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Why fumed and precipitated silica have different mechanical behavior: contribution of discrete element simulations

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Abstract

Precipitated silica (PS) could be an interesting alternative to fumed silica (FS) for the core of Vacuum Insulation Panels (VIP), in particular to reduce their cost and widen their use. However, compacted PS exhibits, for the same density, lower mechanical properties than FS. A better understanding of the mechanical behavior of these materials would help to design PS with optimized mechanical properties for VIP. In this work, complemented with experimental characterization, Discrete Element Method (DEM) simulations are used to investigate the compaction behavior and post-compaction tensile behavior of a set of numerically generated silica aggregates with varying neck size, surface energy and morphology (primary particle size, fractal dimension and gyration radius). During the compaction stage, neck size has the largest influence on the mechanical behavior, whereas during the tensile stage the influence of surface energy predominates. These results should be taken with caution as the task of modeling such a complex system necessarily involves

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bias due to simplifying assumptions. However, it is believed that the experimentally observed differences between PS and FS in compaction behavior and strength may lie not only in aggregates morphological differences, but also in different surface energies and neck sizes.

Keywords: Discrete Element Method, Vacuum Insulation Panels, powder compaction, nanostructured silica, fractal aggregates

1. Introduction

Energy consumption to heat or cool buildings is an important contributor to greenhouse gas emission and leads to other environmental damages. Efficient insulation can largely contribute to reduce the amount of energy required. While in many countries new constructions are low-energy ones thanks to regulations imposing efficient insulation, old buildings are often badly insulated and need to be retrofitted. Thermal retrofitting of housing is an important lever for the reduction of greenhouse gas emissions.

A wide range of retrofitting materials and techniques exists on the market, the most commons being mineral wool and expanded polystyrene foam. Their thermal conductivity varies between $\lambda = 30$ to 35 mW/(m.K) for a cost of 10 to 15€/m² (for a thermal resistance $R_T = 3$ m²K/W). For the same insulation performance, a larger thickness is required for materials with higher thermal conductivity. While having a thick layer is generally not too detrimental for insulation from the outside, insulation from the inside is often required (outside space shortage, conservation of the original historical facade) and thick insulation layer is in this case a barrier to thermal retrofitting.

Thin panel for insulation from the inside can only be achieved with super-

19 insulation materials ($\lambda < 25 \text{ mW}/(\text{m.K})$). The most mature super-insulation
20 technology, Vacuum Insulation Panels (VIP), consists of a highly porous
21 nanostructured silica core wrapped under vacuum (pressure $\leq 5 \text{ mbar}$) in-
22 side a sealed envelope [1, 2, 3]. VIP cost is high ($> 100\text{€}/\text{m}^2$ [4]), mainly
23 because of the nanostructured silica core, but thermal conductivities as low
24 as $5 \text{ mW}/(\text{m.K})$ are reached. Even if a cost analysis including the saved
25 floor area makes VIP an economically viable choice in high housing price
26 areas [4, 5], their high initial cost is detrimental for their wider use. The
27 nanostructured nature of the silica core is essential in VIP as it allows the
28 reduction of thermal conductivity by the Knudsen effect [6, 7], which leads
29 to significantly longer service life than non-nanostructured materials such as
30 glass fibers [4]. The use of precipitated silica (PS) in place of fumed (also
31 called pyrogenic) silica (FS) as nanostructured core material would signif-
32 icantly reduce the cost of VIP [2]. Precipitated silica is indeed a widely
33 available material, in particular because of its use as a filler in the tire in-
34 dustry [8]. Also, because of its production by a low temperature process, PS
35 may help to decrease the embodied energy of VIP [9]. Indeed, FS is obtained
36 from an energy consuming high temperature ($> 1200 \text{ °C}$) pyrolysis of silicon
37 tetrachloride. Primary particles of 7 to 50 nm in diameter form in flame
38 and coalesce in stable aggregates [10]. Polydispersity in primary particle size
39 arises from temperature gradients in flame and has been observed within a
40 single aggregate by Transmission Electron Microscopy (TEM) [11]. The ag-
41 gregates have a fractal morphology [11, 12] with a fractal dimension that may
42 vary depending on the flame temperature and other process parameters. Ag-
43 gregates also exhibit a polydispersity in size as shown by Small Angle X-ray

44 Scattering (SAXS) [11]. The silica surface is made of both silanol groups (Si-
45 OH) and siloxane bridges (Si-O-Si) leading to an intermediate hydrophilic
46 character [13]. PS are obtained via acid or base precipitation in an aque-
47 ous solution of silicates, resulting in a more hydrophilic surface with a high
48 density of silanol groups. The primary particle size is slightly larger than
49 for FS [14] and the fractal dimension is also generally larger than for FS
50 [8, 15]. Aggregates of FS and PS form at a larger scale agglomerates (few
51 hundred nanometers) and then powder grains at the macroscale (few mi-
52 crons). However, the mechanical properties of VIP core made of precipitated
53 silica appear very limited. It has been shown for example that to reach a
54 compressive strength of 100 kPa (considered as a minimum required for han-
55 dling and vacuuming), PS has to be compacted to at least 220 kg/m^3 versus
56 160 kg/m^3 for FS [2]. A recent study by instrumented indentation confirms
57 the lower mechanical properties of PS compacts with indentation modulus
58 half as low for PS as for FS for a similar apparent density [16]. Thermal
59 conductivity greatly depends on the core material density hence the need
60 of a larger compaction density, or the addition of reinforcing fibers, for PS
61 core degrades strongly thermal properties. In short, the thermal/mechanical
62 compromise is presently not optimal to allow the replacement of FS by PS.

63 Fumed and precipitated silica are nonetheless very similar materials and
64 the origin of the observed differences in mechanical behavior is not clear. It
65 has been suggested that the aspect ratio of the aggregates and their capac-
66 ity to entangle influence the mechanical behavior [16]. Differences in surface
67 chemistry and primary particle size also play a role [17]. Last, the influence of
68 ageing should also be considered. While the influence of ageing on the ther-

69 mal properties and the service life time has been studied [7, 13], the effect of
70 ageing on mechanical properties has been less investigated. A better under-
71 standing of the mechanical behavior in relation with aggregate morphology
72 and surface chemistry would be highly valuable to improve the mechanical
73 properties of precipitated silica. Conversely to FS and PS compacts, the
74 mechanical behavior of silica aerogels have been extensively studied through
75 both experiments and modeling [18, 19, 20, 21, 22, 23, 24]. In particular, the
76 necklace structure of primary particles have motivated mesoscale modeling
77 using the Discrete Element Method (DEM) [20] and coarse-grained molecular
78 dynamics [21]. Also, the significant impact of surface energy on mechanics
79 in these nanostructured highly porous materials has been demonstrated by
80 molecular dynamics [22].

81 In this work, a better understanding of the peculiar contrasted mechanical
82 behavior of FS and PS is sought based on macroscale experimental mechan-
83 ical characterization and mesoscale DEM modeling. In particular, the use of
84 DEM allows independent assessment of the influence of various morphological
85 or material parameters such as fractal dimension, primary particle size, ag-
86 gregate size, neck size and surface energy. The paper is organized as follows.
87 First, the mechanical behaviour of FS and PS is investigated experimen-
88 tally during oedometric compaction to confirm and measure the differences
89 between both silica. Experiments will also be used for comparison with mod-
90 eling. The modeling approach and the contact laws are detailed in section 3.
91 The generation of realistic numerical samples, based on recent morphological
92 characterization of the nanostructured silica [11, 25], is described in section
93 4. Results are presented in section 5 and discussed in section 6.

94 **2. Experimental characterization**

95 *2.1. Materials and methods*

96 A commercial FS (Konasil 200, OCI, Korea) and two commercial PS
97 (Tixosil 365 & Tixosil 43, Solvay, France) have been investigated. While the
98 FS silica has a hydrophobic character (1 to 2.5 OH/nm²[26, 27, 28]), the
99 PS silicas are highly hydrophilic (4 to 16 OH/nm² [27, 29]). The intrinsic
100 (skeletal) densities reported by the manufacturers are 2200 kg/m³ for the FS
101 and 2100 kg/m³ for the PS. Oedometric compression tests were performed
102 with a 20 mm diameter cylindrical die using a sapphire pellet in contact
103 with the powder to ensure a flat surface. The same initial mass of powder
104 was used for the three silicas. A conventional testing machine (Zwick-Roell,
105 Germany) was used and the displacement of the punch was recorded with
106 a LVDT sensor. The crosshead speed was 10 mm/min during loading and
107 5 mm/min during unloading. The same maximum force (400 N, leading to
108 a maximum pressure of 1.27 MPa) was used for all powders. This value was
109 chosen to obtain final pellets with a density close to what is required for
110 the final application (i.e. 200 kg/m³ for FS [3]). It must also be mentioned
111 that the silica powder compaction behavior is highly sensitive to humidity
112 and temperature during the test. The conditions of the tests were similar
113 in terms of relative humidity (35% to 45%) and temperature (20°C to 24°C)
114 between the three silicas.

115 *2.2. Results*

116 The initial relative densities (volume fractions of solid) after pouring the
117 powder in the die were ca. 3% for Konasil 200, and 7.5% for T365 and T43

118 silica powders. This simple observation already demonstrates significant dif-
119 ferences between FS and PS, the former having a significantly lower initial
120 relative density. The compaction curves (average over several tests) are dis-
121 played in Fig. 1. A significant difference in compaction behavior of FS and
122 PS is observed, with the FS being significantly harder to compact. The final
123 densities reached after a 1.27 MPa compaction are ca. 290 kg/m^3 ($\approx 13\%$) for
124 PS compacts versus ca. 210 kg/m^3 ($\approx 10\%$) for FS compacts. The oedomet-
125 ric elastic modulus has also been assessed during the first 10% of unloading:
126 $22.4 \pm 0.5 \text{ MPa}$, $17.5 \pm 1.0 \text{ MPa}$ and $18.7 \pm 1.0 \text{ MPa}$ for Konasil 200,
127 Tixosil 43 and Tixosil 365 respectively. These values are not directly com-
128 parable as the difference in density at 1.27 MPa is large between FS and
129 PS. Still, it is remarkable that even at a significantly lower density the FS
130 compact is stiffer than the PS one. Directly comparable data was obtained
131 from iso-density compaction of the three powders to ca. 10%. Compaction
132 pressure and oedometric modulus at 10% density are reported in Table 1
133 and confirm that FS compacts are significantly stiffer than PS ones. These
134 results are consistent with a recent instrumented indentation study showing
135 that, for a similar density of compacts ca. 10%, FS is twice stiffer than PS
136 [16]. The measurement of tensile strength of the compacted silica pellets is a
137 challenging task. Still, preliminary biaxial flexural test have shown that for
138 a density of 200 kg/m^3 PS exhibits extremely low strength ($< 0.1 \text{ MPa}$), 3
139 to 5 times lower than FS (ca. 0.3 MPa) at the same density. These results
140 confirm the contrasting behavior between the two types of nanostructured
141 silica.

142

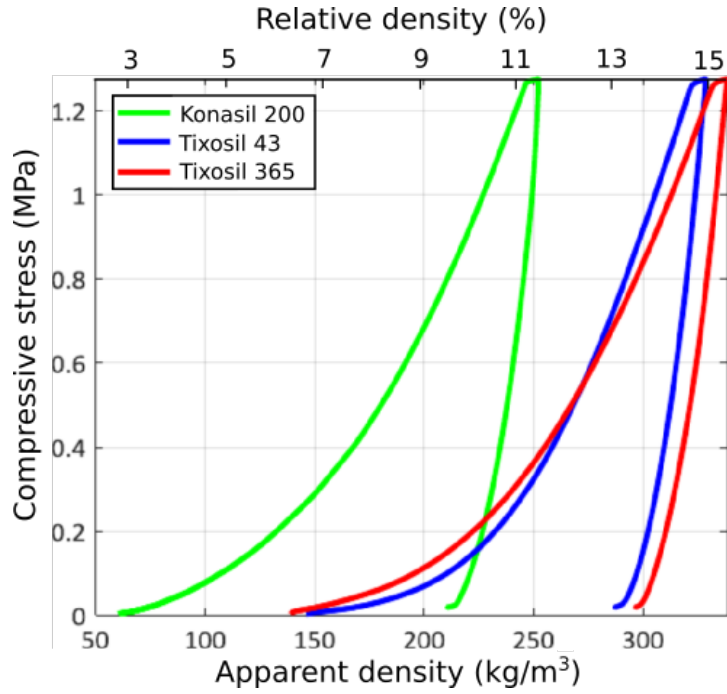


Figure 1: Compaction behavior of fumed (Konasil 200) and precipitated (Tixosil 365 & Tixosil 43) silica. The relative density has been computed based on an intrinsic density of 2200 kg/m³

	Compaction pressure (MPa)	Apparent density (kg/m ³)	Relative density (%)	Oedometric modulus (MPa)
Konasil 200	0.64	218 ± 2	9.9 ± 0.1	10.4 ± 0.2
Tixosil 43	0.16	198 ± 2	9.5 ± 0.1	2.9 ± 0.2
Tixosil 365	0.16	200 ± 2	9.5 ± 0.1	3.7 ± 0.2

Table 1: Comparison of oedometric modulus of compacts at iso-density

143 **3. Model description**

144 *3.1. Discrete Element Method framework*

145 The classical DEM approach [30] is used with Hertzian and bonded con-
146 tacts [31]. In DEM the dynamic motion of discrete entities (generally spher-
147 ical particles) is computed by an explicit time integration of the second law
148 of Newton. Each particle transmit forces to its neighbors through their con-
149 tacts. The open source version of LIGGGHTS [®][32] was used with our
150 own implementation of bonded contacts and numerical damping. For post-
151 processing and visualization OVITO [33] was used. In short, at each time
152 step, the DEM algorithm is as follows:

- 153 • for each particle a neighbor (or contact) list is established;
- 154 • for each contact, forces (and resisting moments) are computed accord-
155 ing to contact laws;
- 156 • forces (and moments) are summed for each particle;
- 157 • Newton’s second law and time integration (Velocity-Verlet) are used to
158 get the new particle position.

The mechanical loading is performed by changing the size of the simulation box in one or more directions according to a prescribed strain rate. All particles are moved according to the corresponding affine displacement at the beginning of the timestep. In the present work a quasi-static approach is sought by using low enough strain rates. The quasi-static strain rate is reached once further decrease in strain rate does not affect significantly the results. In order to dissipate the kinetic energy in the system and damp

oscillations, viscous forces and moments are added. They oppose the contact normal displacements and rotations. Following the work of Agnolin and Roux [34], the damping coefficient was chosen as a fraction $\beta = 0.1$ of the critical damping coefficient. A non-viscous damping force, that opposes the particle velocity and proportional (with a coefficient $\alpha = 0.7$) to the total force acting on the particle, is also applied to each particle [30]. The macroscopic stress tensor on the simulation box of volume V is computed as follows [35]:

$$\sigma_{ij} = \frac{1}{V} \sum_{contacts} F_i l_j \quad (1)$$

159 where F_i is the i^{th} component of the contact force vector, and l_j is the j^{th}
 160 component of the branch vector connecting the centers of the two particles
 161 in contact. The reader will find more details on the DEM method in the
 162 following works: [30, 31, 32, 34, 36, 37]. Here we will only focus on the
 163 description of the contact laws.

164 3.2. Contact laws

165 Two types of contacts are distinguished: bonded contacts that can trans-
 166 mit normal and tangential forces and resisting moments [31], and Hertzian
 167 contacts with Derjaguin-Muller-Toporov (DMT) adhesion [38]. Initially, all
 168 intra-aggregates contacts are bonded. New contacts appearing during the
 169 simulation are then considered as Hertzian. The latter are mainly inter-
 170 aggregate contacts but Hertzian contacts may also appear within an aggre-
 171 gate during its compaction if initially close (but not bonded) particles of an
 172 aggregate contact each other.

173 The contact law proposed by Jefferson et al. [39] and Jauffres et al. [40],
 174 to model the elastic behavior of a solid neck between two sintered particles,

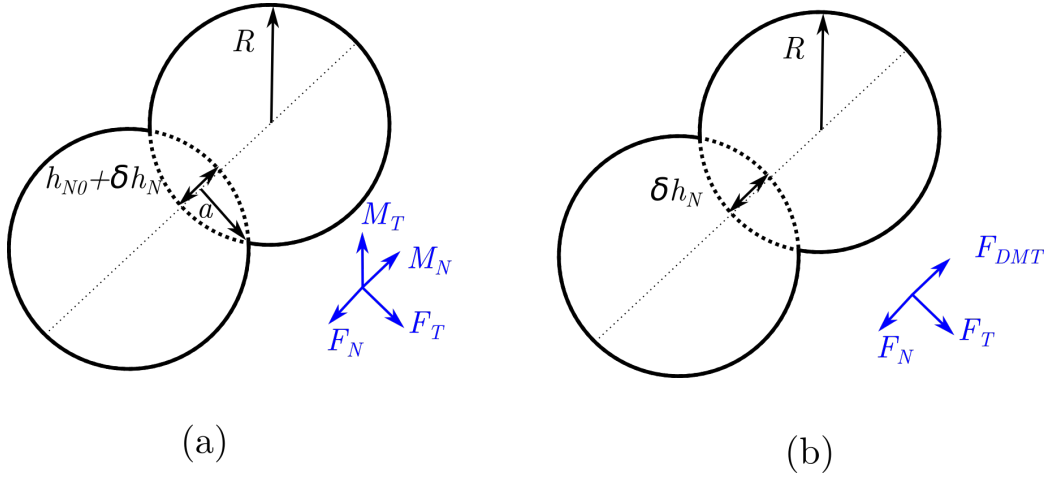


Figure 2: Contact laws. (a) bonded contact. (b) Hertzian contact

175 is used for bonded contacts. This model has been successfully used for silica
 176 aerogels by Liu et al. [20]. It is given here for a monomodal set of particles
 177 of radius R but has been also developed for particles with different radii [40].

Normal force F_N , tangential force F_T , resisting bending M_T and twisting moments M_N (Fig. 2) are given as a function of the contact size a and the elastic properties of the particles, i.e., the Young's Modulus E and the Poisson's ratio ν :

$$F_N = k_N \delta h_N, \quad k_N = \frac{E}{1 - \nu^2} f_N a \quad (2)$$

$$F_T = k_T \delta h_T, \quad k_T = \frac{2E}{(2 - \nu)(1 + \nu)} f_T a \quad (3)$$

$$M_N = k_{MN} \alpha_N, \quad k_{MN} = \frac{a^2 k_T}{2} \quad (4)$$

$$M_T = k_{MT} \alpha_T, \quad k_{MT} = \frac{a^2 k_N}{4} \quad (5)$$

where k_N , k_T , k_{MN} and k_{MT} are stiffnesses; δh_N and δh_T are the normal relative displacement and tangent accumulated displacement; α_N and α_T are

the accumulated relative rotations. The coefficients f_N and f_T have been obtained from finite element simulations at the scale of one sintered neck by McMeeking et al. [41]:

$$f_N = \frac{1 + a^* \left(\frac{\pi}{6} (1 - \nu^2) (1 + 2a^*) - a^* \right)}{\sqrt{1 - (a^*)^2 - \frac{c_0 + 4c_1}{\pi} (a^* + (a^*)^2 \left(\frac{\pi}{6} (1 - \nu^2) (1 + 2a^*) - a^* \right))}} \quad (6)$$

$$f_T = \frac{1 + (a^*)^2 \left(\frac{\pi}{6} (1 - \nu^2) (1 + 2a^*) - a^* \right)}{\sqrt{1 - (a^*)^2}} \quad (7)$$

with

$$a^* = \frac{a}{R} \quad (8)$$

$$c_0 = 0.5650 + 0.04864\nu^2 + 1.036\nu^4 \quad (9)$$

$$c_1 = 0.1396 - 0.03061\nu + 0.3395\nu^2 \quad (10)$$

178 Typical elastic properties of dense amorphous silica were used: $E = 70$ GPa
 179 and $\nu = 0.2$. Equations (4) and (5) are derived from beam theory [31]. Prac-
 180 tically, the linear stiffness coefficients k_N , k_T , k_{MN} and k_{MT} are computed
 181 according to a given contact size a in a pre-processing step. The same con-
 182 tact size a is used for all bonded contacts. For the sake of simplicity, and
 183 also because aggregates are generally considered as unbreakables, no explicit
 184 fracture criteria is used. Still, if the normal force is such that the distance
 185 between two particles become larger than twice their radius the bond will
 186 disappear leading to a geometric breakage of the bond. To limit this artifi-
 187 cial behavior an initial overlap h_{N0} (Fig. 2) is used between the particles as
 188 detailed in section 4.1.1.

Newly formed contacts during simulation are of Hertzian type with Coulomb friction and DMT adhesion [38]:

$$F_N = \frac{\sqrt{2R}}{3} \frac{E}{1-\nu^2} (\delta h_N)^{1.5} \quad (11)$$

$$F_T = \min\left(\frac{E\sqrt{2R}}{(2-\nu)(1+\nu)} \sqrt{\delta h_N} \delta h_T, \mu F_N\right) \quad (12)$$

$$F_{DMT} = -2\gamma_S \pi R \quad (13)$$

189 with μ the friction coefficient, γ_S the surface energy (J/m²). F_{DMT} is an
 190 attractive force normal to the contact that adds up to the repulsive Hertzian
 191 force F_N . A simple dimensional analysis on Eq. (1) shows that the only force
 192 that introduces a size effect is the DMT adhesion (Eq. (13)) as it introduces
 193 a term with an inverse size dependence ($1/R$) in the macroscopic stress σ_{ij} . It
 194 is also worth noting that while during synthesis or ageing surface energy and
 195 particle size are correlated, these two parameters can be set independently
 196 in the DEM simulations.

197 4. Simulation methods

198 4.1. Numerical preparation of initial silica powder bed

199 4.1.1. Initial gas with controlled aggregate morphology

200 The porous Eden growth model [42] was used to generate aggregates,
 201 i.e. random assemblies of spherical primary particles in contact. The porous
 202 Eden model allows the generation of aggregates with a controlled morphol-
 203 ogy through two parameters: the number of particles N and the inactivation
 204 probability P . The random inactivation of particles with the probability

205 P allows the local blocking of the growth to create porous structures. Ag-
 206 gregates are successively generated inside a periodic (in all three directions)
 207 simulation box to form an initial gas of aggregates. When attempting to
 208 place a new particle, the non-overlapping condition applies within the grow-
 209 ing aggregate and with the other aggregates already in the simulation box.
 210 Experimentally observed initial density (3% for FS and 7.5% for PS) are
 211 sufficiently low to ensure that no significant bias exists in the generation of
 212 aggregates due to this globally applied non-overlapping condition. In ad-
 213 dition, the particle radii are multiplied by a factor ξ to create overlapping
 214 contacts (required to limit the geometric breakages) which introduces a third
 215 generation parameter. It is important to underline the model nature of the
 216 gas of aggregates numerically generated: perfect spheres are used, large scale
 217 organization (agglomerate, powder particle) is not considered and no dis-
 218 persion is used on the particle radius. **The fractal dimension and gyration**
 219 **radius are not generation parameters: they are computed after the aggregate**
 220 **generation as described in [42].** Briefly, the gyration radius is computed us-
 221 **ing the classical definition $R_g = \frac{1}{N} \sqrt{\sum_{i,j>i}^N (r_{ij})^2}$, where r_{ij} is the distance**
 222 **between particles i and j , and the fractal dimension is obtained through the**
 223 **slope of the structure factor versus q (modulus of the scattering vector) plot.**
 224 **Consequently there is a small dispersion on these two aggregate character-**
 225 **istics, inherent to the random nature of the generation procedure.** As the
 226 two selected PS (Tixosil 43 & 365) have a quite similar mechanical response
 227 under oedometric compaction, only Konasil 200 and Tixosil 365 silica were
 228 studied numerically. Their fractal dimension d_f , aggregate gyration radius
 229 R_g and primary particle radius R were obtained from SAXS [11, 25]. Their

	SAXS [11, 25]			Numerical					
	d_f	R_g	R	d_f	R_g	R	N	P	ξ
Konasil 200 (FS)	2.0	64	7	2.0	64	8.3	133	61 %	1.3
Tixosil 365 (PS)	> 2.4	35	13	2.4	38	12	35	0 %	1.3

Table 2: Morphological properties (fractal dimension d_f and radius of gyration R_g) and generation parameters (particle radius R , number of particles per aggregate N , inactivation probability P and radius increase factor ξ) of numerically generated aggregates. The radius R reported is after enlargement by the factor ξ . R_g and R are in nanometers. Morphological properties from SAXS experiment used as input to the optimization algorithm are also reported. While a meticulous extraction of d_f from aggregates dispersed in a very low volume fraction suspension was possible for FS [11], the d_f value used for PS may be overestimated due to aggregate interaction [25].

230 numerical counterparts were generated using an optimization algorithm as
231 described in [42]. Morphological properties used as inputs and the numerical
232 parameters resulting from the optimization are reported in Table 2. Images
233 of typical aggregates are provided in Fig. 3 (see also supplementary videos).
234 In total, 30,000 particles, leading to a gas of at least 200 aggregates and a
235 simulation box of $\approx 1 \mu\text{m}^3$ (vs. a few mm^3 for the experiment), were used to
236 ensure a good reproducibility during the subsequent mechanical simulations.

237 4.1.2. Sample preparation by compression-tension cycling

238 Performing directly a compression of the low density gas of aggregate to
239 simulate the experimental oedometric compaction is not realistic. Indeed,
240 starting with an initial gas, by definition with no inter-aggregates contacts,
241 do not correspond to the experimental initial aggregate packing for which
242 silica aggregates exhibit contacts. We noted several anomalies during the

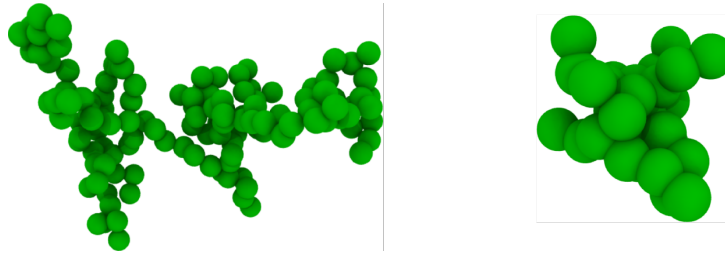


Figure 3: Typical aggregates numerically generated based on SAXS morphological characterization. Left: Konasil 200 (FS), primary particle radius $R = 8.3$ nm. Right: Tixosil 365 (PS), primary particle radius $R = 12$ nm. Note that the enlargement of the particles by the factor ξ has created overlaps

243 compaction of a gas of aggregates that might be related to this unrealistic
 244 initial state:

- 245 • large amount of geometric bond breakages (5%),
- 246 • still increasing number of Hertzian contacts during tensile loading,
- 247 • underestimation of the stresses (ca. 0.3 MPa vs 1.2 MPa in experi-
 248 ment).

249 A procedure to create more realistic initial packings has been developed based
 250 on compression-tension cycling at low density. Packing by gravitation might
 251 be a possible alternative but with the drawback of breaking the periodic
 252 boundary condition in at least one direction. From a given initial gas, 8
 253 uniaxial compression-tension cycles of amplitude 0.025 (i.e. from 3% to 5.5%
 254 for FS) are performed to create Hertzian inter-aggregate contacts. Creation
 255 of new contacts due to adhesive forces and rearrangement occurs during the
 256 cycling, leading to a more realistic initial state. The number of cycle has been
 257 limited to 8 as more cycles lead to a large amount of unwanted geometrical

258 bond breakages. 8 cycles also corresponds to the threshold from which the
259 number of Hertzian contacts start decreasing during the tensile loading stage
260 (Fig. 4). Fig. 5 shows that after cycling, although a fully continuous network
261 is not achieved, large structures of several aggregates linked by adhesion are
262 formed. To maximize the rearrangements and creation of Hertzian contacts,
263 the friction coefficient has been set to 0 and surface energy to 1.2 J/m^2 for
264 this preparation stage. The other contact law parameters are the same than
265 in the subsequent simulation of compaction and tensile tests. It should be
266 noted that to keep reasonable CPU time, the strain rate has been increased
267 by a factor 10 above the quasi-static strain rate for the preparation stage.
268 This is not problematic considering the fact that the preparation procedure
269 is purely numerical and does not seek to reproduce the material behavior.

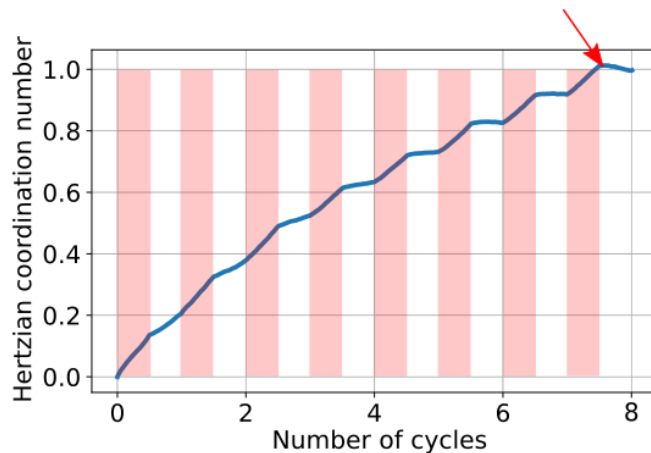


Figure 4: Evolution of the Hertzian coordination number (i.e. the average number of Hertzian contacts per particle) with compression-tension cycling during sample preparation. The compression stages are indicated in red. The Hertzian coordination increases both during compression and tension, until the last cycle where it decreases during tension (red arrow).

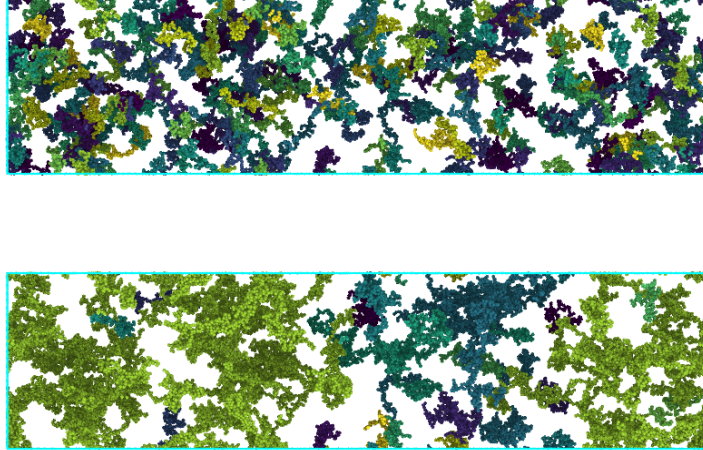


Figure 5: Influence of cycling. (top) No cycling, a different color is assigned to each aggregate indicating that each aggregate is isolated. (bottom) After 8 cycles, colors show the class of equivalence of contacting aggregates indicating a large number of inter-aggregate contacts. The relative density is 3% for both and only a slice of the simulation box is shown.

270 *4.2. Compaction of a silica powder bed to VIP core density followed by tensile*
 271 *test*

272 First, a uniaxial compaction is performed up to a given nominal density
 273 and then a uniaxial tensile loading is imposed in the same direction. Five
 274 simulations on different initial gas of aggregates were run for each set of pa-
 275 rameters to provide an error bar. A typical stress-density curve is reported
 276 in Fig. 6. For the sake of clarity the compressive and tensile parts will be
 277 reported in two separate graphs. **The state of the initial assembly of aggre-**
 278 **gates (in particular the number of Hertzian contacts) affects the result but**
 279 **primarily the beginning of the compaction and only moderately the maxi-**

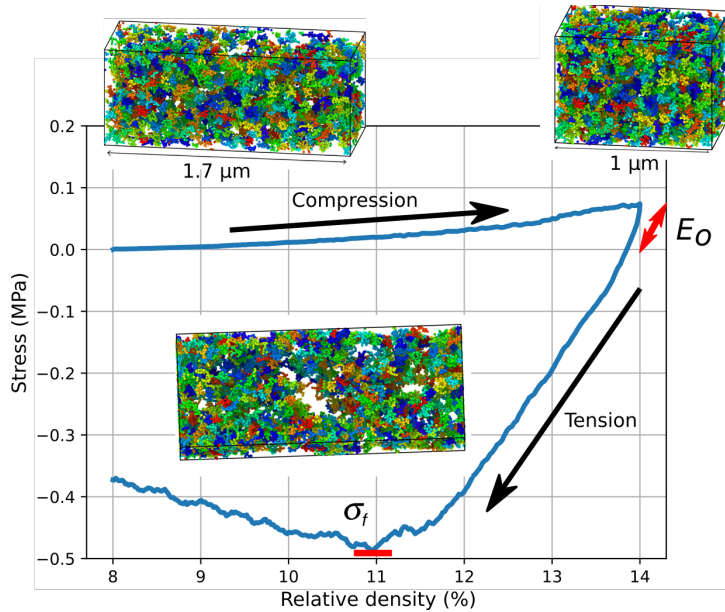


Figure 6: Typical simulation: compaction of a silica powder bed to VIP core density followed by a tensile test. Odoemetric modulus E_0 and strength σ_f are extracted from the simulation to characterize the mechanical behavior of the silica core produced by the compaction stage.

280 mum stress and tension stage. In the extreme case of no hertzian contacts
 281 (no cycling during the preparation stage) the maximum compressive stress
 282 is ca. 25 % lower than for 8 cycles during the preparation stage (1 Hertzian
 283 contact per particle). The oedometric modulus E_o is computed during the
 284 first 0.5% of unloading. During the tensile loading, a maximum tensile stress
 285 σ_f is reached and will be defined as the material strength. The fracture is
 286 progressive and does not exhibit any sudden drop in stress. We identified
 287 two main reasons for this non-brittle behavior. First and as observed in MD
 288 [24, 22] or DEM simulations [20], surface energy plays a predominant role in
 289 the mechanics of these materials with large surface to volume ratio and nano-

metric particles. The adhesive forces (modelled here with the DMT model, Eq. (13)) that appear when aggregates resume contact do not allow for a brittle failure. Second, when dealing with small scale simulation, no large defect of micron size that may lead to a catastrophic failure at the macro scale is included in the modeling. The strength values may thus be overestimated for this reason but are still relevant for relative comparison of various silica types. It is also worth noting that in this system, the adhesive DMT forces have a significant influence on the compressive behavior. For example, even during compaction, the Hertzian contacts maintain an attractive character ($F_N + F_{DMT} < 0$) and thus contribute negatively to the macroscopic compressive stress.

5. Results

5.1. Influence of contact law parameters

The stiffness of the bonded contacts between two particles in the aggregates depends, apart from the Young's modulus of the particle, on the contact size a (Eq. (11)), a parameter difficult to assess, even with TEM images [14]. Liu et al. have assessed the ratio $\frac{a}{R}$ in a silica aerogel by considering, during gelation, neck formation by Johnson-Kendall-Roberts (JKR) adhesion [43]. This approach would also be applicable for PS and interestingly leads to $\frac{a}{R} = 0.26$ for a primary particle of radius 13 nm (value reported for PS, Table 2). It is also worth noting that $\frac{a}{R}$ is expected to increase with ageing of the material [7, 13]. In this work we used $\frac{a}{R} = 0.3$ as a rough estimate and performed a parametric study around this value for FS aggregates (morphological parameters in Table 2 with surface energy $\gamma_s = 1.2 \text{ J/m}^2$

314 and friction coefficient $\mu = 0.3$). The compaction stress-density curves and
 315 tensile stress-strain curves are reported in Fig. 7. As expected increasing $\frac{a}{R}$
 316 leads to a stiffer aggregate packing due to an increase of the stiffness of the
 317 aggregates. The behavior is highly non-linear with a relatively low increase
 318 of the maximum compressive stress between $\frac{a}{R} = 0.15$ and $\frac{a}{R} = 0.3$ and a
 319 much larger one between $\frac{a}{R} = 0.3$ and $\frac{a}{R} = 0.6$. This comment also holds for
 320 the oedometric modulus that takes the values $E_0 = 5.8, 8.8$ and 21.0 MPa
 321 for $\frac{a}{R} = 0.15, 0.3$ and 0.6 , respectively. The tensile strength also increases
 322 with the contact size as the aggregates becomes stiffer, even if the number of
 323 newly formed Hertzian contacts is lower (rearrangement of stiff aggregates is
 324 more difficult).

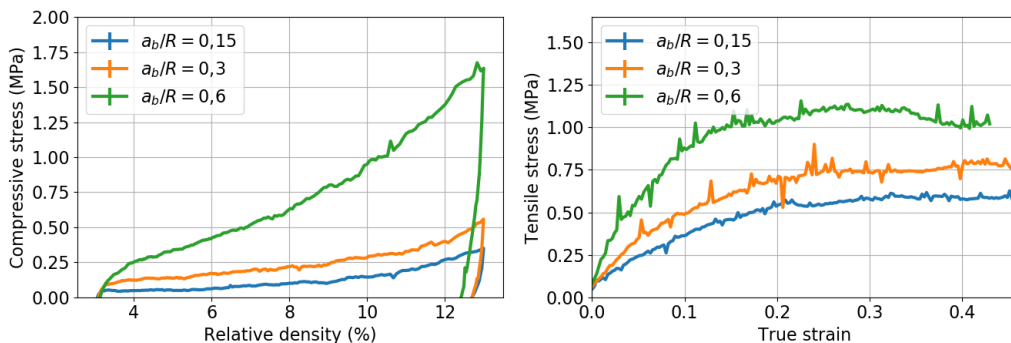


Figure 7: Influence of contact size on the compaction behavior (left) and the tensile behavior (right). FS aggregates with $\gamma_s = 1.2 \text{ J/m}^2$ and $\mu = 0.3$. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 10\%$.

325 Moreover, the behavior of Hertzian contacts is largely dependant on the
 326 value of surface energy γ_s . 1 J/m^2 is generally considered as a good esti-
 327 mate for oxides [44]. A surface energy of approximately 1 J/m^2 has been
 328 calculated by MD simulations for pure Silica [45]. However, in the case of

329 silica, the chemical nature of the surface (density of silanol groups and physi-
 330 cally adsorbed water), that depends on the processing route (pyrogenic or in
 331 aqueous solution), the degree of ageing and the relative humidity [7, 13, 46],
 332 plays an important role. Indeed, chemically or physically adsorbed water
 333 can screen Van der Waals and electrostatics interactions in favor of capillary
 334 forces leading to a lower surface energy [47]. In consequence silica surface
 335 energy varies from 5 J/m² in ultradry conditions [48] to 0.1 J/m² for pure
 336 capillary interaction [47]. To assess the influence of surface energy, a para-
 337 metric study on γ_s was performed for FS aggregates with $\frac{a}{R} = 0.3$ and
 338 $\mu = 0.3$. The results in Fig. 8 show that γ_s has a relatively low impact
 339 on the compaction behavior but a significant influence on the strength and
 340 oedometric modulus ($E_0 = 2.5, 6.7$ and 8.8 MPa for $\gamma_s = 0, 0.4$ and
 341 1.2 J/m², respectively). Values larger than 1.2 J/m² are not reported as the
 342 amount of unrealistic geometrical bond breakages become non-negligible and
 343 may impact the macroscopic result.

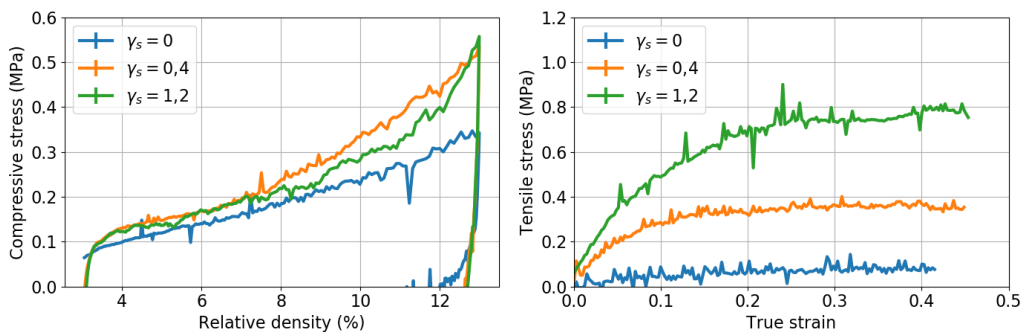


Figure 8: Influence of surface energy on the compaction behavior (left) and the tensile behavior (right). FS aggregates with $\frac{a}{R} = 0.3$ and $\mu = 0.3$. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 10\%$.

344 No statistically significant influence of the friction coefficient varying from
 345 $\mu = 0.1$ to 0.9 has been noted, but simulations with $\mu = 0$ exhibit sig-
 346 nificantly lower compaction stresses. The negligible effect of μ might sounds
 347 surprising but is a consequence of very adhesive hertzian contacts. Indeed,
 348 the indentation is very large ($\delta h_N/R \approx 0.1$) because of the adhesive forces
 349 and consequently F_T is, even with $\mu = 0.1$, very rarely capped by μF_N
 350 ($F_N \propto \delta h_N^{1.5}$ and $F_T \propto \delta h_N^{0.5}$ see equations 11 and 12), which explains
 351 the very limited influence of μ .

352 5.2. Influence of aggregate morphology

353 The influence of the morphological parameters of aggregates has been
 354 studied with the following values for the contact law parameters: $\gamma_s = 1.2 \text{ J/m}^2$,
 355 $\frac{a}{R} = 0.3$ and $\mu = 0.3$. The parametric study has been performed around
 356 the values of FS aggregates (Table 2). In such a nano-sized system, adhesive
 357 interaction are of utmost importance and are directly linked to the size of
 358 particles (equation (13)). Keeping other parameters identical and enlarging
 359 only the primary particle radius up to a value typical of PS has nearly no in-
 360 fluence on the compaction behavior but decreases the strength (Fig. 9). This
 361 is consistent with the parametric study on γ_s : varying the primary particle
 362 or the surface energy affects similarly the DMT adhesion forces (Eq. (13)).

363 FS aggregates are generally more branched and elongated than PS, which
 364 is quantified by a smaller fractal dimension d_f [8, 11, 42] (Fig. 10). When the
 365 initial density (set by the compression-tension preparation stage) and the gy-
 366 ration radius are kept constant, the fractal dimension of the aggregates shows
 367 only a limited effect on the compaction behavior, oedometric modulus and
 368 strength for d_f varying from 1.7 to 2.8 (Fig. 11). It is worth noting that the

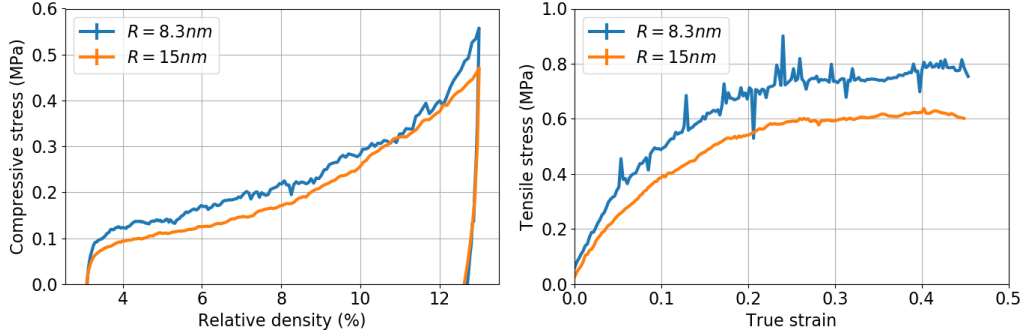


Figure 9: Influence of primary particle radius on the compaction behavior (left) and the tensile behavior (right). $\gamma_s = 1.2 \text{ J/m}^2$, $\frac{\sigma}{R} = 0.3$, $\mu = 0.3$. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 10\%$.

369 number of Hertzian contacts formed during the compression-tension prepara-
 370 tion stage is larger with low d_f as more elongated and branched aggregates
 371 tend to interpenetrate each other more than rounded aggregates. During the
 372 compaction stage, it is also noted that samples with low d_f form more new
 373 Hertzians contacts than samples with high d_f .

374 Lastly, the influence of the gyration radius is investigated. Fig. 12 dis-
 375 plays typical aggregates with increasing radius of gyration used in the simu-
 376 lation. d_f is kept constant but because of the increasing number of particles
 377 the aggregates are more elongated with large R_g for the porous Eden growth
 378 model [42]. It is observed in Fig. 13 that the compaction is more difficult for
 379 large R_g values. The oedometric modulus follows the same trend than the
 380 compaction stress and increases with R_g ($E_0 = 6.3, 8.8$ and 9.1 MPa for
 381 $R_g = 30, 64$ and 128 nm, respectively). Strength is nearly unaffected by
 382 R_g (Fig. 13).

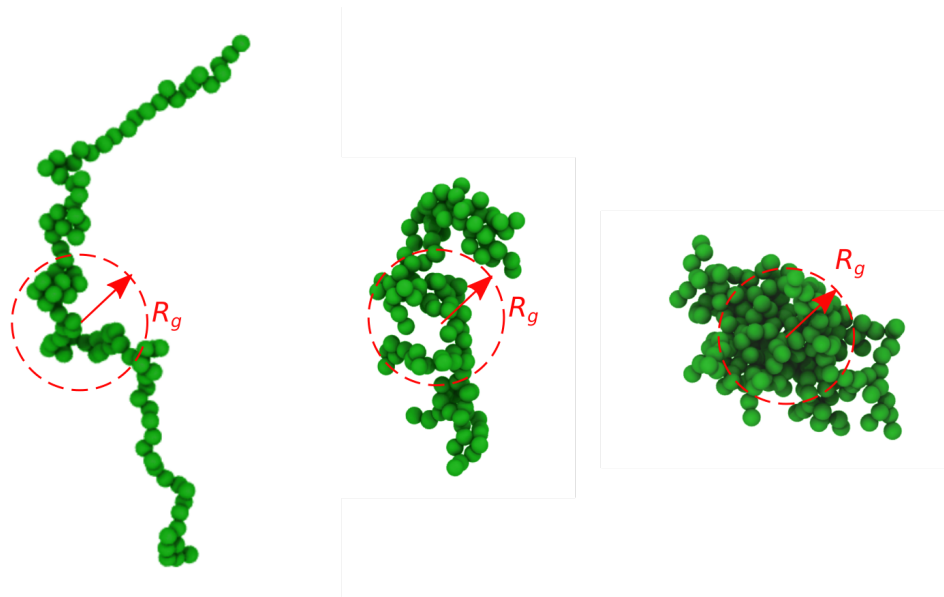


Figure 10: Aggregates with increasing fractal dimension d_f at constant radius of gyration $R_g = 64 \text{ nm}$. From left to right $d_f = 1.7$, $d_f = 2.0$ and $d_f = 2.8$. Aggregates with larger d_f have a larger number of primary particles to keep R_g constant [42].

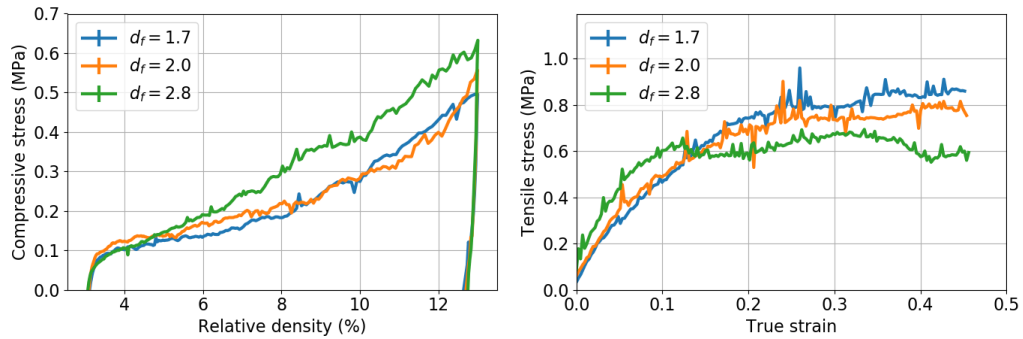


Figure 11: Influence of aggregate fractal dimension on the compaction behavior (left) and the tensile behavior (right). $\gamma_s = 1.2 \text{ J/m}^2$, $\frac{a}{R} = 0.3$, $\mu = 0.3$. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 15\%$.

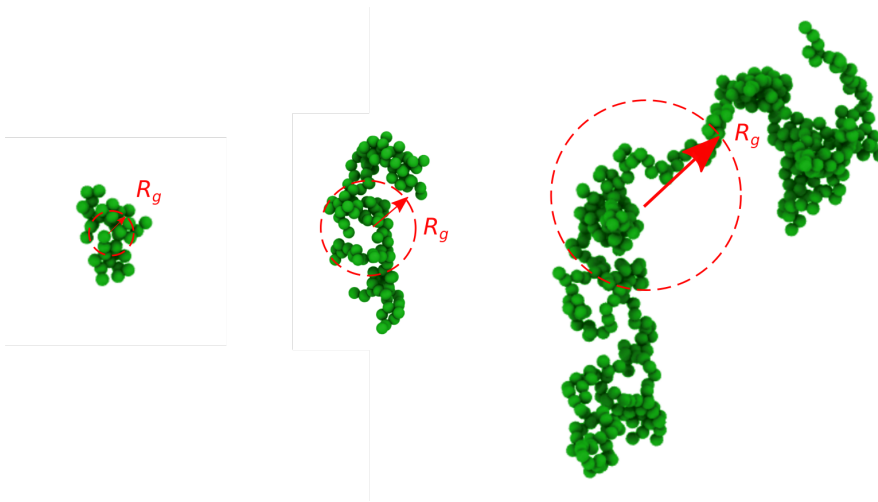


Figure 12: Aggregates with increasing radius of gyration R_g at constant $d_f = 2.0$. From left to right $R_g = 30$ nm, $R_g = 64$ nm and $R_g = 128$ nm. Aggregates with larger R_g are more elongated [42].

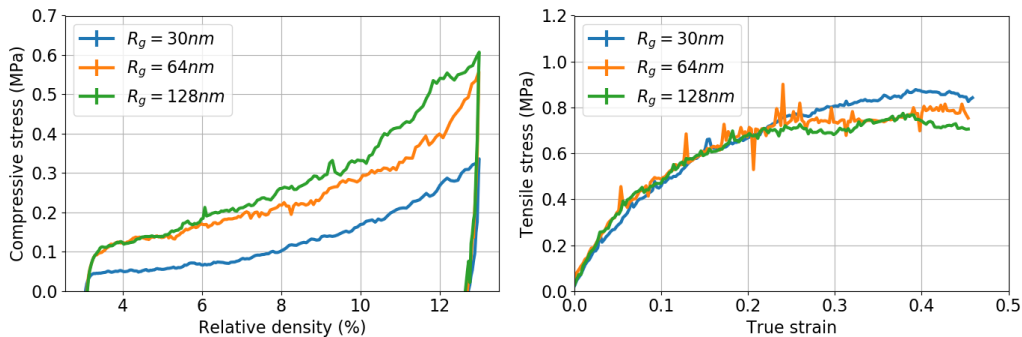


Figure 13: Influence of aggregate radius of gyration on the compaction behavior (left) and the tensile behavior (right). $\gamma_s = 1.2$ J/m², $\frac{\sigma}{R} = 0.3$, $\mu = 0.3$. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 21\%$, 5% and 13% for $R_g = 30$, 64 and 128 nm respectively.

383 5.3. Comparison with experiment

384 For the sake of comparison with the experimental study reported in sec-
 385 tion 2, compaction and tensile behavior of numerically generated FS and PS

386 were simulated. In the absence of reliable assessments of the surface energy
387 and the neck size, the same values were used for FS and PS ($\gamma_s = 1.2 \text{ J/m}^2$
388 and $\frac{a}{R} = 0.3$). The experimentally observed initial relative densities were
389 targeted during the initial sample preparation by compression-tension cy-
390 cling. To follow the experiment, the final density of PS was set to a larger
391 value than the FS one. Compaction curves and tensile stress-strain curves are
392 reported in Fig. 14. Qualitatively the initial part of the compaction curves is
393 very steep, which is not observed experimentally. However, we believe this is
394 an artifact due to the non quasi-staticity of the compression-tension cycling,
395 that may lead to a system slightly out of equilibrium at the beginning of the
396 compaction. Quantitatively, the simulation compressive stresses are lower
397 than the experimentally observed ones but the order of magnitude is correct.
398 This is satisfactory considering the fact that no parameter has been fitted
399 and that neck size, which has a tremendous effect on the stress (Fig. 7),
400 has only been very roughly estimated and fixed constant for all the particles.
401 **The fact that the simulations underestimate the compressive stresses sug-**
402 **gests however that the actual neck size maybe larger than the one estimated**
403 **from JKR model.** The simulation odeometric moduli (8.8 MPa for FS at 13
404 % and 14.5 MPa for PS at 17 %) are lower than the experimentally measured
405 values at lower densities (22.4 MPa for FS at 11 % and 18.7 MPa for PS at
406 15 %) but the correct order of magnitude is also obtained. For the fracture
407 behavior, only a rough experimental estimation of the strength is known,
408 and again the order of magnitude is correct, at least for FS (ca. 0.3 MPa at
409 a density of 9 % experimentally versus 0.75 MPa but at a density of 13 %
410 numerically). As for PS, the difference in density (9 % experimentally versus

411 17 % numerically) makes the comparison difficult. The fact that PS has a
 412 larger oedometric modulus and strength than FS is difficult to interpret due
 413 also to the large difference in density of the two compacts.

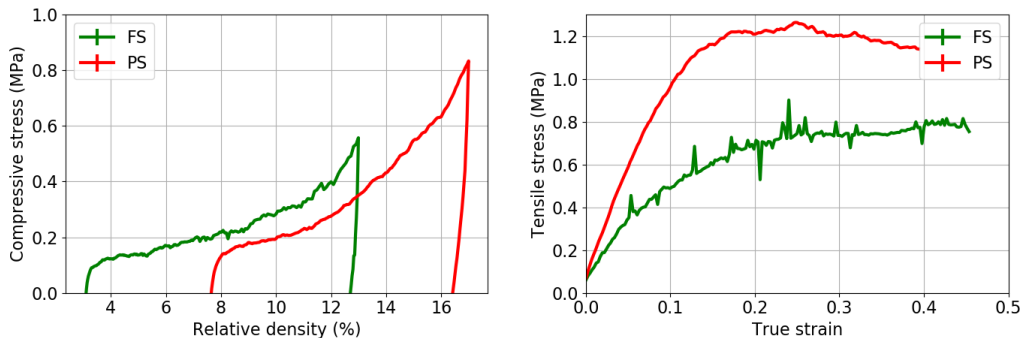


Figure 14: Comparison of the compaction behavior (left) and the tensile behavior (right) of fumed (K200) and precipitated (T365) silica powders. Averaging is done over 5 timesteps and 5 simulations, relative standard deviation $\leq 10\%$.

414 5.4. Scaling law for oedometric modulus

415 In order to compare the two silica over similar density range, unloading
 416 steps during the compaction were used to evaluate the oedometric modulus
 417 of the packing versus its density. The results are reported in log-log plot in
 418 Fig. 15, showing that at similar density FS is stiffer than PS but only by a
 419 small amount, ca. 20%. The data follow a scaling law of the form $E_0 \propto d^\kappa$.
 420 The computed exponents of the scaling have intermediate values between
 421 what is expected for an open foam structure ($\kappa = 2.0$ [49]) and a silica
 422 hydrophobized aerogel ($\kappa = 3.8$ [22]).

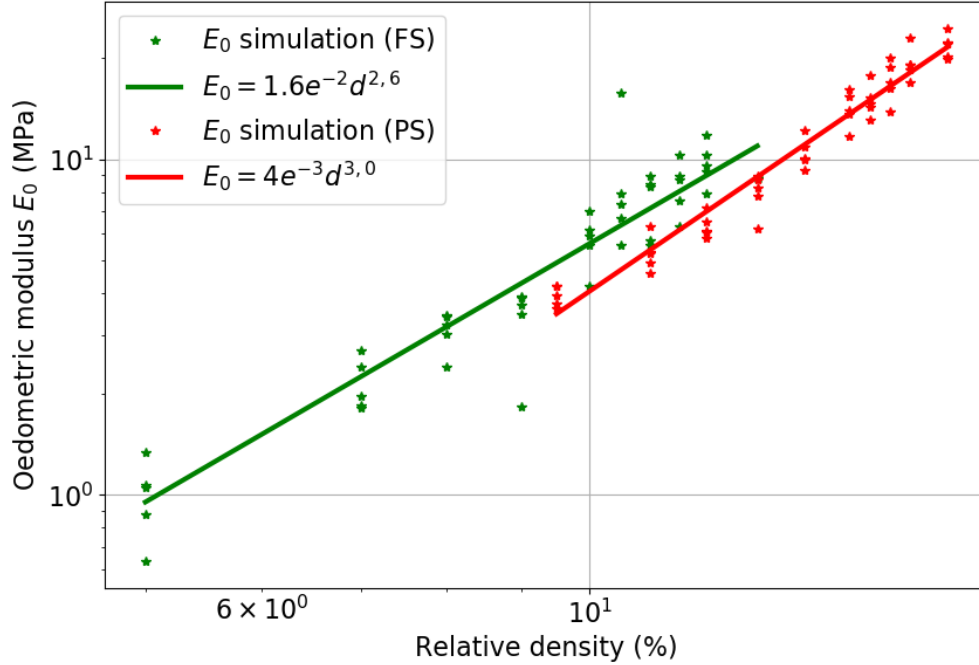


Figure 15: Scaling law between oedometric modulus E_0 and relative density d for PS and FS.

423 6. Discussion

424 The parameters governing the mechanical behavior in compaction of nanos-
 425 tructured silica powders in the simulations are, by increasing order of signif-
 426 icance:

- 427 • neck size between bonded primary particles
- 428 • gyration radius of the aggregate
- 429 • surface energy (or primary particle radius)

430 The fact that the fractal dimension has very limited influence appears sur-
 431 prising as more elongated and branched aggregates have been suggested as
 432 a possible explanation for the observed stronger mechanical behavior under
 433 compaction and indentation of FS powders [16]. First, the elongation, for-
 434 mally defined as the square root of the ratio of the minimum and maximum
 435 eigenvalues of the inertia matrix, is not just related to its fractal dimension
 436 but also to its number of particles N : for the same d_f the elongation increases
 437 with N or R_g for the porous Eden growth model [42] (Fig. 12). Secondly,
 438 decreasing d_f will also affect the number of bonded contacts within the aggre-
 439 gates as a larger amount of new bonded contacts are formed when increasing
 440 the particle radius during the preparation stage (see 4.1.1). The initial co-
 441 ordination number (only bonded contacts, i.e. before tension-compression
 442 cycling) goes from 2.7 for $d_f = 1.7$ to 3.5 for $d_f = 2.8$. On the con-
 443 trary, for $d_f = 2.0$ increasing R_g will not significantly change the initial
 444 coordination number. The influence of lowering d_f is thus twofold:

- 445 • Because of a more elongated and branched structure, more Hertzian
 446 contacts are formed which hinders the reorganizations and tends to
 447 increase the compaction stress.
- 448 • Aggregates are less stiff because of a lower number of bonded contacts
 449 per particles, which tends to decrease the compaction stress.

450 These two competing effect may compensate each other, and finally lead
 451 to the apparent very limited influence of d_f on compaction noted on Fig.
 452 11. On the contrary, increasing R_g does not affect the initial number of
 453 bonded contacts and the compaction stress is governed only by the amount of

454 Hertzian contacts which increases with R_g leading to the expected behavior:
455 more elongated aggregates are more difficult to compact.

456 The observed relatively weak influence of γ_s on the compaction behavior
457 is not consistent with recent experimental results. Indeed, moderate ageing of
458 FS has a significant effect on the compaction behavior [25] that is attributed
459 to a decrease of surface energy (gain of hydrophilicity [13]). The simulations
460 have two possible bias that might explain the inconsistency with experiments:

- 461 • increasing amount of geometrical bond breakages with increasing sur-
462 face energy may lead to an artificially too soft compaction behavior;
- 463 • preparation by compression-tension cycling was done with $\gamma_s = 1.2 \text{ J/m}^2$
464 for all samples, which may lead to an unrealistically large number of
465 Hertzian contacts, at the beginning of the compaction, for low γ_s and
466 hinder the reorganization.

467 When focusing on tensile behavior, the effect of surface energy predom-
468 inates. The oedometric modulus and tensile strength are influenced, in our
469 simulation, by order of significance, by:

- 470 • surface energy (or primary particle radius)
- 471 • neck size between bonded primary particles
- 472 • the aggregate morphology (R_g for E_0 and d_f for σ_f)

473 The parametric study shows that contact law parameters (neck size a and
474 surface energy γ_s) impact more the mechanical behavior (compaction and
475 post-compaction) than the morphology of the aggregates (fractal dimension

476 d_f and gyration radius R_g). However the transposition of this result to real
477 silica powder systems is delicate because of the model nature of the numerical
478 aggregates, the omission of larger scale structures (agglomerate and powder
479 grain) and the absence of reliable values for surface energy and neck size.
480 Still, higher surface energy is expected for FS because of its less hydrophilic
481 surface, and neck size might be influenced by the process. The possibly
482 large influence of these last two parameters on the mechanical behavior of
483 silica powders could thus significantly contribute to the stronger mechani-
484 cal behavior of FS. More insight is provided by the comparison of FS and
485 PS numerically generated according to morphological parameters extracted
486 from SAXS data [11, 25]. It is observed in Fig. 14 that the compaction and
487 tensile behavior of FS and PS are close if only morphological differences are
488 considered (in absence of reliable values, the neck size and surface energy
489 are kept similar for both silicas in the simulations). Morphological differ-
490 ences, i.e. larger aggregate radius of gyration, lower fractal dimension and
491 smaller primary particles of FS, taken alone do not explain completely the
492 experimentally observed large differences in mechanical behavior between FS
493 and PS. In terms of stiffness for example, Fig. 15 shows that morphological
494 differences account for a FS slightly stiffer than PS but experimental instru-
495 mented indentation data around 10% density have shown that FS is actually
496 twice stiffer than PS [16]. The stronger behavior of FS in compaction and
497 the higher strength of its compact are thus attributed to a combined effect
498 of morphology of the aggregate, smaller primary particle size, higher surface
499 energy and possibly larger necks between particles. However, the assessment
500 of the significance of each parameter is difficult due to the limitations of the

501 model and lack of data on surface energies and neck sizes.

502 In light of these findings, the effect of ageing on the mechanical behavior
503 can be discussed. Hygrothermal ageing has two main effects on nanostruc-
504 tured silica: the decrease of the surface energy through water uptake followed
505 by the growth of the necks between primary particles [13]. It has been clearly
506 shown that these effects are detrimental for thermal insulation [7]. For me-
507 chanical behavior, the decrease of surface energy associated with moderate
508 ageing leads to easier powder compaction (formation of less Hertzian contacts
509 leading to easier reorganization). On the contrary, for more severe ageing,
510 the increase of neck size may lead to the reverse. As for the tensile behavior,
511 ageing is expected to decrease the strength as the surface energy is the main
512 factor governing the strength of the compacts.

513 **7. Conclusion**

514 The difference in compaction behavior and post-compaction mechanical
515 properties of a fumed and a precipitated nanostructured silica have been
516 investigated through DEM simulations. A parametric study on a set of mor-
517 phological parameters (R , d_f and R_g) and simulations on realistic aggregates
518 numerically generated based on SAXS measurements have shown that differ-
519 ences in morphology alone may not explain the experimentally observed large
520 differences in mechanical behavior between FS and PS. The study of the in-
521 fluence of neck size and surface energy have shown that these two properties
522 have more effect than the aggregate morphology in the simulations. While
523 the compaction behavior is largely influenced by the neck size, the surface
524 energy is the first governing parameter for strength. The extension of these

525 results to real systems should however be treated with caution because of
526 the lack of reliable surface energy and neck size values, and the questionable
527 realistic character of the numerical silica (omission of particle size dispersion
528 and large scale structures). In particular, particle size dispersion may not
529 have a negligible influence on mechanical behavior, as is the case for scatter-
530 ing behavior [50]. Even with these limitations in mind, it is believed that the
531 stronger mechanical behavior of FS as compared to PS is, at least partially,
532 a consequence of larger neck sizes and surface energy. While it is clear that
533 FS have a larger surface energy than PS, it has never been proposed, to our
534 knowledge, that FS may have larger necks. In practice, it may thus be effi-
535 cient to increase surface energy of PS to improve their mechanical behavior.
536 Increasing the neck size may also improve the mechanical properties but is
537 detrimental for thermal properties [7]. Future research on PS should thus
538 focus not only on adjusting the morphology (e.g. by attempting to decrease
539 their fractal dimension) but also on surface modifications to decrease the
540 hydrophilicity and increase the surface energy as it should be highly bene-
541 ficial for mechanical properties. An experimental investigation of the effect
542 adsorbed water on surface energy and mechanical behavior of silica powders
543 would be of high interest and may help to decouple the morphological and
544 surface energy effects. The proposed modeling approach could also be im-
545 proved, for example a more realistic model would include primary particle
546 size dispersion (observed by Benane et al. on FS [11]). Small dispersion on
547 d_f and R_g exists in the present approach but could be enhanced and tuned.
548 The bonded contact law could allow plastic deformation. Indeed, this would
549 solve the issue related to geometrical breakages by relaxing unrealistically

550 large contact forces. It has been shown that silica glass actually exhibits
551 plasticity when tested at small scales [51, 52].

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