder systems, considers Rosin-Rammler size distributions for the ground clinker and limestone, and optimizes the parameters of the distribution to obtain a composite distribution of the same fineness as the interground system. The model is verified using a cement hydration and microstructure model.

Keywords: Limestone, Interground, Blended, Hydration, CEMHYD3D, Pore Structure, Rosin-Rammler Distribution

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1.0 INTRODUCTION

The use of fine limestone as partial cement replacement is a topic of great interest since it improves the sustainability of portland cement-based concrete and provides comparable properties to that of conventional OPC concrete [1,2]. Two methodologies are commonly used to incorporate fine limestone in cementitious systems: (i) intergrinding the limestone with the portland cement clinker to produce portland-limestone cements (PLCs), or (ii) blending OPC with limestone powder in the concrete production process. Intergrinding of portland cement clinker with limestone results in a finer limestone phase in the composite system due to the fact that limestone is a softer material than the clinker. Blending, on the other hand, would result in a limestone size distribution that can be controlled more directly by the cement or concrete producer. ASTM C595 cements, along with cements conforming to CSA A 3000 (Canada), AASHTO M 240 and EN 197-1 (Europe) among others are permitted to contain 5-15% (by mass) of fine limestone. In the U.S., cements conforming to ASTM C1157 (a performance based cement specification, as compared to ASTM C595 and C150 which prescribe limits on chemical composition) have also been manufactured with 5-15% of limestone.

Several studies have investigated the influence of fine limestone as a partial cement replacement material, blended or interground with OPC [3,4]. Limestone has also been used in conjunction with other cement replacement materials such as fly ash, slag, or metakaolin [5–9]. The early age hydration response, reaction product formation, rheology, strength development, and durability of the binary and ternary systems containing limestone have been reported in detail. A number of studies have focused on the use of limestone which is finer than the cement it replaces, as this has been shown to accelerate hydration reactions [7,10], increase the packing of particles [11], and minimize the strength loss associated with limestone [7]. The formation of carboaluminates in limestone bearing systems that reduces the overall pore volume has been reported in [1,12]. A number of studies on the properties of interground limestone cements have also been reported [13–15].

It is well known that the particle size distribution (PSD) of the cement (OPC or PLC) influences the early-age hydration, reaction product formation and consequently the performance [16,17]. This paper evaluates whether property equivalence between interground PLCs and OPC-limestone blends can be attained, provided the blend is designed to have a similar specific surface area as that of the PLC and is constituted using the same OPC clinker that made up the PLC. This is of significance for limestone suppliers interested in supplying limestone to concrete

producers that blend limestone with the cements they use, because it is the ASTM C150 or equivalent cement that generally is used for general concrete construction. Furthermore, a methodology to extract the PSDs of cement and limestone in an interground PLC is proposed, which will help to choose the parent OPC and limestone particle sizes that permit property equivalence. This methodology is generic enough so as to be implemented to extract the size classes of different particles in a wide array of powder mixtures such as in pharmaceutical, chemical, and food industries.

2.0 EXPERIMENTAL PROGRAM

2.1 Materials

The materials used in this study are a commercially available Type I/II ordinary portland cement (OPC) conforming to ASTM C150 [18], nominally pure limestone powders (> 95% CaCO_3 , by mass) of four different median particle sizes (0.7 μm , 3 μm , 10 μm , and 15 μm), and two different commercially available interground PLCs conforming to ASTM C595 [19] and ASTM C1157 [20]. Figure 1 shows the particle size distribution of these raw materials, and Table 1 presents their respective chemical compositions (provided by the manufacturer) and Blaine's fineness. Both the interground cements are finer than the parent OPC (denoted as C150), with the C1157 cement being markedly finer. It is noted that the major difference between these C595 and C1157 cements is in their fineness alone since they are constituted from the same clinker used for the parent C150 cement.

Figure 1: Particle size distributions of: (a) three different cements, and (b) the limestone powders used in this study.

Table 1: Chemical composition and fineness of the parent cements used in this study

Cement type (ASTM)	Chemical composition (% by mass)								Blaine's Fineness (m ² /kg)
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Loss on ignition	Limestone	
C150 Type I/II	19.60	4.09	3.39	63.2	3.37	3.17	3.17	-	452
C595 Type IL	16.51	3.38	2.66	56.8	2.61	2.80	4.17	11.1	497
C1157 Type HE	16.51	3.41	2.77	56.6	3.01	2.87	3.81	10.5	594

2.2 Experiments

2.2.1 Compressive strength

Compressive strength tests were carried out in accordance with ASTM C109 [21]. The mortar cubes were prepared with a sand volume fraction of 50%. The testing was carried out at ages of 1, 3, 7, 28 and 56 days.

2.2.2 Isothermal calorimetry

The heat evolution from the hydration of cement was determined using isothermal calorimetry (TAM Air microcalorimeter™ 2700 Series) at a constant temperature of 25°C for 72 h. The powders were dry blended prior to adding water. To ensure accurate early age measurements and minimize the time required to attain isothermal conditions, the blended powders and water were conditioned in an oven for 12 hours at 25°C. The pastes were then mixed in accordance with ASTM C305 [22]. Approximately 10 g of sample was extracted immediately, placed in a sealed sample vial to minimize evaporation and placed in the calorimeter. Three samples per mixture were tested and average values are reported.

2.2.3 Mercury Intrusion Porosimetry

Paste samples of approximately 100 g were cured for 3 and 28 days under sealed conditions at a constant temperature of 23±1°C. At the desired age of testing, the samples were crushed to an approximate size of 2 mm, and then pre-treated in an oven for 2 hours at 60°C, as this method was found to produce consistent results in a previous study [23]. Approximately 1 g of

material was selected and weighed using a high precision scale. Testing was completed using a 0.5 cc cell in a Quantachrome Instruments PoreMaster™ mercury intrusion porosimeter to a maximum testing pressure of approximately 410 MPa. The porosity of the sample was determined by dividing the total volume intruded by the determined sample volume. The relationship between pore diameter and intrusion pressure was determined using the Washburn equation. The surface tension of mercury and the mercury contact angle were assumed to be 0.480 N/m and 117° respectively during intrusion [24,25]. The potential inaccuracies in the determination of the pore size distribution through mercury intrusion have been detailed in [26,27]. Thus, to provide indications of the pore structure, the critical (percolating) pore diameter, which is the pore diameter corresponding to the highest rate of volume intrusion into the specimen alone is used [28,29].

3.0 RESULTS AND DISCUSSIONS

3.1 Comparing the Properties of Interground PLCs (C595 and C1157) and Equivalent Size-Matched Blends

OPC-limestone blends were prepared using the four different limestone PSDs (Figure 1(b)) so that the overall PSD of the blend is similar to the PSD of the C595 or C1157 cements. The mass fraction of limestone in the blend is also maintained at the same level (~11%) as that in the PLCs. The individual fraction of limestone of each median size required in the blend was calculated using an iterative solver to minimize the mean square error of the final PSD of the blended and the interground mixtures. Size-matching in such a way ensures that the total solids surface area available for the reaction is similar for the corresponding blended and interground mixtures. However, since OPC is used in the blended mixtures, this does not ensure that the clinker and limestone surface areas in the PLCs and the blends are similar, which likely results in differing reaction rates. The size-matched blends are identified with the letter 'b' after the corresponding parent cement designation (C595 or C1157) in the remainder of this paper. For instance, C595b indicates a blend of C150 and ~11% size-matched limestone such that the final PSD is the same as that of C595 cement.

Figure 2 shows the PSDs of the PLCs and the size-matched blended mixtures. As can be noticed from the figure, the PSD of the blend corresponding to C1157 PLC could not be accurately matched to that of its parent cement using the four available limestone sizes. This is predominantly because of the higher fineness of this cement as noted from Table 1. Thus the blend that provided the closest approximation is used in this study. This blend is deficient in

particles smaller than 20 μm and rich in particles larger than this size, as compared to C1157 PLC.

Figure 2: Particle size distribution of the PLCs ('C595' and 'C1157') and their equivalent size-matched blends ('C595b' and 'C1157b', respectively). The open and closed circles correspond to C595 PLC and the corresponding blend whereas the triangles correspond to C1157 PLC and the corresponding blend. Note that the use of four different limestone sizes along with the chosen OPC is unable to accurately replicate the PSD of C1157 PLC.

In an attempt to compare and contrast the properties of the PLCs and the corresponding size-matched blends, the early age hydration, pore structure and compressive strength of these systems are investigated here. It should be noted that when OPC is blended with limestone of different particle sizes to simulate the PSD of PLCs, it is implicitly assumed that the PSD of the clinker fraction in the PLCs and that of the OPC in the blends are the same. The limestone sizes for the blended mixtures are then chosen to match the PSD of the PLCs. In reality, this is likely incorrect because the limestone could be ground finer in the intergrinding process due to its softness, and the ground clinker fraction in PLC might be finer or coarser than that in OPC. This results in differences in properties between the interground and size-matched blended mixtures as will be explained in this section, even though the attempt is to provide similar equivalent solid surface areas.

Figure 3 shows the isothermal calorimetric response of the parent cements (Figure 3(a)) and the corresponding blends (Figure 3(b)). From Figure 3(a), it can be noticed that the acceleration stage in the heat flow plots occur at earlier times, the acceleration phase is steeper, and the

maximum heat released is higher for the PLCs, the effects being more prominent for the C1157 PLC. This can be attributed to the higher fineness of the PLCs as compared to OPC and the chemical effects of limestone [7]. When limestone is interground with portland cement clinker, the softer limestone phase is ground more readily than the harder portland cement clinker, resulting in a finer limestone phase [11]. The clinker phase could also be ground finer in the composite cements depending on the desired ultimate fineness of the cement. Fine limestone increases the surface area and seed locations available for hydration product nucleation. In addition, an increase in the amount of limestone fines also enhances the interactions with the C_3A phase, thus significantly sharpening the main hydration peak, while also decreasing the thickness of the initial hydration product shell that forms on particles thereby enhancing C_3S reactivity [27].

Figure 3: Isothermal calorimetric response of: (a) parent cement pastes (OPC and PLCs), and (b) the corresponding size-matched blends.

For the size-matched blends (Figure 3(b)), the calorimetric response is more in line with that of a conventional OPC paste. The total heat released for the blended C595 system is almost comparable to that of the corresponding PLC (333.8 J/g for C595 cement and 331.7 J/g for C595b), except for the fact that the heat release peak is sharper in the PLC paste. This is likely because of the enhanced aluminate reaction owing to the presence of much finer limestone particles in the PLC, as will be shown later. An increase in the slope of the acceleration phase attributable to the presence of fine limestone, as described in detail in [7], is observed for the blended pastes as well. The discrepancy between the heat release peaks of the blended and interground systems corresponding to C1157 can be attributed mainly to the inadequacy of size-matching. Note that the blend designed to match C1157 PLC was deficient in the finer fraction as depicted in Figure 2.

Figure 4 shows the porosities and critical pore diameters of interground and size-matched blended systems after 3 and 28 days of hydration. At 28 days, as expected, the intruded pore volume decreases for all the pastes, and the pore structure becomes more refined as compared to 3 days. OPC has the lowest 28-day porosity among all the pastes while the blended and interground limestone containing pastes show slightly higher porosities because of the reduced clinker fraction in these pastes. Further, it is noted that the interground samples have lower porosities than the corresponding blended samples. This is a result of: (i) increase in the particle packing of these systems due to pore filling by the finer limestone particles, and/or (ii) enhancement in cement hydration due to finer cement particle sizes or fine limestone seeding. When the critical pore diameters are compared, the interground limestone paste (C1157) demonstrates the lowest pore size. This is also because of the fact that the limestone in this cement is much finer, along with a higher overall composite Blaine fineness of this cement (Table 1) that enables better particle packing and increased reactivity. Even though the total reaction product volume is slightly lower in this case than that of the OPC paste due to the fact that limestone is not as reactive as that of the OPC, the finer particles result in pore size refinement. The blended pastes are noted to have a larger critical pore size than the PLC pastes, and comparable to that of the OPC paste.

Figure 4: Comparison of: (a) porosity and (b) critical pore diameter for the interground and size-matched blended cement pastes at 3 and 28 days.

Figure 5 shows the compressive strengths of the PLC mortars (Figure 5(a)) and the corresponding blended mixtures (Figure 5(b)) as a function of time. It is noted that the PLC mortars result in higher strengths at all ages than the OPC and the size-matched blended

mortars. This can be attributed to the higher fineness of the PLCs and the consequent increased packing and enhanced reactivity [31]. Comparing the early age strengths, it is seen that the finer PLC (C1157) shows the highest strength. This is because of the increased participation of the fine limestone in reactions with C_3A and acting as nucleation site for the formation of hydration products. The compressive strength results are in line with the trends in porosity described above.

Figure 5: Compressive strength development with time for: (a) PLC mortars, and (b) size-matched blended mortars. OPC is shown for comparison.

To proportion blended systems that are performance-equivalent to PLCs, it is necessary to understand the size distribution of the components (clinker and limestone) in the PLCs. The need to understand the size distribution of components that constitute the final product exists in several critical industries such as pharmaceuticals, food processing, and chemical synthesis where the size distribution influences rates of heat and mass transfer or chemical reaction. The forthcoming section sheds more light on this aspect by developing an analysis method to separate the sizes of the component solids. The method is generic and versatile, though it has been implemented in this study only to separate the PSDs of clinker and limestone fractions in PLCs.

3.2 Extracting the Component Size Distributions in Interground Systems

As noted above, the disparity in the pore structure and properties between the PLCs and the corresponding blended mixtures is indicative of the fact that the OPC and limestone size distributions in the blended systems are not true representations of the ground clinker and limestone PSD in the interground PLCs. The inherent assumption that the PSD of the ground clinker fraction of the PLCs is the same as that of C150 is incorrect (to varying degrees based on whether the comparison is with C595 or C1157 cement).

An understanding of size distribution of components in multi-particle blends is important for several applications [32,33]. There have been attempts at determining the individual PSDs of components from the composite particle size distributions experimentally [34]. Laser diffraction has been employed to obtain the PSDs of gypsum and cement based on the difference in the refractive indices of the two materials [35]. For particulate blends with comparable refractive indices such as cement and limestone, this method is inapplicable. A sedimentation method using Andreasson apparatus has been used to obtain the independent PSD of two or more blended solid species [36]. This method, based on the steady-state settling of spherical particles according to Stoke's law, employs periodic determination of concentration of solids at a given depth in a vertical settling tube. While useful for mixtures containing larger particles, the sedimentation technique is extremely tedious for determining PSDs with size fractions finer than 1 μm . This is because the quadratic relationship between settling time and particle diameter in Stokes' equation makes the intervals between samples extremely long for sampling smaller (~ 1 μm) particles. Back-scattered electron microscopy and thin section image analysis have also been used to identify the distributions of particle classes in a powder mixture [37]. This method is rather tedious and demands adequate optical or microscopic contrast between the particles imaged, which is not always achieved. In order to overcome these limitations, a novel

optimization technique is discussed in this work, which has the potential to deconvolute the PSDs of the clinker fraction and limestone from that of the composite cement.

3.2.1 The optimized Rosin-Rammler distribution-based PSD deconvolution technique

Rosin-Rammler (R-R) distribution (which essentially is a Weibull distribution but called R-R because it was first applied by Rosin and Rammler to describe PSDs [39]), is widely accepted as a method to describe the PSDs of materials processed by grinding, milling, crushing, or comminution operations, such as in the cement manufacturing process [40,41]. R-R distribution is defined by the characteristic diameter and the shape parameter. The characteristic diameter (d_0) represents the cumulative volume fraction that is finer than 63.2%, which makes it a measure of the fineness of the distribution, whereas the shape parameter (n) is a measure of spread of the distribution. The R-R cumulative distribution function, $Q(d)$, where d is the particle size, is defined, as shown in Equation 1, as a function of d_0 and n . The parameters of the R-R distribution can be obtained by re-factoring the distribution function to the form shown in Equation 2. For the three parent cements used in this study (C150, C595, and C1157), the R-R parameters obtained are shown in Table 2.

$$Qd = 1 - e^{-dd_0^n}$$

(1)

$$\ln \ln \frac{1}{1-Qd} = n(\ln d - \ln d_0) \quad (2)$$

An optimization procedure was employed to obtain the values of the characteristic diameter (d_0) and the shape parameter (n) of the clinker and limestone present in interground cements, from which their individual PSDs can be deduced. The constraint used in the optimization procedure was the equivalence of specific surface areas from the PSDs of the actual interground cements and their PSDs obtained using the R-R parameters of both clinker and limestone fractions. Specific surface area (SSA) can be calculated from the PSD using Equation 3 [42], where F_s is a constant that accounts for the shape of particles (considered as 1.0 assuming spherical particles), f_d is the mass fraction of particles with size ' d ' μm and ρ is the density of material.

$$SSA = 6 \times 10^3 \times F_s \times \sum \frac{f_d}{d} \times \rho \quad (m^2/kg)$$

(3)

Table 2: Rosin-Rammler parameters and SSA of the parent cements used in the study.

Cement type	R-R parameters		SSA (m ² /kg)	
	d ₀ (μm)	n	Predicted SSA using Eq. 3	Experimental Blaine fineness
C150	17.95	1.32	492.4	452
C595	16.99	1.28	508.1	497
C1157	12.48	1.32	604.1	594

The optimization function is defined as the summation of the absolute relative errors in the values of d₀, n, and SSA of the actual interground cement and the predicted distribution from the R-R parameters, as shown in Equation 4.

$$Z = \Delta d_0 d_0 + \Delta n n + \Delta SSA SSA$$

(4)

A rigorous search was carried out to obtain the d₀ and n values associated with each of the individual components in the composite material; in this case, the clinker and limestone. Multiple iterations were carried out using trial d₀ and n values for clinker and limestone fractions selected from a pre-specified range and step interval. These trial combinations were used to calculate the respective PSDs using Equation 1. The composite distribution was then calculated knowing that these PLCs contain 12.7% of limestone by volume. Subsequently, d₀ and n values of the composite distribution were determined using Equation 2 and SSA was calculated using Equation 3. Finally, these values were used in Equation 4 to calculate the optimization function. The optimization function was found to converge to a minima for certain combinations of d₀ and n for the clinker and limestone phases. The region of convergence was used to redefine the range for d₀ and n values for the next iteration cycle. The step interval was reduced in order to explore the region of convergence in search of a better solution. The tolerance value for the optimization function was also subsequently refined so as to finally reach the value of ~ 0.5%. The values of d₀ and n at the minima at an acceptable level of tolerance (~ 0.5% in this case) were taken as the optimized values. A flowchart describing this approach, which has been developed into a computer program, is shown in Figure 6. The optimized R-R parameters for the clinker and limestone phases present in the PLCs are shown in Table 3. The median size (and d₀) of the clinker particles in the C595 PLC is higher than that of OPC whereas for the C1157 PLC, it is lower than that of OPC. The spread of the distribution of the clinker particles

are rather invariant between the three parent cements. As expected, limestone is ground finer in the C1157 PLC than in the C595 PLC. Figure 7 shows the comparison between the actual PSDs of the C595 and C1157 cements and the composite distribution predicted using the optimization scheme that extracted the individual PSDs of clinker and limestone. The adequacy of the proposed optimization approach is evident from this figure.

Figure 6: Flowchart to demonstrate the steps for the optimized R-R method

Table 3: Summary of the parameters of Rosin-Rammler distribution for clinker and limestone in the OPC and PLCs obtained using the optimization approach. d_{50} values are also shown for comparison

Cement type	Clinker fraction			Limestone			Error
	d_0 (μm)	n	d_{50} (μm)	d_0 (μm)	n	d_{50} (μm)	
C 150	17.95	1.32	11.20	--	--	--	--
C595	19.00	1.28	14.26	2.20	1.90	1.82	0.51%

C1157	13.90	1.35	10.61	1.93	1.80	1.57	0.53%
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Figure 7: Comparison of the actual PSDs of: (a) C595 PLC and (b) C1157 PLC with those obtained from the R-R parameters.

3.3 Validation of the Proposed Model through Virtual Microstructure-and-Hydration Modeling

While Figure 7 established the correspondence between the PSDs of the interground cement and those extracted from individual clinker and limestone PSDs, it is onerous to experimentally generate blended mixtures of these PSDs separately for validation studies. Thus, virtual microstructures and a well-accepted and validated cement hydration model is used in this study to evaluate the efficiency of the PSD extraction approach. The individual PSDs of the clinker and limestone phases obtained using the R-R optimization approach were used to calculate the composite distributions as shown in Figure 7, which were used as inputs in microstructural modeling. The composite PSDs were discretized to get the number of particles of the different components in a representative volume element of side length 300 μm . The packing fraction corresponded to a water-solids ratio of 1.26 by volume (approximately 0.4 by mass). Figure 8 shows representative slices from the initial digitized microstructures of the blended mixtures (where OPC and four limestone sizes are used to match the PSD of the PLCs – Figure 2) and the composite mixtures after extraction of PSDs of individual components. An observation of these virtual microstructures indicate the drawbacks of the PSD-matching approach adopted in the first part of the study. While the clinker fraction particle sizes are taken to be similar for the

blended mixtures (Figures 8(a) and (c)) because of the use of parent OPC in the blends, simulation of the optimized PSDs in Figures 8(b) and (d) show that the clinker fraction is much finer for the C1157 cement. Similar, but subtler variations exist for the C595 cement also, which are elucidated in more detail using microstructural quantifiers described below.

Figure 8: Comparison of virtual microstructures (in the unhydrated state) for the PSD-matched blends corresponding to Figure 2 (Figure 8(a) and (c)) and the simulated PSDs based on R-R method and optimization (Figures 8(b) and (d)). Clinker fraction is indicated in red, gypsum in violet and limestone in green. Note the large discrepancy in particle sizes of both clinker fraction and limestone between the blended and simulated PSDs for the C1157 cement.

The interactions between the nearest neighbors in the random multi-component microstructure can be extracted from microstructural simulations such as the ones shown in Figure 8. Quantification of the interactions through contact fractions is useful to obtain a perspective on the reaction rates in the mixtures. The particle contact fraction is calculated as the fraction of

nearest neighbor pairs in the microstructure. For instance, the cement-limestone contact fraction is calculated as the ratio of the total number of contacts between cement and limestone to the total number of contacts in the system (which includes cement-cement, limestone-limestone, and cement-limestone contacts). Since limestone is known to contribute both physically and chemically to the hydration of cement, albeit to a minor extent, the interaction between cement and limestone particles is vital towards understanding the nucleation process. As is well known, this is highly dependent on the PSDs of both limestone and cement in the mixture. Figure 9 shows the like and unlike particle contact fractions in the interground PLCs and the corresponding blended mixtures. The blended mixtures exhibit higher cement-cement interaction than the interground PLCs, indicating that the limestone particles are larger in this case (and thus more separated, given the same volume fraction). This results in the cement-limestone interactions being lower also. The proximity between the cement and limestone particles, coupled with the increased fineness of limestone leads to increased hydration rates since limestone is known to accelerate the hydration of cement. This aspect is evident when the C1157 and C595 PLCs are compared.

Figure 9: Percentages of contact between like and unlike particles obtained from the microstructure model. C-C indicates the % contact between cement particles, L-L between limestone particles and C-L cement and limestone particles.

Cement hydration was modeled using the hydration and microstructure modeling tool CEMHYD3D [43]. The process of hydration of a cement with known particle size distribution is simulated using a set of cellular automata rules. The model has been validated for a number of

different types of portland cements as well as portland cements containing limestone [16,44]. After the construction of virtual microstructures (Figure 8), the volume fractions of individual phases in the parent cements were obtained from Bogue's calculations. The hydration was simulated for 72 hours under isothermal conditions in a sealed environment [43]. A cycles-to-time conversion factor of $0.00035 \text{ hours/cycles}^2$ was used to represent the hydration results as a function of time [43]. Figure 10 shows the simulated cumulative heat release curves based on the PSD-matched blends of OPC and limestone (labelled C595b-Sim or C1157b-Sim in the figures) as well as those based on the individual PSDs extracted from R-R optimization method (labelled C595-Sim or C1157-Sim in the figures). It is noted that the simulations based on the extracted PSDs match very well with the experimental data for both the PLCs. Since the PSD matching was rather satisfactory for the C595 PLC (Figure 2), the heat release responses are not very different. However, the adequacy of the PSD extraction process described earlier can be noticed from Figure 9(b) where the C1157 cement is simulated. Since CEMHYD3D has been shown in the past to predict the hydration heat accurately when limestone is present in the mixture, the use of such a model to compare the efficiency of the methodology developed in this study to separate PSDs is valid. However, the possibility of careful physical testing to validate the modeling strategy is also being considered.

Figure 10: Cumulative heat flow curves for the PSD-matched blends (C595b and C1157b) and the PLCs from hydration simulation and their comparison with experiments. Simulation data shown as continuous and dashed lines; experimental data shown as discrete symbols.

Figure 11 shows the comparison between the porosities calculated at 3 days using the hydration model and the experimental porosity values obtained using MIP. The porosities calculated by the hydration model for the interground PLCs using the composite distributions in

Figure 7 are comparable to the experimental values obtained using MIP, whereas the simulated porosities for the blended mixtures are much higher in comparison. This further validates the composite PSDs calculated using the R-R optimization approach.

Figure 11: Comparison of experimental and simulated porosities at after 72h of hydration

4.0 CONCLUSIONS

This paper has compared the hydration response, pore structure, and strength of cementitious systems proportioned using two interground portland-limestone cements (conforming to ASTM C595 and C1157) to those of corresponding particle size-matched blends. The PSD-matched blends were proportioned using limestone powders of four different median sizes. The inability of blended systems to match the properties of interground PLCs even with similar or comparable overall solids surface area is brought out in this paper. This behavior is based on the difference in the relative size distribution of clinker and limestone in the interground PLCs as compared to the size-matched blends. In order to determine the unknown PSDs of clinker and limestone in the interground PLCs, a novel method was proposed which can aid in better design of blended mixtures to achieve performance equivalence to the PLCs. The approach uses Rosin-Rammler (R-R) distributions for the clinker and limestone fractions in the interground PLCs and determines the corresponding characteristic diameter (d_0) and shape parameter (n) using an optimization procedure. Such an approach will be of interest to other areas of particle and powder technology such as food processing, pharmaceuticals etc. The validation of the

technique was carried out using CEMHYD3D modeling of cement hydration and microstructure, given the potential difficulties in physical testing that requires both cement and limestone to be ground separately to match the PSDs predicted by the R-R based modeling approach.

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