

1 **Improving discrete particle packing models for the microstructural** 2 **formation simulation of Portland cement**

3 Mingzhi Wang^{a,*}, Abir Al-Tabbaa^b, Wei Wang^c

4 a. School of Civil Engineering, Harbin Institute of Technology, 150006, CN

5 b. Department of Engineering, University of Cambridge, CB2 1PZ, UK

6 c. School of Civil Engineering, Harbin Institute of Technology, 150006, CN

7 *Corresponding author at School of Civil Engineering, Harbin Institute of Technology,

8 150006, CN

9 E-mail address: kevin18289@outlook.com

10 **Abstract**

11 The 3D solid phase spatial distribution strongly influences the electrical, mechanical and
12 chemical properties of Portland cement microstructure. The commonly applied random
13 sequential addition (RSA) method in cement microstructure formation simulation is
14 causing **over-computation of volume expansion** due to the unrealistic initial geometry
15 condition. However, it is difficult to search for a suitable model to represent the initial 3D
16 pore structure with sufficient pore density range and compatibility with existing 3D cement
17 microstructure models. An approach is proposed based on introducing a pseudo-contact
18 mechanics analysis step to the RSA-discrete particle packing simulation scheme. The key
19 control parameter to obtained specific pore density is identified to be the coefficient of
20 friction after adjusting relative velocity distribution, lattice elastic constant and
21 particle/domain size ratio. The proposed method enables the generation of random 3D pore
22 structure with the same lattice configuration of major discrete cement microstructure
23 formation models and Lattice Boltzmann Method (LBM), allowing more realistic 3D
24 structure input and coupled modelling.

25 **1. Introduction**

26 The problem of particle packing has been studied intensively for decades both
27 experimentally [1,2] and numerically [3-19]. In terms of mono-sized **sphere packing**, it was
28 mathematically proved that 0.74 is the highest packing fraction [20]. However, the random
29 particle packing is unlike artificial placement and the highest packing fraction 0.74 hardly
30 exists in practise. Random loose packing (RLP) is commonly defined as the stable packing

31 phenomenon with minimum packing fraction and random close packing (RCP) is
32 commonly defined as the densest packing phenomenon formed by random particle packing
33 without chemical reaction and deformation. Through the previous study, a packing fraction
34 of around 0.55 and a coordination number of 5 were observed for monosized sphere
35 packing [2-4,12,23] in the case of RLP. On the other hand, a packing fraction of 0.64 and
36 a coordination number of 6 were determined [1,4, 13-15] in the case of RCP. From this
37 point of view, packing fraction and coordination number are often used as the macroscopic
38 parameters to determine the packing degree when a visual 3D pore structure is not directly
39 available. In this paper, random pore structure with a packing fraction of 0.55 and 0.64 and
40 the corresponding coordination numbers are referred to as RLP and RCP structure,
41 respectively. The debate about a better definition of RLP can be noticed through the
42 development of particle packing models regarding the cohesive control and frictional
43 control [2,12,23]. It has been as well debated that no lower packing fraction limit exists for
44 RLP[23]. As a result, the packing fraction value of 0.64 is a better-recognised validation
45 than that of RLP. In fresh cement microstructure, monosized distribution is seldom
46 observed and Rosin-Rammler function has been widely used to represent the particle size
47 distribution of cement particles [40]. In terms of polydisperse spheres, the packing fraction
48 was found to be a function of the standard deviation if log-normal particle size distribution
49 (PSD) is applied [6].

50 The computer simulation of a porous structure made of particles can be realized with
51 various algorithms. To name a few, random sequential addition (RSA) [16,17] algorithm
52 provides a straightforward solution by sequentially adding pre-defined geometry at a
53 random position and overlap is not allowed. However, the upper packing fraction limit of
54 RSA is almost always lower than RLP. Particle growth algorithm [5] simulates the packing
55 process by increasing the radius of point or sphere placed with RSA. The size of the
56 individual particle is often not under control to achieve a dense pore structure.
57 Overlapping-relocation algorithm [14, 15] adjusts the particle's position by assigning a
58 movement opposite to its overlapping with the other particles. The domain size is not under
59 control since the sample volume keeps expanding with this method. For the purpose of
60 having a user-defined sample size and PSD, the following two algorithms are considered
61 to be well-developed. DigiPac [8] and the related DigiDEM [21] and DigiCGP [22] provide

62 a reliable solution for the issue of arbitrary shape random particle packing in a discrete
63 system. Discrete element method (DEM) [23-25,34,35], which is though not originally
64 designed for the packing issue, emphasizes the particle inter-force during the packing
65 process in a continuous system and the RLP-RCP packing result is as well close to the
66 determined value.

67 One of the important issues that the particle packing aids to solve is the microstructure
68 development simulation of cement-based material as the result of hydration [26-29]. These
69 cement microstructure formation simulations require an initial 3D porous structure with
70 specific sample size and PSD, which is generally generated by RSA simulation. However,
71 it was experimentally observed that fresh bulk cement paste possesses a packing density
72 within the range of 0.480-0.514 measured with dry packing method and the range of 0.622-
73 0.703 measured with wet packing method [30,31], which are higher than the maximum
74 packing density (≈ 0.4) provided with RSA [38]. The inconsistency of the initial packing
75 fraction between simulation and experiments inevitably leads to the over-computation of
76 the volume expansion when the final results consist. This vital problem of unrealistic initial
77 spatial distribution of fresh cement particles became outstanding only after the
78 development of experimental techniques of measuring packing density of fresh cement in
79 2008 [30,31]. In terms of system compatibility, CEMHYD3D series [26,27] applying
80 cellular automaton (CA) in the discrete system are naturally compatible with discrete
81 packing algorithms such as DigiPac series [8,21,22]. On the other hand,
82 HYMOSTRUC/ μ ic series [28,29] applying particle growth algorithm in the continuous
83 system are well compatible with continuous sphere algorithms such as DEM and the
84 original sphere growth algorithm [5]. Data conversion can be applied to link the
85 incompatible simulation systems between particle packing and cement microstructure
86 formation but data distortion is inevitable from the discrete-continuous conversion or the
87 other way around. In the analysis aspect of the 3D pore structure, the Lattice Boltzmann
88 Method (LBM) has become a well-accepted tool to simulate diffusive fluid in cement pore
89 structure [36]. Novel model applying LBM to simulate the microscale cement hydration
90 has recently been initialized [41].

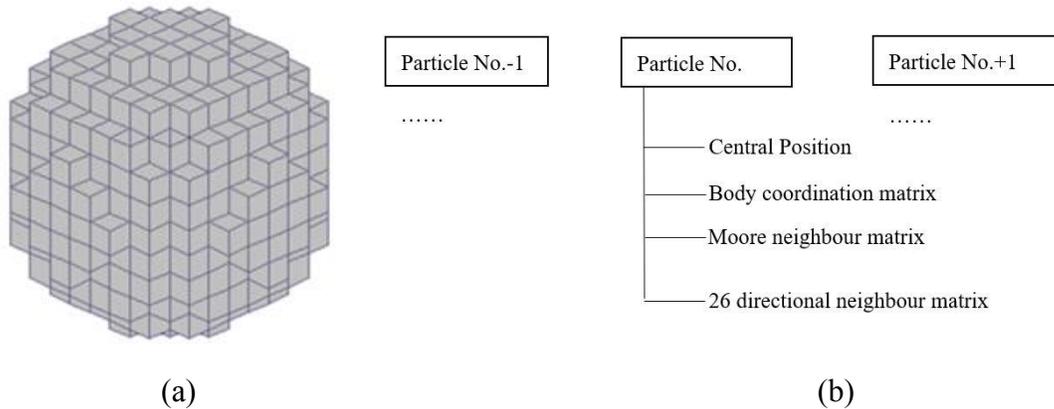
91 Through the author's reproduction of pre-existing discrete models and the available data
92 [2,8,21,22], it was found that the random structure generated had a considerably lower

93 packing fraction than the RCP structure and the experimental measurement of fresh cement.
 94 As previously mentioned, the continuous-discrete data conversion from DEM results will
 95 inevitably cause the change of key properties such as porosity and water/cement ratio. On
 96 the other hand, the un-converted data is unable to perform a sub-particle scale simulation
 97 such as the dissolution of a specific part of a cement particle. As a result, it is necessary to
 98 improve pre-existing discrete models to generate a random 3D pore structure directly in
 99 the discrete system for a wider structure range and better adjustability. This paper presents
 100 the author's solution for the issue and it is believed that this work inclines with the research
 101 interest of the simulation of particle packing and cement microstructure in a discrete system.

102 **2. Methodology**

103 **2.1 Pre-simulation data and optimization**

104 Before the conduction of the simulation, PSD data is independently generated. For general
 105 comparison and validation purpose, monosized particles are initially discussed in this paper.
 106 User-specified PSD can be applied from experimental measurement of fresh cement
 107 microstructure. The Log-normal distribution and Weibull distribution are then applied as
 108 examples for arbitrary PSD input. Structural data as presented by Fig.1(b) are generated with
 109 individual particle's position, size and particle number information in this step.



110

111

112

113

114

115

116

117

Fig.1 (a)A digitized particle used in this model. (b) Structural data used in this model.

One voxel-based particle applied in this simulation is presented by Fig.1(a) which is in the same form with the common particle setting in the discrete packing system [8,21,22] and discrete cement microstructural formation system [26,27]. These particles are generated with Eq.1 in a 3D matrix.

$$X^2 + Y^2 + Z^2 = r^2 \tag{1}$$

118 where X , Y and Z is the coordination array for the particle with a size of r . The length
119 mapping of the simulation was $1 \mu\text{m}$ per lattice (1 lu).
120 The calculation of each particle's body coordination matrix is time-consuming if it is
121 conducted in the packing simulation. Optimization is therefore performed by pre-
122 calculating the relative body coordination to the central coordination for a particle with a
123 radius from 1 to $50 \mu\text{m}$, so the body position update is directly conducted with the central
124 position update during the packing simulation. Another optimization conducted is the pre-
125 calculation of the 3D Moore neighbours of the body voxels and its 26 directional
126 neighbours. The latter is obtained by performing a single lattice movement in one of the 26
127 discrete directions and then erasing the original body coordination. All the results of pre-
128 calculation are stored in the particle structural data so that the contact check and movement
129 assignment step in the packing simulation can be directly performed without real-time
130 calculation.

131 **2.2 Packing Simulation**

132 Fig. 2(a) demonstrates the simulation flow of the programs. Periodic boundary condition
133 is applied to the horizontal four directions and solid wall boundary condition is applied to
134 the top and bottom direction of the 3D matrix named D1. The nature of the discrete system
135 makes the direction of unit movement discrete as well, and 26 discrete directions are the
136 maximum possible number for the 3D cubic lattice. The lattice system is named D3Q26
137 for 3D model with 26 possible movement directions following the naming principle of
138 LBM. Initially, particles with pre-calculated PSD are placed into the 3D matrix with the
139 RSA method. Then a contact analysis is conducted on each particle in its 6 orthogonal
140 directions as illustrated by Fig.2 (b). In this simulation, contact is defined as the existence
141 of the overlap between a particle and the Moore neighbours of the other particles. The
142 movement in a certain direction is blocked if the contact analysis in this direction results
143 in a true value (true=1).

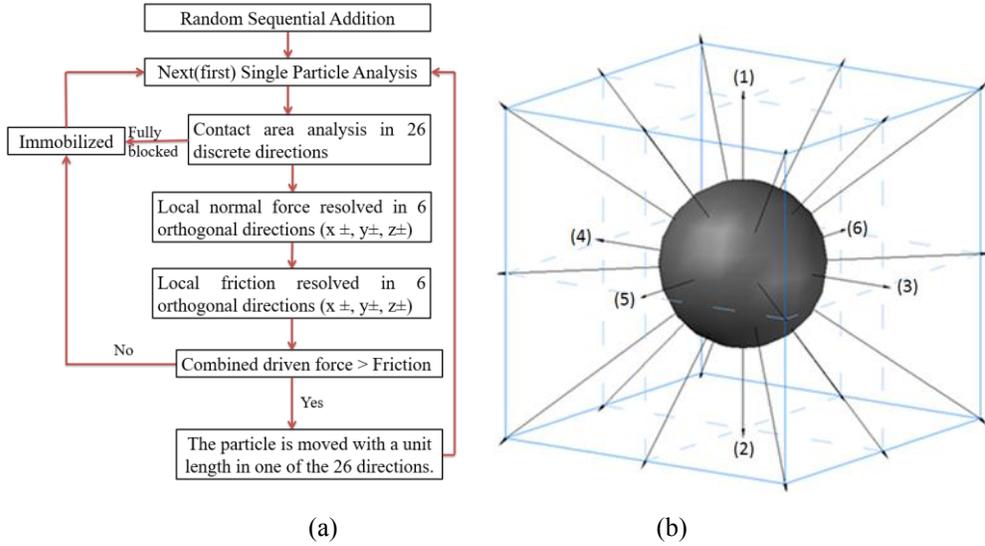


Fig.2 (a)Simulation flow of this method. (b) Directions of contact analysis.

After the contact analysis step, a temporary 3D matrix named D2 is created. The Moore neighbours of all the particles are placed in D2 with the same central position. The overlap voxels in D2 caused by the increasing particle size are counted as the contact area A of the particles as shown in Fig.3(b), which is stored in the structural data during the calculation.

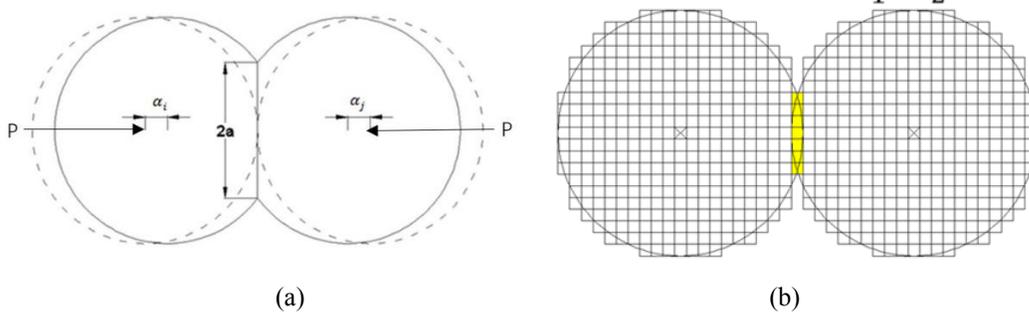


Fig.3 (a)Parameters in contact analysis. (b) Contact area determination.

Then a pseudo-contact mechanics analysis is performed with Hertz repulsive force and the contact properties as shown with Eq.2 and Eq.3:

$$a = \left(\frac{3PR}{4E^*}\right)^{1/3} \quad (2)$$

$$\alpha_{ij} = \frac{a^2}{R} = \left(\frac{9P^2}{16RE^{*2}}\right)^{1/3} \quad (3)$$

where a is the radius of contact area; E^* is a constant relevant to the elastic modulus in the discrete system; $1/R$ is the equivalent contact curvature; α_{ij} is the relative displacement of the two centres, which is calculated as $\alpha_i + \alpha_j$. With equation (2) and (3), the following equation is derived:

162
$$P = \frac{4}{3}E^* a\alpha_{ij} \quad (4)$$

163 Assuming the contact area is a circle, the relation among normal force P , contact area A
164 and relative displacement is obtained as given by Eq.5.

165
166
$$P = \frac{4}{3\sqrt{\pi}}E^*\sqrt{A}\alpha_{ij} = C_E\sqrt{A}\alpha_{ij} \quad (5)$$

167 where C_E is a general constant relevant to the elastic modulus. α_{ij} is treated as the relative
168 velocities of one particle to its surrounding particles since each computation iteration is
169 unit time, and the speed is calculated with Eq.6:

170
$$\alpha_{ij,k}/\Delta t = \sqrt{v_k^2} \quad k = 1,2, \dots,6 \quad (6)$$

171 where $\alpha_{ij,k}$ is the relative displacement of one particle in k th direction, k indicates one of
172 the six orthogonal movement directions, Δt is the time mapping of the simulation, v_k is
173 randomly assigned following a normal distribution with a mean of 0 and a standard
174 deviation of s_v . As a result, thousands of $\alpha_{ij,k}/\Delta t$ values are directly assigned following
175 Maxwell–Boltzmann distribution for the continues calculation of normal repulsive force in
176 this discrete system. Friction threshold in the tangential direction for each particle is then
177 calculated as given by Eq.7.

178
$$f = \mu P \quad (7)$$

179 where μ is the discrete coefficient of friction(*cof*). In this study, *cof* is the major adjustable
180 parameter to control the density of the final packed structure.

181 Besides the local particle interaction, global influences such as gravity and vibration are
182 also introduced as a universal force to all the particles, where the direction of gravity is
183 downwards and the direction of vibration is randomly chosen in one of the four horizontal
184 directions. The vibration is not emphasized in the work presented in this paper since it was
185 experimentally proved that vibration intensity and frequency is not critical in the formation
186 of the packed structure [1], which is also observed from this simulation. The above contact
187 mechanics analysis step differs from ‘real’ contact mechanics calculation in the continuous
188 system since the velocity map is not updated accordingly due to the built-in limitation of
189 the discrete system.

190 With the conduction of the pseudo contact mechanics analysis, the resultant of forces \vec{F}
191 for each individual particle is obtained. A movement update step is then performed in D1.

192 This D3Q26 system only allows a single lattice movement in one of the 26 directions per
193 iteration. The movement direction with the maximum vector scalar product calculation
194 result given by Eq. 8 is determined to be the movement update direction.

$$195 \quad R_i = \vec{F} \cdot \vec{n}_i \quad i = 1, \dots, 26 \quad (8)$$

196 where R_i is the scalar product in i th direction, \vec{F} is the resultant of force vector on
197 individual particle and \vec{n}_i is the unit vector in i th direction. After the movement update,
198 the previously designed procedure is repeated until a stable pore structure is formed. With
199 the above design, no residual overlap exists in D1 and D2 makes use of the overlaps for
200 the contact area calculation.

201 The method described above present an effort to bring the merits of pre-existing algorithms
202 together in order to provide a reliable particle packing simulation directly in the discrete
203 system. It applies the RSA method as the initial condition. The lattice configuration and
204 sphere-like particle are compatible with CEMHYD3D, DigiPac series and D3Q27 LBM.
205 The contact mechanics formula follows the Hertzian principal in DEM [34,35], which is
206 fully functional off-lattice. The alternative contact area determination method and
207 statistically determined relative velocity distribution in contact analysis are originally
208 proposed to settle the problem between discrete and continuous system. Multi-task is
209 conducted using parallel computation and packing result of this model is discussed in
210 section 3.

211 **2.3 Analysis methods**

212 Packing fraction is obtained as the ratio of occupied voxels to the overall number of voxels.
213 The porosity is directly obtained as the ratio of void voxels to the overall number of voxels.
214 The coordination number for each particle is obtained by conducting a single step contact
215 check of the overlaps between the Moore neighbour voxels of an individual particle in the
216 D2 and the body voxels of the rest particles in the D1. Representative elementary volume
217 (REV) analysis is conducted by the extracting samples with increasing sample size from
218 the final packed structure in the D1 and chi-square criterion is applied as given by Eq.9
219 [37].

$$220 \quad \chi^2 = \sum_{i=1}^n \frac{(p_i - \langle p \rangle)^2}{\langle p \rangle} \quad (9)$$

221 where χ^2 is the chi-square coefficient, p_i is the porosity of the extracted sample, $\langle p \rangle$
222 is the average value of p_i , $n=8$ is the amount of extracted samples. In this study, A chi-
223 square coefficient lower than 0.03% is applied as the criterion of REV determination and
224 a cubic volume is then extracted to represent the structure.

225 **2.4 Particle size distribution (PSD)**

226 Simulation with mono-sized PSD is initially conducted to compare with well-recognized
227 results from previous study of mono-sized particle packing. Rosin-Rammler function
228 (Weibull distribution) [40] and log-normal distribution are applied for the polydisperse
229 simulation to demonstrate the more practically simulated initial cement microstructure than
230 previous model [38]. Eq. 10 and Eq. 11 gives the probability density function (PDF) of
231 Weibull distribution and log-normal distribution, respectively.
232

$$233 \quad PDF_{log-normal} = \frac{1}{x\sigma\sqrt{2\pi}} \exp\left(-\frac{(\ln r - \mu)^2}{2\sigma^2}\right) \quad (10)$$

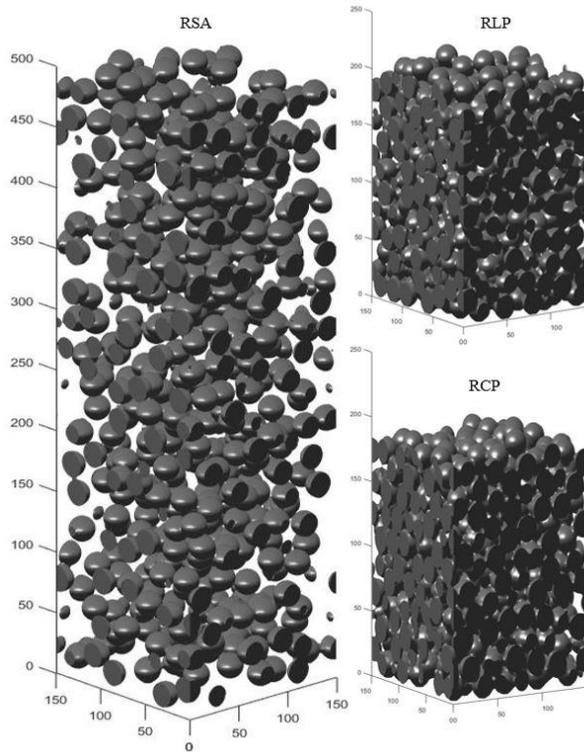
$$234 \quad PDF_{Weibull} = \frac{k}{\lambda} \left(\frac{r}{\lambda}\right)^{k-1} e^{-(r/\lambda)^k} \quad (11)$$

235 where r is the radius of the particles, μ is the mean of log-normal distribution, σ^2 is
236 the standard deviation of log-normal distribution, λ and k are the control
237 parameters of Weibull distribution.

238 **3. Results and Discussion**

239 **3.1 Visualized 3D porous structure**

240 Fig.4 illustrates one visual result of the packing structure applying RSA, RLP and RCP
241 with 500 discrete particles and 150×150 bottom area. The difference in the height of the
242 packing structure can be intuitively observed. The fundamental aim of this research is to
243 fully replace the 3D RSA input with a more realistic packed input for cement microscopic
244 simulation with the consistency of macroscopic properties such as the volumetric ratio
245 among solid phase, pores and fluid phase. Through reapply parametric study, $s_v=3$ and
246 $C_E=500$ were found to be able to generate a sample with wider porosity range and better
247 stability. In order to validate the presented simulation program with the well-recognized
248 RCP phenomenon, parametric study and simulation were initially conducted with mono-
249 sized spheres to observe whether 0.64 can be approached. In a mono-sized particle system,
250 the difference in the size of the particle only influence the 3D resolution and the packing
251 fraction result should be similar. Therefore, simulations were conducted with 5000
252 digitized spheres with radiuses of 8,9 and 10 lu. The early reported DigiPac algorithm is
253 reproduced when $cof=0$, $C_E=0$ and $S_v=0$.



254

255

Fig.4 Three visual output from the model including RSA, RLP and RCP.

256

3.2 Sample volume determination with size ratio and REV analysis

257

Fig. 5 presents the packing fraction development under the influence of size ratio (L/d).

258

L/d ratio is a parameter to describe the horizontal capacity of the domain to contain

259

particles. It can be noticed from the figure that the frictionless packing reaches a packing

260

fraction of around 0.64 when $L/d > 0$, and the 0.64 is not much exceeded afterwards. As a

261

random particle placement process, a low L/d indicates a small horizontal area with a low

262

possibility for particle placement. Such low possibility significantly influences the

263

macroscopic porosity when the number of particles in this area is limited. When the number

264

of the particle is high enough, the change of a few among becomes much less influential to

265

the macroscopic parameter. In this study, it is suggested that $L/d > 20$ should be adopted for

266

the simulation with this method.

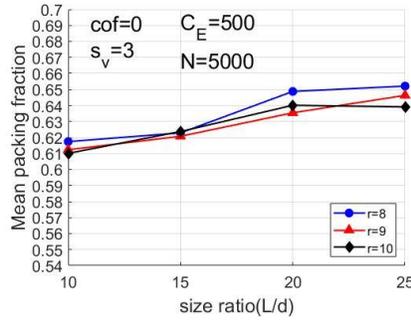


Fig.5 Influence of size ratio (L/d).

267

268

269

270

271

272

273

274

275

276

277

278

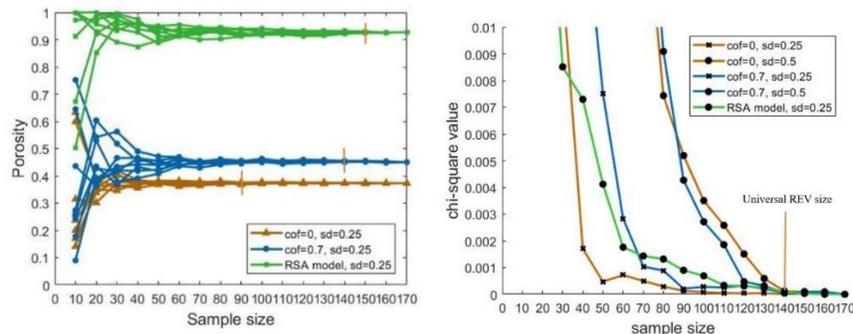
279

280

281

282

In a heterogeneous system, a small extraction from the whole sample may not be representative since such extraction could be a specific part of the sample. An extraction from the fresh cement model as presented in Fig.4 could have an overestimated void ratio if most of the extraction is void phase. A REV analysis with log-normal PSD is conducted in this section to determine the minimum representative sample volume on this model and RSA model. Fig.6 (a) presents the void ratio moving from non-representative zone to the representative zone with the increment of extraction size. In order to quantify the REV size, chi-square criterion is applied as presented in Fig.6 (b). It can be noticed that the REV sizes are within the size range provided by the L/d ratio of 20 as previously discussed. REV requirement increased with both the increment of the standard deviation (*sd*) of the PSD and *cof*, due to the enlarged particle size range and porosity, respectively. A comparison analysis is conducted on the RSA model with *sd*=0.25, and it can be noticed that the REV size requirement of the RSA model in the size determination range of (80,140). 140×140×140 is found to be a universal REV for all current digital samples.



(a)

(b)

283

284

285

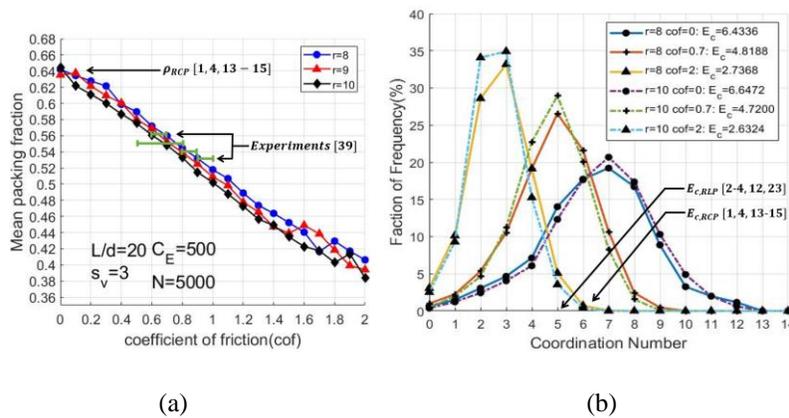
286

287

Fig.6 (a) Void ratios of the extracted samples. (b) Chi-square value development in terms of the extraction size.

288 **3.3 Mono-sized simulation and validation**

289 Fig. 7 present the simulations to generate adjustable pore structures using the *cof* as the
 290 **only** tuning parameter. $L/d=20$, $s_v=3$ and $C_E=500$ are applied for the 5000 particles
 291 simulation. The dependence of particle size is minimised but not entirely removed. As a
 292 matter of fact, the voxelized particles applied both in this and previous discrete models is
 293 not in the same shape as spheres. Due to the meshing, some of the voxels in the sphere
 294 surface is not counted as part of the particle. As a result, the minimized dependence of
 295 radius is actually dependence of particle shape and it is impractical to pursuit a single curve
 296 for every particle size. The voxelization is essential for sub-particle modification for
 297 discrete cement microstructure formation simulation and analysis. In 3D discrete cement
 298 models, the **matrix** representing the particle body can be coupled with mass density matrix
 299 so that a single particle with heterogeneous density distribution can be simulated. Such
 300 heterogeneous density distribution is fundamental to simulate the surface mass lost during
 301 the dissolution of the solid phase. The same argument as well applied to the pore matrix
 302 with which a 3D fluid density distribution can be coupled. In this case, the voxelization
 303 process narrows the homogeneous assumption to the scale of a single voxel before the
 304 construction and solution of the extremely complicated, if not impossible, the 3D
 305 theoretical description of reactive cement microscopic system. It is as well argued that no
 306 purely continuous simulation exists if the fundamental calculation is conducted in a binary
 307 system such as modern computers, where there only 0 and 1 and nothing in-between.



308
 309

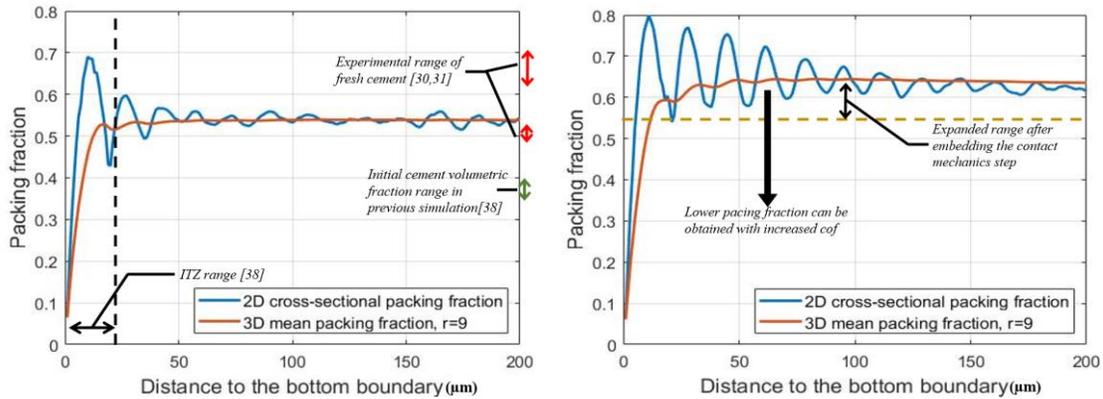
310 **Fig.7 Different pore structure generated with a varying coefficient of friction: (a) Extracted packing**
 311 **fraction development. (b) Extracted coordination number distribution.**

312 Fig. 7(a) presents the packing fraction of the simulated 3D pore structure in terms of the
 313 *cof* changes. The behaviour of loose pore structure formation under increased interparticle

314 friction is quantitatively simulated in the discrete system. At the point of $cof=0.7$, a packing
315 fraction of 0.55 is obtained. Fig. 7(b) presents the coordination number distribution when
316 cof equals 0, 0.7 and 2, respectively. E_c denotes the mean coordination number in the figure.
317 The study shows that the packed structure simulated with this method has an $E_c \approx 6.4$ when
318 the packing fraction is around 0.64 and an $E_c \approx 4.7$ when the packing fraction is around 0.55.
319 In this studied, the stable structure is defined as the status packing fraction change is within
320 0.01% where most of the particles are immobilized. The existence of the pore structure
321 with a packing fraction lower than 0.55 supports the argument that 0.55 is not the bottom
322 limit of the RLP. However, $cof=0.7$ is still used to generated loose pore structure in the
323 polydisperse simulation as discussed in section 3.5.

324 **3.4 Comparison simulation**

325 A comparison simulation without the pseudo contact mechanics analysis step is presented
326 by Fig.8(a) with solid wall boundary condition applied at the bottom. A noticeable
327 improvement in the highest packing fraction, which is very close to 0.64, can be observed
328 as the direct result of the introduction of the pseudo contact mechanics analysis step
329 proposed in this paper. In the comparison study, $r=9$ lu, $L/d=20$ and REV size of the sample
330 are applied. As previously discussed, the range of dimensionless particle size does not
331 significant influence the representativity of a numerical test when the size/domain ratio is
332 fixed since mono-sized particle packing is independent of the particle size. In terms of
333 hardware requirement, single non-parallel computation from RSA to a stable structure
334 made of 6000 particles in $400 \times 400 \times 2300$ matrix takes Intel(R) Xeon(R) CPU E5-1630
335 9482s to complete, with a peak RAM demand of 3 GB and 10% CPU occupation. The
336 introduction of the pseudo contact mechanics analysis step increased the computation time
337 by 20.6% with the same program setting. The proposed algorithm can be implied in the
338 previously mentioned models for different performance without amending the simulation
339 framework. Fig.8(b) presents the simulation result of the proposed algorithm and the
340 increment of the maximum packing fraction is demonstrated. The increment is necessary
341 because the experimental measurement of the packing fraction of fresh cement process
342 higher limits than previous discrete packing model, and the RSA model applied in previous
343 cement hydration simulation.



344

345

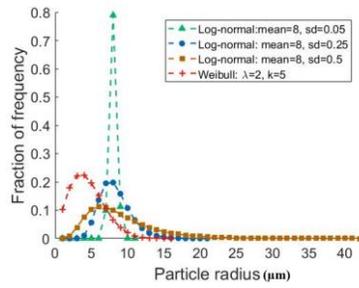
(a)

(b)

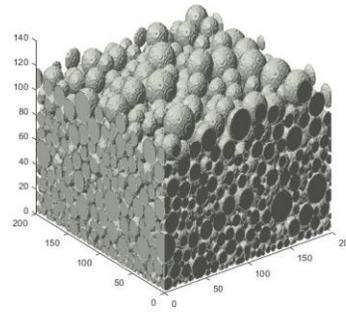
346 **Fig.8 (a) Simulation without the contact mechanics step. (b)Simulation including contact mechanics step.**
 347 One noticeable packing behaviour related to the cement microstructure is that the porosity
 348 is increased when the measurement 2D cross-section is closer to the bottom boundary. This
 349 behaviour corresponding well to the original of the ITZ between bulk cement paste and
 350 aggregates as a result of the wall effect. The ITZ thickness simulated with this comparison
 351 simulation is 20 μm . It needs to be mentioned that properties such as ITZ thickness, porosity
 352 and coordination number are extracted from the more important random 3D structural data.
 353 The traditional RSA can also reproduce this phenomenon to some extent, but the porosity
 354 is significantly higher than practical value. **Embedding particle packing model can solve**
 355 **this vital problem of unrealistic initial input to some extent, and this work presents a further**
 356 **improvement of a suitable packing algorithm by extending the maximum packing fraction**
 357 **limit.**

358 3.5 Polydisperse simulation

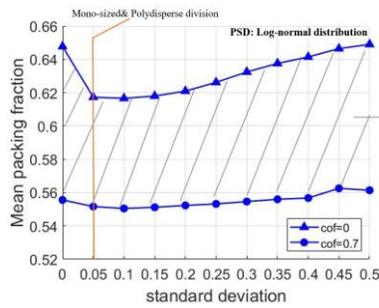
359 **Monosized particles are seldom observed in fresh cement paste.** Simulations are conducted
 360 in this section to model the fresh Portland cement sample with cement particles following
 361 log-normal distribution **and Weibull distribution as presented in Fig.9.** In log-normal
 362 distributed PSD, the mean particle radius is set to be the commonly applied 8 μm and the
 363 coefficient of friction is set to be within the range of (0,0.7). The pre-hydrated cement
 364 particles are assumed to be digitized spheres. **In practice, microscale PSD can be artificially**
 365 **tuned with fundamental methods such as sieving so that the requirement for the modelling**
 366 **work is actually the ability to have arbitrary PSD input.**



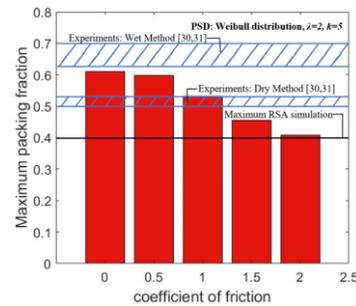
(a)



(b)



(c)



(d)

367

368

369

370

371 Fig.9 (a) Polydisperse PSD applied in the simulation. (b) Visualized result of the polydisperse simulation.

372 (c) Simulation result with log-normal distribution. (d) Simulation result with Weibull distribution.

373 It can be noticed from Fig.9(c) that the packing fraction of simulated cement paste appears

374 to be a function of the PSD standard deviation. The increment of the particle density caused

375 by applying PSD is due to the fact that smaller particles can fill the pore made of bigger

376 particles. When the standard deviation is low, the actual PSD in a continuous system is

377 better graded than that in a discrete system, which is presented by the markers in Fig.9(a),

378 because there is no limitation of the resolution. This limitation can be reduced through the

379 application of higher resolution such as using $r=16$ to represent the $8\mu\text{m}$ cement particles.

380 Higher resolution increases the amount of the available particle sizes, which has the same

381 effect as increasing the PSD standard deviation with dimensionless consideration. Another

382 common method is to increase the standard deviation to obtain a better grade as presented

383 in Fig.9(a). In terms of cement particles, particles with radius significantly larger than the

384 mean radius are often observed, indicating that low standard deviation may not apply to

385 cement particles. In this study, the largest pre-calculated particles applied is $r=54\mu\text{m}$ when

386 the standard deviation reaches 0.65. When the standard deviation is above 0.1, the discrete

387 simulation result shows that the particle density increases with the standard deviation,
388 which is the same as the continuous simulation. The results indicate that a higher resolution
389 is required for the model when PSD of cement particles has a very low standard deviation,
390 at the cost of increased computation demand. This simulation also presents that some
391 macroscopic parameters of cement past such as void ratio is insufficient to represent the
392 microscopic properties since different microstructures can offer the same macroscopic
393 parameter. The shaded area indicates that the pore range provided by the method is
394 (0.53,0.65) when cof is within (1, 0.7), corresponding to a void ratio range of (0.35,0.47).
395 In the simulation with Weibull distribution, the result demonstrates an overlapping range
396 with the experimental measurement using dry method [30,31]. Further simulation with the
397 exact PSD of the fresh cement requires more determined experimental techniques to
398 measure the packing density and microscale PSD, which is unfoundatly not widely
399 available.

400 **3.6 Implement in discreet cement microstructural simulation**

401 The previous simulations bring out the discussion of the necessity of this work. 3D
402 Hydration models require a 3D pore structure of the fresh cement matching the
403 experimental observation as the input. Initial properties such as void ratio, w/c ratio are
404 calculated from the three-dimensionally distributed solid phase, void phase and fluid phase.
405 The commonly adopted RSA method and the original model without the pseudo contact
406 mechanics analysis step presents a limitation in terms of the available porosity range and a
407 lack of the porosity control. With the presented model, a 3D pore structure is generated
408 with a wider density range and specific porosity can be generated using cof as the only
409 control parameter. As an important branch of the cement microstructure formation
410 simulation, discrete models have the ability to conduct sub-particle modification.
411 Continuous-discrete conversion can provide input, but the microscopic changes of the
412 particle surface will assemble to become a macroscopic difference in the initial properties.
413 This problem is more severed if coupled modelling is conducted since the changes can
414 assemble through thounds of iteration. The proposed discrete packing algorithm is fully
415 compatible with discrete cement hydration model (CEMHYD3D and so on). The above
416 discussion also applies to the LBM simulation of fluid in porous media, which is as well a
417 part of research interest in the cementitious material since LBM is the upgrade of the

418 random walk algorithm widely applied in CEMHYD3D. The particles growth behavior in
419 HYMOSTRUC can as well be reproduced with a well-constructed LBM simulation as
420 presented in Fig.10 (b).

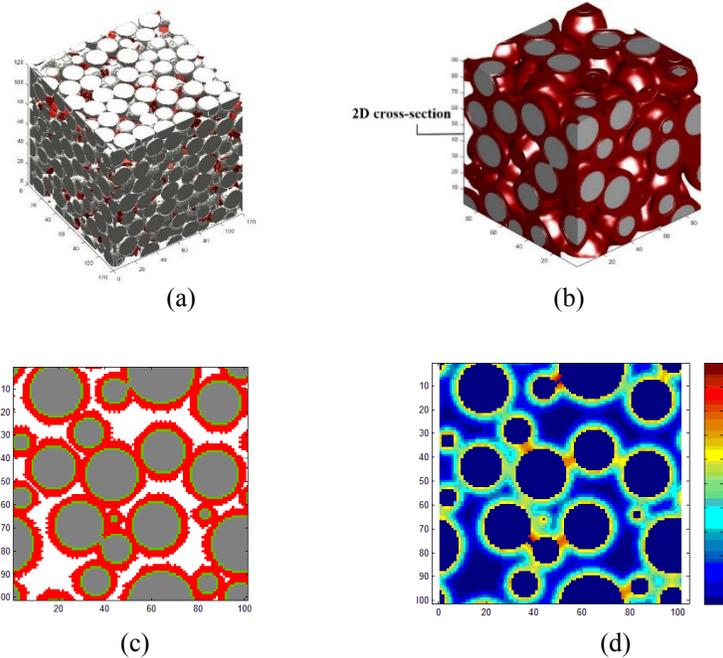
421

422

423

424

425



426

427

428

429

430

431 Fig.10 (a) Simulation with spheres and plates. (b) 3D particle growth behavior from the initial condition
432 generated with this model. (c) 2D cross-section of the 3D structure. (d) LBM simulation of cement
433 hydration with structure generated with this model.

434

435 Due to the same lattice configuration, the 3D pore structure generated with the proposed
436 method can be directly embedded in the LBM simulation of diffusion behaviour in porous
437 media (Fig.12(d)) and the discrete cement microstructural formation simulation (Fig. 10(b))

438

439 as geometry input. It can be noticed from Fig. 10 (d) that the geometry of a single particle
440 become irregular during the cement hydration simulation, indicating a sub-particle

441

442 modification on the heterogeneous distributed solid phase. In the voxelized system, each
443 voxel of the particle can be amended according to the local diffusion-reaction mechanism.

444

445 As a result, irregular hydration products with non-predefined shapes can be formed during
446 the simulation.

444

445 Another advantage of the proposed packing algorithm is that it inherits the strong ability
446 to simulate particle packing with arbitrary shape from the original discrete packing

446

447 algorithm, which cannot be properly realized with current DEM. Modern experimental

447 cement system often contains non-spherical particles such as carbon black (plate-like),
448 fibre (tube-like) in microscale and aggregates (arbitrary shape) in mesoscale. Fig.12(a)
449 demonstrates a sphere-plate packing structure generated with this model as an example of
450 fresh cement system containing non-sphere particles.

451 The packing density range provided by this model is 0.40-0.64. Though the highest packing
452 density of 0.708 observed from the experiment on fresh cement is still not realized due to
453 the lack of information on the PSD, considerable improvement has been made in terms of
454 the density range and adjustability. Fluid density distribution can be assigned to the void
455 phase matrix and solid mass density distribution can be assigned to the solid phase matrix
456 both in macroscopic level or molecular level in order to perform the hydration simulation
457 with the certain void ratio, w/c ratio, etc. In terms of volumetric w/c ratio, a packing density
458 of 0.4 can result in a w/c ratio within the range of 0-1.5 and a packing density of 0.64 can
459 result in a range of 0-0.5625 if the free water in the pore is the only consideration.

460 **4. Summary**

461 In this paper, a discrete particle packing algorithm is proposed to extend the maximum
462 packing fraction to a value closer to experimental measurement of fresh cement. A pseudo
463 contact mechanics analysis is introduced to enlarge the packing density range and the
464 adjustability of the generated 3D pore structure. It was found that a local velocity
465 distribution standard deviation of 3, a lattice elastic constant of 500 and an L/d ratio of
466 above 20 is sufficient to be set as the fixed parameters in order to provide stable results
467 with minimum size dependence. Coefficient of friction was applied as the only tuning
468 parameter to obtain specific pore density. RCP packing fraction of around 0.64 was realized
469 in the frictionless simulation. One RLP packing fraction of around 0.55 is realized when
470 $cof=0.7$. Lower packing fraction was obtained with increased cof . Randomly assigned
471 relative displacement following Maxwell–Boltzmann distribution is able to provide a
472 packing fraction development matching previous experiment of frictional particle packing.

473 A comparison simulation was conducted to find that the introduction of the proposed
474 pseudo contact mechanics analysis step indeed extends the packing density range. Single
475 non-parallel computation from RSA to a stable structure made of 6000 particles in
476 $400 \times 400 \times 2300$ domain takes Intel(R) Xeon(R) CPU E5-1630 9482s to complete, with a

477 peak RAM demand of 3 GB and 10% CPU occupation. The introduction of the pseudo
478 contact mechanics analysis step increased the computation time by 20.6% with the same
479 program setting. Polydisperse simulation indicates that a resolution higher than 1 μ m per
480 lattice is needed when the PSD standard deviation is lower than 0.1. Limitation of the
481 discrete simulation on the available particle sizes still exists on the PSD assignment when
482 the spherical assumption is applied.

483 The proposed packing model is in natural compatibility with discrete cement hydration
484 simulation system and LBM system. Voxelization enables the hydration models to perform
485 sub-particle modification as a result of the local diffusion-reaction mechanism. The strong
486 ability to simulate particle packing with arbitrary shape is inherited from the original
487 discrete packing algorithm. Though the highest packing density recorded in the
488 experimental reports is still not reached, an improvement has been made for the discrete
489 cement microstructure formation simulation with the expanded packing density range up
490 to 0.64 and lower REV size requirement.

491 **Conflict of interest**

492 The authors declare that they have no conflict of interest.

493

494 **References**

- 495 [1] McGEARY, R. K. (1961) 'Mechanical Packing of Spherical Particles', *Journal of the*
496 *American Ceramic Society*, 44(10), pp. 513–522.
- 497 [2] Onoda, G. Y. and Liniger, E. G. (1990) 'Random loose packing of uniform spheres and
498 the dilatancy onset', 64(22), pp. 2727–2730.
- 499 [3] Song, C., Wang, P. and Makse, H. a (2008) 'A phase diagram for jammed matter',
500 *Nature*, 453(7195), pp. 629–632.
- 501 [4] Valverde, J. M. and Castellanos, a (2007) 'Random loose packing of cohesive granular
502 materials', *Europhysics Letters (EPL)*, 75(6), pp. 985–991.
- 503 [5] Lubachevsky, B. and Stillinger, F. (1990) 'Geometric Properties of Ran- dom Disk
504 Packings', *Journal of statistical physics*, 60(5/6), pp. 561–583.
- 505 [6] Brouwers, H. (2006) 'Particle-size distribution and packing fraction of geometric
506 random packings', *Physical Review E*, 74(3), p. 31309.
- 507 [7] a.B. Yu *et al.* (2003) 'Computer simulation of the packing of fine particles',
508 *International Journal of Materials and Product Technology*, 19(3/4), p. 324.
- 509 [8] Byholm, T., Toivakka, M. and Westerholm, J. (2009) 'Effective packing of 3-
510 dimensional voxel-based arbitrarily shaped particles', *Powder Technology*. Elsevier B.V.,
511 196(2), pp. 139–146.
- 512 [9] Caulkin, R. *et al.* (2006) 'An investigation of packed columns using a digital packing

513 algorithm', *Computers & Chemical Engineering*, 30(6–7), pp. 1178–1188.

514 [10] Corwin, E. I. *et al.* (2010) 'Model for random packing of polydisperse frictionless
515 spheres', *Soft Matter*, 6(13), p. 2949.

516 [11] Cundall, P. A. and Strack, O. D. L. (1980) 'A discrete numerical model for granular
517 assemblies', *Géotechnique*, pp. 331–336.

518 [12] Farrell, G. R., Martini, K. M. and Menon, N. (2010) 'Loose packings of frictional
519 spheres', *Soft Matter*, 6(13), p. 2925.

520 [13] a.C.J. de Korte and Brouwers, H. J. H. (2013) 'Random packing of digitized particles',
521 *Powder Technology*, 233, pp. 319–324.

522 [14] He, D., Ekere, N. N. and Cai, L. (1999) 'Computer simulation of random packing of
523 unequal particles.', *Physical review. E, Statistical physics, plasmas, fluids, and related
524 interdisciplinary topics*, 60(6 Pt B), pp. 7098–7104.

525 [15] Jia, X. and Williams, R. . (2001) 'A packing algorithm for particles of arbitrary shapes',
526 *Powder Technology*, 120(3), pp. 175–186.

527 [16] Williams, S. R. and Philipse, a P. (2003) 'Random packings of spheres and
528 spherocylinders simulated by mechanical contraction.', *Physical review. E, Statistical,
529 nonlinear, and soft matter physics*, 67(5 Pt 1), p. 51301.

530 [17] Xu, W. X. and Chen, H. S. (2012) 'Microstructural characterization of fresh cement
531 paste via random packing of ellipsoidal cement particles', *Materials Characterization*, 66,
532 pp. 16–23.

533 [18] Yang, R. Y. *et al.* (2007) 'Simulation of the packing of cohesive particles', *Computer
534 Physics Communications*, 177(1–2 SPEC. ISS.), pp. 206–209.

535 [19] Corwin, E. I. *et al.* (2010) 'Model for random packing of polydisperse frictionless
536 spheres', *Soft Matter*, 6(13), p. 2949.

537 [20] T. C. Hales, 'The status of the Kepler conjecture', *Math. Intelligencer*, 16, no. 3, (1994),
538 47–58.

539 [21] Caulkin, R. *et al.* (2015) 'Impact of shape representation schemes used in discrete
540 element modelling of particle packing', *Computers and Chemical Engineering*. Pergamon,
541 76, pp. 160–169. doi: 10.1016/j.compchemeng.2015.02.015.

542 [22] Jia, X. *et al.* (2008) 'Property predictors for packed columns using Monte Carlo and
543 Discrete element digital packing algorithms.pdf', *Computer Modeling in Engineering and
544 Sciences*, 23(2), pp. 117–125.

545 [23] Dong, K. *et al.* (2006) 'Role of Interparticle Forces in the Formation of Random Loose
546 Packing', *Physical Review Letters*, 96(14), p. 145505.

547 [24] Powell, M. S. *et al.* (2011) 'DEM modelling of liner evolution and its influence on
548 grinding rate in ball mills', *Minerals Engineering*. Elsevier Ltd, 24(3–4), pp. 341–351.

549 [25] Thakur, S. C., Ooi, J. Y. and Ahmadian, H. (2016) 'Scaling of discrete element model
550 parameters for cohesionless and cohesive solid', *Powder Technology*. Elsevier B.V., 293,
551 pp. 130–137.

552 [26] Bentz, D. P. (1997) 'Three-Dimensional Computer Simulation of Portland Cement
553 Hydration and Microstructure Development', *Journal of the American Ceramic Society*,
554 pp. 3–21.

555 [27] Bentz, D. P. (2007) 'Cement hydration: building bridges and dams at the
556 microstructure level', *Materials and Structures*, 40(4), pp. 397–404.

557 [28] Ye, G., van Breugel, K. and a.L.a. Fraaij (2003) 'Three-dimensional microstructure
558 analysis of numerically simulated cementitious materials', *Cement and Concrete Research*,

- 559 33(2), pp. 215–222.
- 560 [29] Bishnoi, S., Joseph, S. and Kaur, A. (2018) ‘Microstructural modelling of the strength
561 of mortars containing fly ash using μic ’, *Construction and Building Materials*. Elsevier
562 Ltd, 163, pp. 912–920.
- 563 [30] Wong, H. H. C. and Kwan, a. K. H. (2008) ‘Packing density of cementitious materials:
564 measurement and modelling’, *Magazine of Concrete Research*, 60(3), pp. 165–175.
- 565 [31] Wong, H. H. C. and Kwan, A. K. H. (2007) ‘Packing density of cementitious materials:
566 part 1—measurement using a wet packing method’, *Materials and Structures*, 41(4), pp.
567 689–701.
- 568 [32] Wang, M. and Al-Tabbaa, A.(2014) ‘Computer simulation of the packing of digitized
569 reactive magnesia particles’. *Proceeding of the RILEM International Symposium on*
570 *Concrete Modelling 2014* (pp.36-43). Tsinghua University, Beijing.
- 571 [33] Wang, M. and Al-Tabbaa, A.(2015) ‘Computer simulations of the hydration-
572 carbonation processes in reactive magnesia cement systems.’ *5th International Conference*
573 *on Accelerated Carbonation for Environmental and Material Engineering*. Columbia
574 University, New York.
- 575 [34] Vu-Quoc, L., Zhang, X. and Lesburg, L. (2000) ‘A Normal Force-Displacement Model
576 for Contacting Spheres Accounting for Plastic Deformation: Force-Driven Formulation’,
577 *Journal of Applied Mechanics*, 67(2), p. 363.
- 578 [35] Vu-Quoc, L., Zhang, X. and Lesburg, L. (2001) ‘Normal and tangential force-
579 displacement relations for frictional elasto-plastic contact of spheres’, *International*
580 *journal of solids and structures*, 38, pp. 6455–6489.
- 581 [36] Zhang, M., Ye, G. and Van Breugel, K. (2012) ‘Modeling of ionic diffusivity in non-
582 saturated cement-based materials using lattice Boltzmann method’, *Cement and Concrete*
583 *Research*. Elsevier Ltd, 42(11), pp. 1524–1533.
- 584 [37] Gitman, I. M., Gitman, M. B. and Askes, H. (2006) ‘Quantification of stochastically
585 stable representative volumes for random heterogeneous materials’, *Archive of Applied*
586 *Mechanics*, 75, pp. 79–92. doi: 10.1007/s00419-005-0411-8.
- 587 [38] Zhang, M. (2013) Multiscale Lattice Boltzmann-Finite Element Modelling of Transport
588 Properties in Cement-based Materials. Figure 5.17. Technische University Delft.
- 589 [39] Farrell, G. R., Martini, K. M. and Menon, N. (2010) ‘Loose packings of frictional
590 spheres’, *Soft Matter*, 6(13), p. 2925. doi: 10.1039/c0sm00038h.
- 591 [40] Breugel, K. Van (1991) Simulation of hydration and formation of structure in
592 hardening cement-based materials. Phd thesis. Delft University Press.
- 593 [41] M. Wang (2017) Numerical modelling of the kinetics and microstructural development
594 of carbonated magnesia-based cements. Phd thesis. University of Cambridge.