



HAL
open science

Investigation into the mercury intrusion porosimetry (MIP) and micro-computed tomography (μ CT) methods for determining the pore size distribution of MX80 bentonite pellet

Jin-Wen Yang, Yu-Jun Cui, Nadia Mokni, Emmanuel Ormea

► To cite this version:

Jin-Wen Yang, Yu-Jun Cui, Nadia Mokni, Emmanuel Ormea. Investigation into the mercury intrusion porosimetry (MIP) and micro-computed tomography (μ CT) methods for determining the pore size distribution of MX80 bentonite pellet. *Acta Geotechnica*, 2024, 19, pp.85-97. 10.1007/s11440-023-01863-y . irsn-04311821

HAL Id: irsn-04311821

<https://irsn.hal.science/irsn-04311821v1>

Submitted on 7 Dec 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Copyright

22 **Abstract**

23 The pore size distribution (PSD) plays an important role in the hydro-mechanical behaviour for
24 porous materials. In this study, the PSD of MX80 bentonite pellets under various imposed suctions
25 from 262 to 1.5 MPa was determined by both Mercury Intrusion Porosimetry (MIP) and Micro-
26 Computed Tomography (μ CT). The void ratios e_{18-344} in the overlapping pore range (18-344 μ m)
27 identified by MIP and μ CT were compared to clarify the difference between the two techniques.
28 Results showed that the MIP-detection e_{18-344} nearly overlapped with the μ CT-detection one at
29 suction $s \geq 57$ MPa, indicating the reliability of MIP and μ CT results for pellets at $s \geq 57$ MPa.
30 However, the μ CT-detection e_{18-344} became larger than the MIP-detection one at $9 \text{ MPa} \leq s \leq 38$
31 MPa, while the changes of MIP-detection and μ CT-detection e_{18-344} with suctions were opposite at
32 $s \leq 4.2$ MPa. As the difficulty of interpreting the variation of μ CT attenuation coefficient at low
33 suctions undermined the reliability of μ CT thresholding, the segmentation of μ CT images was
34 suggested to be determined by making the μ CT-detection e_{18-344} equal to the MIP-detection one.
35 Because the reliability of MIP results at $s \leq 4.2$ MPa was reduced by the difficulty of keeping the
36 integrity of freeze-dried samples, the MIP-detection e_{18-344} determined in a previous study without
37 the sample integrity problem was chosen as reference for the μ CT thresholding at $1.5 \text{ MPa} \leq s \leq 4.2$
38 MPa. The corrected μ CT-detection e_{18-344} calculated by the new thresholds matched well with the
39 MIP-detection e_{18-344} , completing the μ CT-detection at suctions smaller than 57 MPa. Since the
40 MIP-detection PSD only covers the pores smaller than 344 μ m, the μ CT-detection PSD with pores
41 larger than 344 μ m was then integrated into the MIP-detection PSD, enlarging the MIP-detection to
42 millimetric pores.

43 **Keywords:** bentonite pellet; suction; Mercury Intrusion Porosimetry; Micro-Computed
44 Tomography; pore size distribution.

45

46

47 **1. Introduction**

48 In the European concepts of deep geological disposal for high-level waste, a multi-barrier system
49 consisting of metal canisters, natural geological barrier (host rock), concrete lining and
50 sealing/backfill elements (bentonite-based materials) has been adopted [11, 37]. To well understand
51 the hydro-mechanical behaviour of the involved porous materials (host rock, bentonite-based
52 materials and concrete), it is important to identify their pore size distributions (PSDs) [2, 5, 14, 37].
53 Indeed, the PSDs can help reveal the microstructure [19, 23, 33], determine the damage coefficient
54 by extracting the macro-porosity [18, 30].

55 Mercury Intrusion Porosimetry (MIP) that is based on the measurement of the volume of mercury
56 intruded into pores with distinct sizes under different intrusion pressures, is a widely-applied
57 technique in detecting the PSDs of porous media, due to its advantages including high efficiency,
58 great accuracy and a broad pore-detection range (from several nano-meters to several hundreds of
59 micro-meters) [23, 30]. However, the MIP technique is unable to detect pores with sizes larger than
60 several hundreds of micro-meters and smaller than several nano-meters. By contrast, Micro-
61 Computed Tomography (μ CT) is a non-destructive technique that can visually reveal the pore
62 structure of porous materials in high resolution (tens of micrometers) without particular sample
63 preparation [13]. The μ CT can detect pores larger than the μ CT resolution, but the difficulty and
64 uncertainty in image segmentation is a major concern [3, 13] because a tiny adjustment of grey
65 threshold can significantly affect the final result. Hence, it is important to study the PSD with both
66 MIP and μ CT techniques in order to extend the detection pore range from several nano-meters to
67 several millimeters.

68 A few studies were performed on the PSD of porous materials with MIP and μ CT techniques [17,
69 39]. Zong et al. [39] conducted Nitrogen Adsorption/desorption Isotherms (NAIs), MIP tests and
70 Synchrotron-Radiation-based X-ray computed microtomography (SR- μ CT) on four types of soils,
71 including black soils, Shajiang black soil, paddy soil and latosolic red soil. They observed that for
72 the overlapping pore region with the three methods, the PSDs detected by the MIP and SR- μ CT
73 methods agreed well for the pores larger than 3.75 μ m and smaller than 360 μ m, while NAIs highly

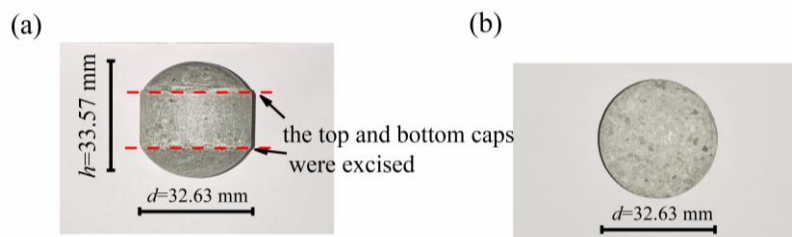
74 underestimated the PSD compared with MIP for the pores larger than 0.003 μm and smaller than
75 0.15 μm . Li and Shao [17] performed one MIP test and two μCT scans with two resolutions (10 μm
76 and 40 μm) on loess. The equivalent sphere diameter was employed for the comparison of MIP and
77 μCT results in their common range. It was observed that the MIP-detection void ratio was larger
78 than the two μCT -detection ones for the pores larger than 15.6 μm and smaller than 200 μm , whereas
79 the MIP-detection void ratio became smaller than the two μCT -detection ones for the pores larger
80 than 200 μm and smaller than 400 μm . Additionally, the μCT -detection void ratio with resolution of
81 10 μm was closer to the MIP-detection void ratio compared with resolution of 40 μm , showing that
82 the lower the μCT resolution, the smaller the difference between MIP and μCT results.

83 Some studies did not aim at PSD investigation, but compared MIP and μCT from a perspective
84 of visualizing mercury by μCT after MIP tests [34–36]. Zeng et al. [36] and Zeng et al. [35]
85 conducted μCT scan on post-MIP porous cement and the μCT results revealed that most detected
86 pores were entrapped by mercury with a few unfilled pores (possibly resulting from the ink-bottle
87 effect after mercury extrusion [35], showing a good agreement between MIP and μCT . The study
88 with μCT scanning on post-MIP compacted clay also showed that the μCT can well identify the
89 mercury entrapped by the ink-bottle effect [34]. Zeng et al. [36] and Zeng et al. [35] pointed out that
90 nearly all mercury-entrapped pores within porous cement were spherically-shaped due to the
91 naturally hydrophobic feature of mercury. Moreover, the smaller the pore diameter, the larger the
92 sphericity of pores. However, Yuan et al. [34] reported that the most mercury-entrapped pores within
93 clay are non-spherically-shaped, suggesting that the mercury intrusion or extrusion would not
94 misrepresent the pore structure. Hence, from the aforementioned studies, it appears that there is
95 generally a good agreement between μCT and MIP in their overlapping pore range. However, to the
96 authors' knowledge, no studies tried to make an extension of the detection pore range using both the
97 MIP and μCT techniques, in particular for soils at different suctions.

98 In this study, the μCT and MIP techniques were employed to determine the PSD of bentonite
99 pellets under different suctions from 262 to 1.5 MPa. The void ratio of the pores with overlapping
100 pore range from 18 to 344 μm (e_{18-344}) were analysed to compare the two techniques. A method for
101 extending the PSDs was finally proposed.

102 **2. Materials and Methods**

103 The investigated material is MX80 bentonite pellet. This bentonite in powder form comes from
104 Wyoming, USA, containing a high smectite content (80%) and some other non-clay minerals (8%
105 anorthite, 4% quartz, 4% muscovite, 2% albite and < 1% pyrite) [20]. Bentonite powder was rapidly
106 and powerfully compacted into a mould of approximately 32 mm in diameter and 32 mm in height
107 to fabricate the pellets (Fig. 1(a)) which have a commercial name of Expangel SP32 [20]. The top
108 and bottom semi-spherical caps were excised using a cutting machine and smoothed using
109 sandpapers to produce cylinder-shaped pellets (Fig. 1(b)) in order to ensure an easier measurement
110 of volume and a better definition of stress state. The initial hydro-mechanical properties of pellets
111 are presented in Table 1. The treated pellets were carefully placed in desiccators with desired
112 saturated salt solutions at constant 20 °C temperature for imposing suctions from 262 to 4.2 MPa.
113 According to Tang and Cui [28], various salt solutions were chosen, including LiCl for 262 MPa,
114 MgCl₂ for 149 MPa, K₂CO₃ for 113 MPa, Mg(NO₃)₂ for 82 MPa, NaCl for 38 MPa, (NH₄)₂SO₄ for
115 25 MPa, KNO₃ for 9 MPa and K₂SO₄ for 4.2 MPa. Some pellets were also placed inside a plastic
116 box with deionized water on the bottom for the target suctions smaller than 4.2 MPa. After two
117 months, a filter paper was pasted onto the top cover and deionized water was evenly sprayed on the
118 filter paper every two days to accelerate the wetting process with target suctions. The pellets were
119 regularly taken out to measure the mass, height and diameter for determining the water content w
120 and the total void ratio e_T . In order to avoid the damage on pellets at $s \leq 4.2$ MPa, only the mass was
121 measured and thus only the water content was determined for these pellets.



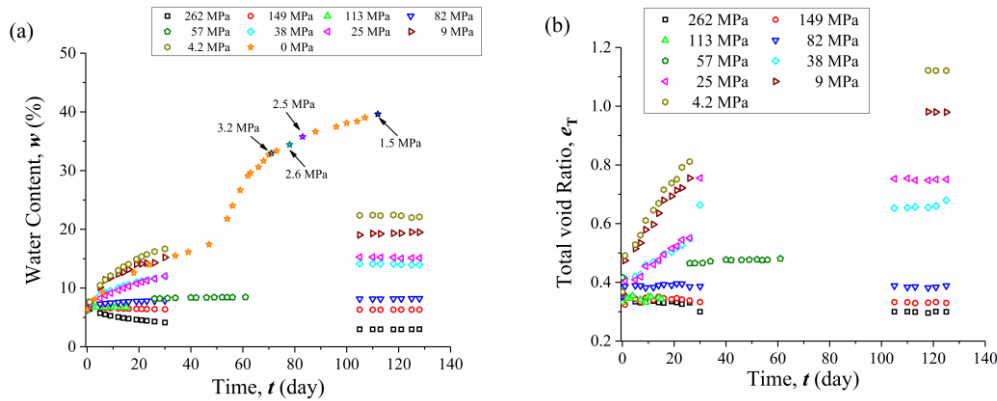
122

123 Fig. 1. MX80 bentonite pellets: (a) original pellet; (b) machined pellet.

124 Table. 1. Initial hydro-mechanical properties of pellets

Property	Value
Dry density, ρ_d : Mg/m ³	2.08
Void ratio, e	0.37
Water content, w %	6.32
Diameter, D : mm	32.63
Height, H : mm	11.51
Suction, s : MPa	114.36

125 The variations of water content w and total void ratio e_T with time are presented in Fig. 2. The
 126 absence of data from the 30th to 100th day was due to the lockdown of France in March and April
 127 2020. It is observed that the pellets at $s \leq 82$ MPa swelled with absorption of water and the pellets
 128 at $s \geq 149$ MPa shrank with loss of water, suggesting that the initial suction of pellets was between
 129 82 and 149 MPa. All the pellets finally reached the target suctions.



130

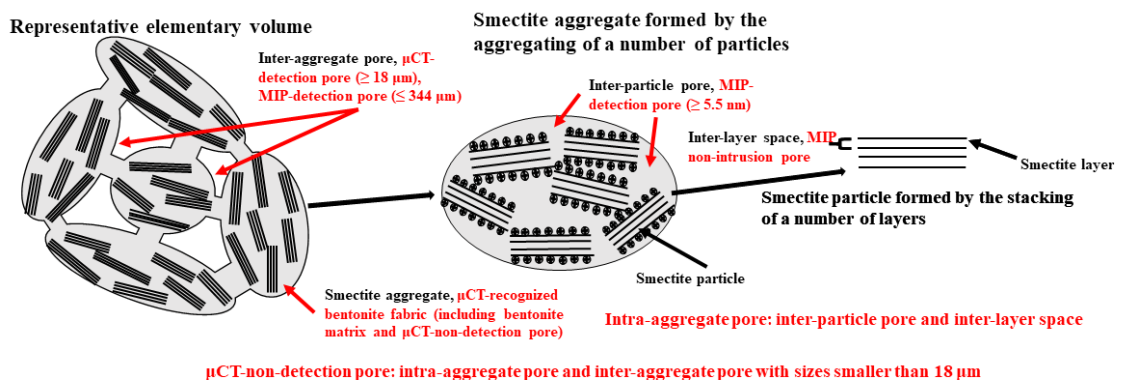
131 Fig. 2. (a) Water content w versus time; (b) Total void ratio e_T versus time.

132 After the pellets reached the target suctions, several centimetric samples were cut out from the
 133 centre and the perimeter of pellets, which were then freeze-dried according to the procedure
 134 proposed by Delage et al. [6]. A Micromeritics Auto-pore IV 9500 mercury intrusion porosimeter
 135 was used to explore the porous structure of samples under a working pressure from 3.4 kPa to 227.5
 136 MPa, allowing identification of the entrance diameters from 344 μm to 5.5 nm. Some other pellets
 137 were waxed to avoid water loss by evaporation for future μCT scans by Skyscanner-1173. The
 138 voltage and current of X-ray sources are 130 kV and 61 μA , respectively, with a 0.25mm-thick
 139 copper filter placed in front of the sources. These settings allowed reducing the noise and increasing

140 the image quality and contrast [8, 16, 29]. The whole pellet was scanned using 2240×2240 pixels
 141 into 16-bit BMP-format images with voxel size of 18 μm. After scans, the bentonite pellet was 3D
 142 reconstructed by assembling around 700 horizontal slices using Bruker software NRecon with
 143 median noise reduction.

144 **3. Calibration of MIP-Detection and μCT-Detection e_{18-344}**

145 The MIP and μCT techniques have distinct detection ranges of pores as presented in Fig. 3. Within
 146 a particle, the smectite layers are disposed one above another in a face-to-face orientation, with the
 147 planar interlayer space between the elementary smectite layers, inside the smectite particles. The
 148 smectite particles are assembled together inside the aggregates with inter-particle pores. Between
 149 aggregates there are large inter-aggregate pores [6]. The intra-aggregate pores comprise the
 150 interlayer space and the inter-particle pores. The interlayer space and the inter-particle pores smaller
 151 than 5.5 nm and the inter-aggregate pores larger than 344 μm are undetectable by the MIP technique.
 152 By contrast, the μCT can only detect the inter-aggregate pores larger than 18 μm (the μCT-detection
 153 pores). Therefore, the μCT-recognized bentonite fabric includes the bentonite matrix and the μCT-
 154 non-detection pores (intra-aggregate pores and inter-aggregate pores smaller than 18 μm). The pores
 155 between 18 and 344 μm (with the void ratio e_{18-344}) are the overlapping pore size range that both the
 156 MIP and μCT can detect. Thus, the MIP-detection and μCT-detection e_{18-344} are compared and
 157 analysed in this study.



159 Fig. 3. Classification of pores detectable by both MIP and μCT.

160 **3.1 Calibration of MIP-detection e_{18-344}**

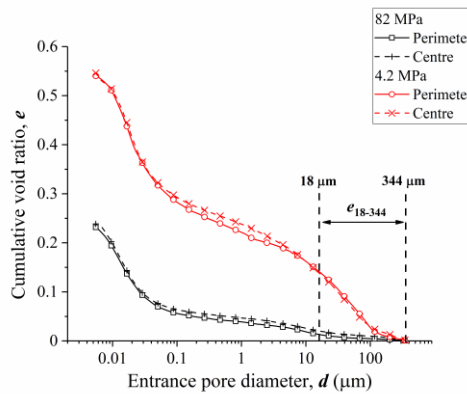
161 In MIP tests, the Washburn equation was used in calculating the corresponding pore entrance
 162 diameter D (μm) [32]:

$$163 \quad D = \frac{4T_s \cos \alpha}{P} \quad (1)$$

164 where P (MPa) is the mercury pressure, T_s is the interfacial tension (taken equal to 0.485 N/m), α is
 165 the contact angle between the mercury-air interface and soil (taken equal to 130° as in plenty of
 166 literatures for bentonite [12, 27, 30, 38]).

167 In MIP tests, 10 seconds were adopted for pressure lower than 0.21 MPa and 120 seconds were
 168 adopted for pressure larger than 0.21 MPa between each pressure step. It is worth noting that
 169 sufficient time must be let to allow the quasi-static condition to be reached, so that a constant contact
 170 angle could be adopted [1, 23].

171 Fig. 4 shows the cumulative void ratio versus the entrance pore diameter for the bentonite pellets
 172 at suctions 82 and 4.2 MPa. The MIP-detection e_{18-344} was extracted from the cumulative curves.



173

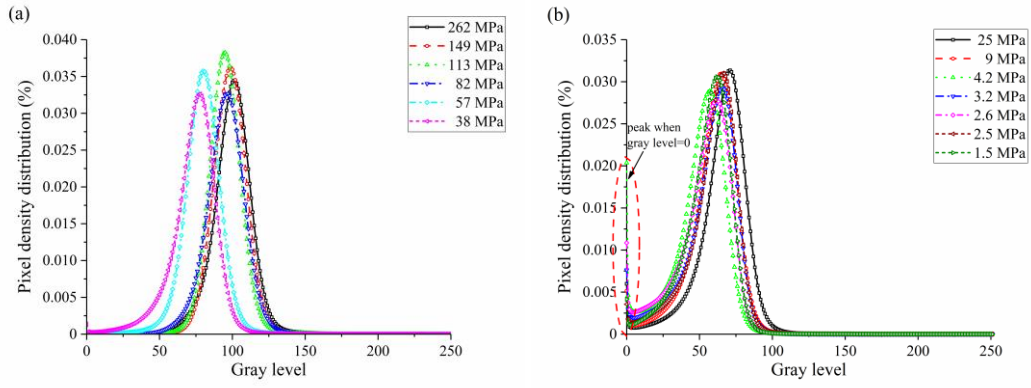
174 Fig. 4. MIP-detection cumulative void ratios of pellets at suctions 82 and 4.2 MPa.

175 **3.2 Calibration of μCT -detection e_{18-344}**

176 The μCT -scanned specimen usually consists of several discrete phases with distinct phase contrasts
 177 (in this study, one phase was bentonite fabric and another μCT -detection pores). The segmentation

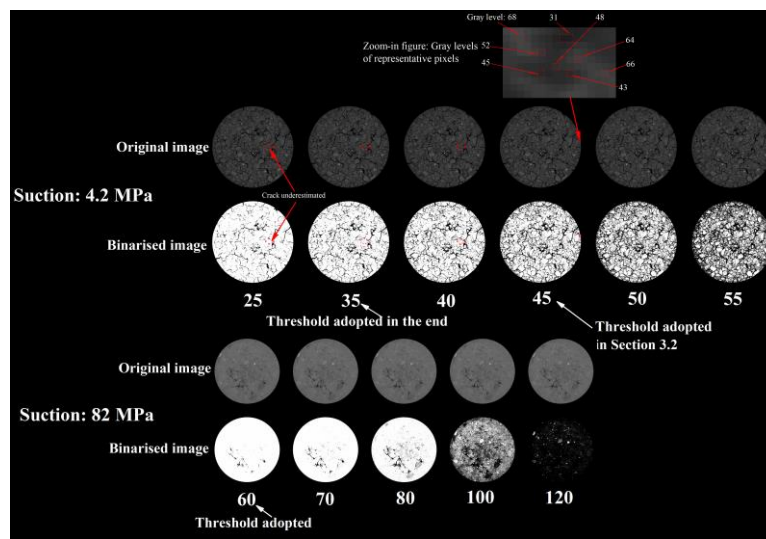
178 of bentonite fabric and μ CT-detection pores is of great interest for the computational purpose - the
179 determination of the grey level threshold. The thresholding process is thus essential in image
180 analysis. The automatic thresholding and the manual thresholding are two methods commonly used
181 in determining the grey level threshold. The automatic thresholding is based on either the histogram
182 of pixel density distribution along grey level such as the OTSU method [22, 25], the Valley-emphasis
183 method [9], or the distribution and contrast of pixels within images such as the Watershed method
184 [21] and the Neural network [4]. A minor change in automatic thresholding results in largely
185 different characterisation of microstructure. The manual thresholding directly analyses the μ CT
186 images by distinguishing different scanned phases through their distinct grey levels in pixels. Thus,
187 it can be used in assisting the determination of grey level threshold. In this study, the Stanford
188 segmentation that applies the automatic thresholding and the manual thresholding [3] was used.

189 The automatic thresholding that employed the OTSU method [22, 25] and the Valley-emphasis
190 method [9] worked on the histogram of pixel density distribution along grey level (Fig. 5), but failed
191 when this histogram was unimodal or close to unimodal for suctions 262-38 MPa. The 2nd and 3rd
192 columns of Table 2 show the grey level thresholds calculated from OTSU and Valley-emphasis
193 methods. The manual thresholding is presented in Fig. 6 for suctions 82 and 4.2 MPa as examples.
194 For suction 82 MPa, the automatic thresholding recommended the value 100 as the threshold, but
195 the manual thresholding shows that some minerals were mistakenly treated as pores when choosing
196 threshold greater than 70. As a result, the porosity of pellet was irrationally overestimated. It appears
197 that the binarized pictures at threshold 60 can represent the characteristics of pores. Therefore, 60
198 was taken as the threshold at $s = 82$ MPa. As for $s = 4.2$ MPa, the automatic thresholding suggested
199 the value between 45.9832 and 35.1569. However, the manual thresholding in Fig. 6 shows that the
200 binarized pictures with threshold ≤ 40 failed to depict the profile and shape of the cracks inside the
201 red dotted-line ellipse in the original pictures. Additionally, the grey levels of representative pixels
202 from a small rectangle are presented in the zoom-in figure, with different colours of pixels for grey
203 level below and above 45 (more black and more grey, respectively). Therefore, the value of 45 was
204 chosen as the threshold at suction 4.2 MPa. The thresholds determined are presented in the fourth
205 column of Table 2.



206

207 Fig. 5. Pixel density distribution with gray level.



208

209 Fig. 6. Manual thresholding at suctions 82 and 4.2 MPa.

210 Table 2. Summary of grey level thresholds.

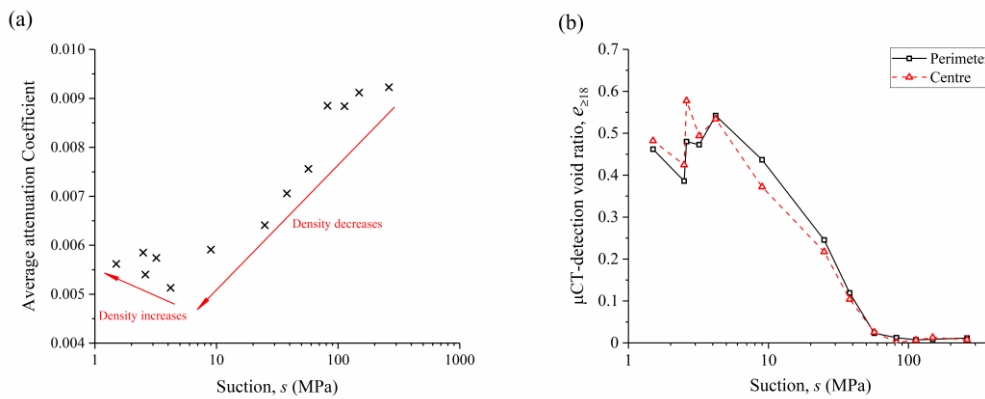
Suction (MPa)	OTSU	Valley-emphasis	Thresholds adopted
262	102.1783	139.8733	70
149	102.7892	141.4752	70
113	103.2123	123.3823	65
82	102.7974	123.8752	60
57	79.5246	97.7145	50
38	69.3227	54.1365	50
25	59.5523	45.5459	50
9	54.3526	42.1858	50
4.2	45.9832	35.1569	45
3.2	47.9171	41.2372	45

2.6	46.6723	40.5973	45
2.5	50.5592	44.1436	45
1.5	47.3634	39.4350	45

211 The attenuation coefficient is a measure of how easily a material can be penetrated by an incident
212 energy beam of X-rays. Table 3 shows the average attenuation coefficients and densities of different
213 phases, with the larger attenuation coefficient for higher density. Fig. 7(a) shows that the average
214 attenuation coefficient of sample decreased with suction decreasing from 262 to 4.2 MPa and then
215 increased with further suction decrease. According to Van Geet et al. [10], the larger the average
216 attenuation coefficient of the whole sample, the larger the μ CT-recognition density, the smaller the
217 μ CT-detection void ratio $e_{\geq 18}$. Therefore, the variation trends of the average attenuation coefficient
218 of whole sample and $e_{\geq 18}$ should be opposite with suction decrease, as shown in Fig. 7(a) for the
219 average attenuation coefficient and in Fig. 7(b) for $e_{\geq 18}$. Additionally, the average attenuation
220 coefficients with similar magnitudes corresponded to the same or similar thresholds.

221 Table 3. Average attenuation coefficient of different phases in μ CT scan.

Phase	Attenuation coefficient	Density (g/cm ³)
Aluminium	0.00991	2.7
Glass	0.00972	2.5
Free water	0.00278	1.0
Wax	0.00194	0.9
Air	0.001	0.001205



222

223 Fig. 7. (a) Average attenuation coefficient of whole sample versus suction; (b) μ CT-detection void
224 ratio $e_{\geq 18}$ versus suction.

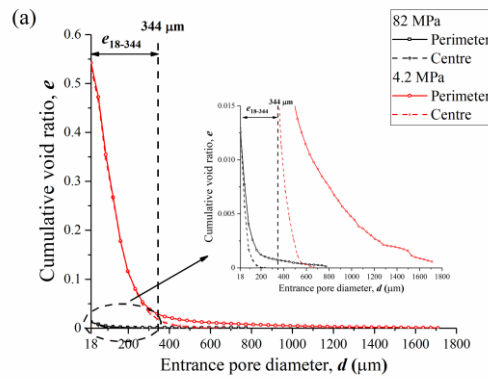
225 The μ CT images were then transformed into binarized images with only black and white colours,

226 by replacing the pixels below and above the threshold adopted with 0 (black) and 255 (white),
 227 respectively. Note that black represents crack and white bentonite fabric. The void ratio of each pore
 228 range i with sizes $18i-18(i+1)$ μm was calculated by Eq. (2):

$$229 \quad de_i = \frac{dV_{\text{pore},i}}{m} G_s \quad (2)$$

230 where $V_{\text{pore},i}$ is the volume of i^{th} pore range, m the mass, w the water content and G_s the specific
 231 gravity (taken as 2.77).

232 The variation of cumulative void ratio with entrance pore diameter was calculated using Eq. (2)
 233 and presented in Fig. 8. The μCT -detection e_{18-344} was extracted from the cumulative curves.



234

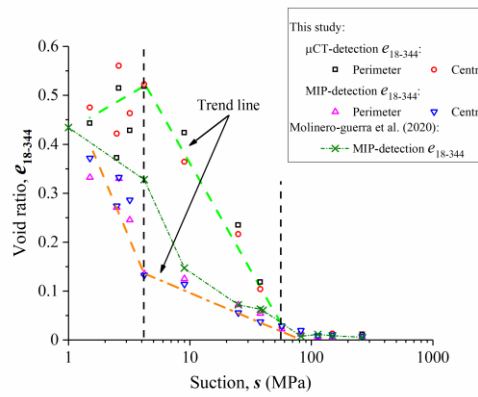
235 Fig. 8. μCT -detection cumulative void ratios of pellets at suctions 82 and 4.2 MPa.

236 4. Comparison and Discussions

237 4.1 Comparison between MIP-detection and μCT -detection e_{18-344}

238 The pores between 18 and 344 μm are the overlapping pore size range that both the MIP and μCT
 239 can detect, with their void ratios e_{18-344} compared and analysed in this study. Note that the initial dry
 240 densities, void ratios and water contents of 7mm-in-size MX80 bentonite pellet of Molinero-Guerra
 241 et al. [19] and 32-mm pellet in this study were close to each other. The fabrications of these two
 242 pellets were the same, by heavily compacting powder grains in the mould of different sizes. Fig. 9
 243 depicts the variations of MIP-detection and μCT -detection e_{18-344} with suctions, together with the

244 results of Molinero-Guerra et al. [19] on 7-mm pellet. The difference between MIP-detection and
 245 μ CT-detection e_{18-344} appears negligible at $s \geq 57$ MPa, whereas the μ CT-detection e_{18-344} was
 246 remarkably larger than the MIP-detection one at $4.2 \text{ MPa} \leq s \leq 38 \text{ MPa}$. Both MIP-detection and
 247 μ CT-detection e_{18-344} show a large scatter at $1.5 \text{ MPa} \leq s \leq 4.2 \text{ MPa}$. The trend lines were drawn and
 248 it appears that the μ CT-detection e_{18-344} decreased with suction decreasing, unlike the MIP-detection
 249 e_{18-344} which exhibited a remarkable increase in this suction range. The difference between the MIP-
 250 detection e_{18-344} of this study and Molinero-Guerra et al. [19] remained limited at $s \geq 9$ MPa, but
 251 large at $s \leq 4.2$ MPa.



252

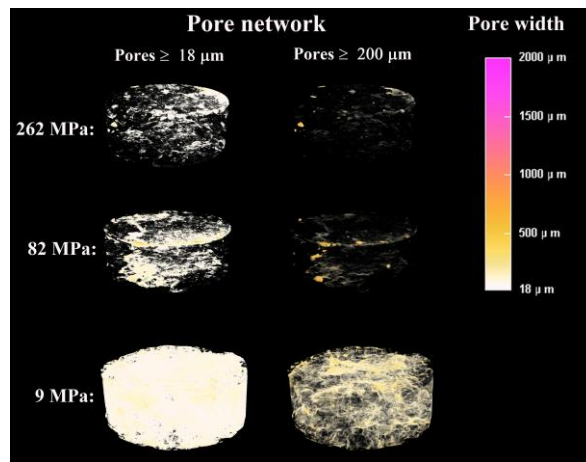
253 Fig. 9. e_{18-344} versus suction.

254 4.2 Discussions on MIP results

255 Although the MIP technique is a widely-recognized technique in determining pore size distribution,
 256 it presents some limitations [23, 30]: (1) closed pores: pores are completely surrounded by the
 257 aggregated solid particles and isolated from any surrounding mercury-filled pores, even though such
 258 closed pores are not significant in soils [23]; (2) constricted pores: large pores that are accessible
 259 only through smaller ones, cannot be detected until the smaller pores are penetrated, leading to an
 260 underestimation of diameter of some large pores.

261 The 3D reconstruction of bentonite pellet and pore network at suctions 262, 82 and 9 MPa are
 262 presented in Fig. 10, allowing the problems of the closed pores and constricted pores to be analysed.
 263 As for high suctions (262 and 82 MPa), it is observed that the pores with sizes $\geq 200 \mu\text{m}$ were mainly

264 located at the boundary part of pellet and the pores with sizes $\geq 18 \mu\text{m}$ appeared to extend from
 265 boundary to centre and to clump together. Therefore, mercury can always enter the bentonite pellet
 266 from the larger pores into the smaller ones. The effects of closed pores and constricted pores were
 267 thus quite limited on the PSDs of pellets at high suctions. For pellet at $s = 9 \text{ MPa}$, both pores with
 268 sizes $\geq 200 \mu\text{m}$ and pores with sizes $\geq 18 \mu\text{m}$ appear to be omnipresent within pellets and highly
 269 interconnected, indicating that the problem of closed pores and constricted pores can be ignored for
 270 the bentonite pellets at low suctions.

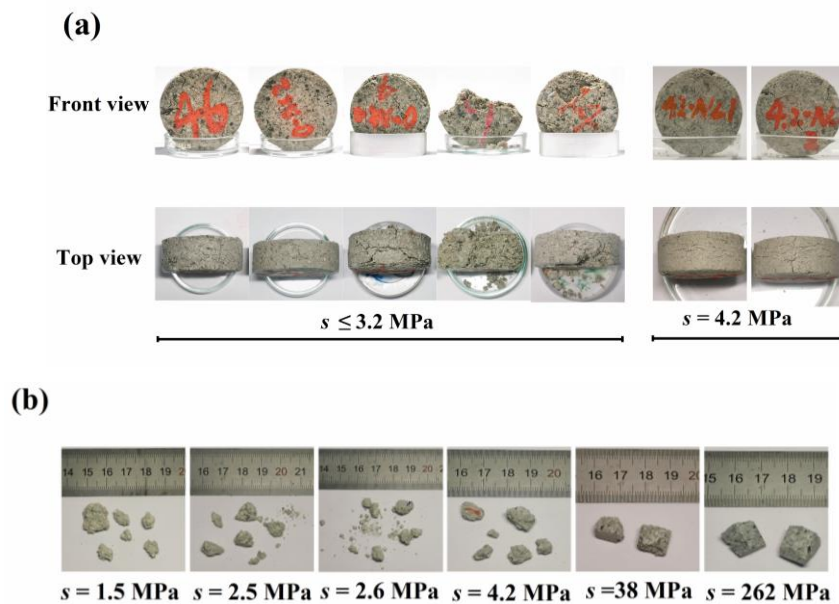


271
 272 Fig. 10. 3D reconstruction of bentonite pellet and pore network at suctions 262, 82 and 9 MPa.

273 The exfoliation of particles is significant for bentonite materials at low suctions [6, 31]. The
 274 average number of layers per clay particle may decrease from 350 to 10 layers as the suction
 275 decreases from 100 to 2 MPa [24]. This leads to increasingly spatially-separated disruption,
 276 dispersion of smectite layers and exfoliated particles. Under the electrostatic effect, the
 277 microstructure of whole bentonite pellet appears to be of a honeycomb type [7]. The large data
 278 scatter at $s \leq 4.2 \text{ MPa}$ observed in Fig. 11(a) resulted from the hydration under a very low suction,
 279 which made the sample shape difficult to be kept as shown in Fig. 11(a). This large data scatter led
 280 to a large discreteness between MIP-detection and μCT -detection e_{18-344} at $1.5 \text{ MPa} \leq s \leq 4.2 \text{ MPa}$
 281 in Fig. 9.

282 The observed difference in MIP-detection e_{18-344} between this study and Molinero-Guerra et al.
 283 [19] at $s \leq 4.2 \text{ MPa}$ might come from the sampling procedure. Molinero-Guerra et al. [19] directly
 284 freeze-dried and conducted MIP tests with three 7mm-in-size bentonite pellets in the penetrometer

285 tube, avoiding the disturbance of MIP samples. On the contrary, in this study, one centimetric freeze-
 286 dried sample at $s \geq 9$ MPa or two or three millimetric freeze-dried samples at $s \leq 4.2$ MPa were
 287 taken out from the 32mm-in-size bentonite pellet because such 32mm-in-size pellet was too large
 288 for the penetrometer tube employed (Fig. 11(b)). In fact, the relatively fragmentary millimetric
 289 freeze-dried sample at $s \leq 4.2$ MPa was apt to be taken out from a pellet along large crack, causing
 290 some underestimation of pore volume. Summarising, the MIP technique is appropriate for
 291 identifying the PSD of bentonite pellets. However, the difficulty of keeping good sample shape and
 292 the possible effect of sampling should be taken into account while analysing the results for suctions
 293 lower than 4.2 MPa.



294

295

296 Fig. 11. (a) The fragility of bentonite pellets at $s \leq 4.2$ MPa; (b) The freeze-dried samples at $s \leq 4.2$
 297 MPa, with samples at suctions 38 and 262 MPa selected as reference.

298 4.3 Discussions on μ CT results

299 As far as the grey level threshold on μ CT results is concerned, Haugen and Bertoldi [13] pointed
 300 out that the thresholding step performed by visual and histogram estimation was user-dependent,
 301 possibly resulting in inaccurate structural characterization. In fact, some pixels contained pores (i.e.,
 302 pores with sizes < 18 μ m or the border part with large pores) and bentonite matrix simultaneously,

303 and the contrast of pore and bentonite matrix is the main concern in that case. For instance, the
 304 pixels with grey levels around 45 in the zoom-in figure (Fig. 6) may include μ CT-non-detection
 305 pores and bentonite matrix. The larger the threshold adopted, the more the pores of 18 μ m and the
 306 larger the pores > 18 μ m. Nevertheless, when comparing the thresholds adopted between 25 and 45
 307 for $s = 4.2$ MPa in Fig. 6, it appears that the large pores that were constituted by dozens of pixels
 308 tended to expand insignificantly, while the point-shaped pores that comprised several pixels
 309 remarkably increased with the increase of the adopted threshold, indicating that the thresholding has
 310 limited effect on the large pores. In other words, the size of large pores identified by μ CT is not
 311 significantly depending on the thresholding accuracy.

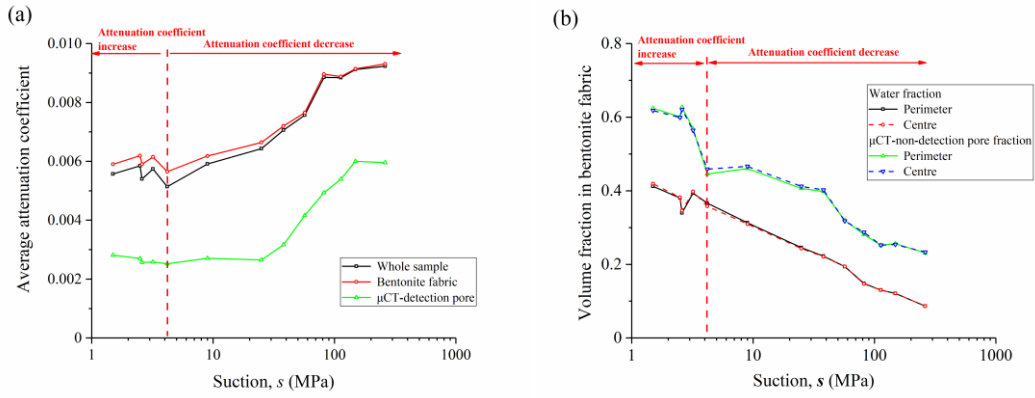
312 Because the MIP technique appears appropriate for determining the PSD of bentonite pellets at s
 313 ≥ 9 MPa, the thresholding of μ CT images was suggested to be adapted to the MIP results, by making
 314 μ CT-detection e_{18-344} equal to MIP-detection one at $s \geq 9$ MPa. The thresholds for pellets at $s \geq 57$
 315 MPa were adopted as the previous values in Table 2, while the value 35 was selected as the
 316 thresholds at $9 \text{ MPa} \leq s \leq 25 \text{ MPa}$ and the value 40 was selected as the threshold at $s = 38 \text{ MPa}$.

317 The determination of the thresholds for the pellets at $s \leq 4.2$ MPa seems to be less straightforward.
 318 Fig. 12(a) shows that the average attenuation coefficients of whole sample, bentonite fabric and
 319 μ CT-detection pore decreased with the suction decrease from 262 to 4.2 MPa. On the contrary, a
 320 slight increase in the average attenuation coefficients of whole sample, bentonite fabric and μ CT-
 321 detection pore are observed when the suction decreased from 4.2 to 1.5 MPa. It is worth noting that
 322 the attenuation coefficients of whole sample and bentonite fabric had exactly the same trend,
 323 showing that the bentonite fabric itself dominated the attenuation coefficient of whole sample. The
 324 average attenuation coefficient of μ CT-detection pores up to 0.006 was due to some pixels
 325 containing μ CT-non-detection pores and bentonite matrix simultaneously. The water fraction and
 326 μ CT-non-detection pore fraction in bentonite fabric were determined using Eqs. (3) and (4)
 327 respectively and presented in Fig. 12(b).

$$328 \text{ Water fraction} = \frac{V_w}{V_{V, \leq 18} + V_s} = \frac{wG_s}{1 + e_T - e_{\geq 18}} \quad (3)$$

$$329 \quad \mu\text{CT} - \text{non} - \text{detection pore fraction} = \frac{V_{V, \leq 18}}{V_{V, \leq 18} + V_s} = \frac{e_T - e_{\geq 18}}{1 + e_T - e_{\geq 18}} \quad (4)$$

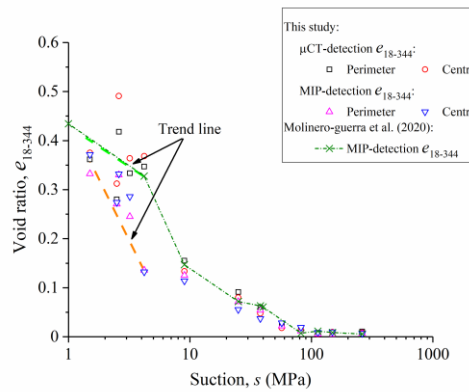
330 where G_s is the specific gravity of bentonite matrix (taken as 2.77), and V_w , V_s and $V_{V, \leq 18}$ are the
331 volumes of water, bentonite matrix and pores smaller than 18 μm , respectively. The water content
332 w at suctions 262-1.5 MPa and the total void ratios e_T at suctions 262-4.2 MPa could be taken as the
333 value when reaching suction equilibrium (Fig. 2(b)) and the total void ratios e_T at suctions 3.2, 2.6,
334 2.5 and 1.5 MPa were measured before the μCT scans, being 1.57, 2.01, 1.73 and 1.86 respectively.
335 The lower the suction the larger the e_T , which held for suctions larger than 4.2 MPa. However, upon
336 wetting to suction smaller than 4.2 MPa, the volume change of pellets became unstable - the pellets
337 started to lose their good shape, leading to a relatively large scatter of e_T data at low suctions. It is
338 observed from Fig. 12(b) that the water fraction and μCT -non-detection pore fraction increased with
339 the suction decrease. Jacinto et al. [15] pointed out that the water density for MX80 bentonite sample
340 at a dry density of 1.6 Mg/m^3 decreased from around 1.165 Mg/m^3 at suction 113 MPa, to 1.13
341 Mg/m^3 at suction 38 MPa, to 1.093 Mg/m^3 at suction 4.2 MPa and to 1.085 Mg/m^3 at suction 1.5
342 MPa. Thereby, the decreasing average attenuation coefficient of bentonite fabric at $s \geq 4.2$ MPa was
343 due to the increasing μCT -non-detection pore fraction, the increasing water fraction and the
344 decreasing water density, in agreement with the decrease in attenuation coefficient for the Callovo-
345 Oxfordian claystone upon wetting [26]. However, the increasing average attenuation coefficient of
346 bentonite fabric at $s \leq 3.2$ MPa was hard to be quantified. Considering the difficulty in considering
347 the suction effect on the attenuation coefficient, the MIP results of Molinero-Guerra et al. [19] was
348 taken as reference and the threshold at 1.5 MPa $\leq s \leq 3.2$ MPa was selected as 40 and the threshold
349 at 4.2 MPa was selected as 35. The corrected μCT -detection e_{18-344} calculated by the new thresholds
350 matched well with the MIP-detection e_{18-344} , as shown in Fig. 13, completing the μCT -detection in
351 the low suction range. Since there was a limited effect of μCT thresholding on large pores as
352 mentioned previously, the μCT -detection PSD for pore larger than 344 μm was used to extend the
353 upper limit of MIP-detection pore sizes.



354

355 Fig. 12. (a) Average attenuation coefficients of whole sample, bentonite fabric and μ CT-detection

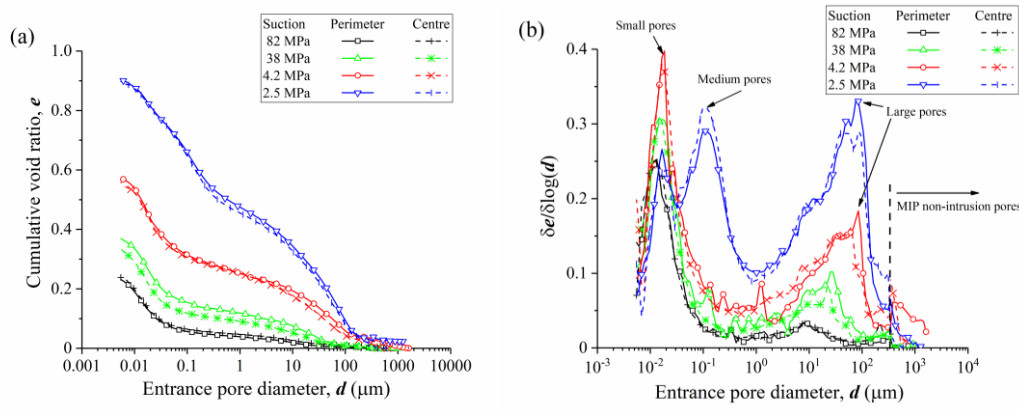
356 pore; (b) Volume fractions of water and μ CT-non-detection pore in bentonite fabric.



357

358 Fig. 13. Corrected e_{18-344} versus suction.

359 The corrected PSDs by the proposed combined MIP/ μ CT method for the bentonite pellets at
 360 suctions 82, 38, 4.2 and 2.5 MPa are shown in Fig. 14. It appears from Fig. 14(a) that the smaller
 361 the suction, the larger the cumulative void ratio. From Fig. 14(b) it is observed that the PSDs
 362 displayed a bimodal porosity at $s \geq 4.2$ MPa, but a trimodal porosity at $s = 2.5$ MPa. Moreover, the
 363 smaller the suction, the larger the large and small pores. The large pores that the MIP tests cannot
 364 identify were not negligible especially at low suctions (Fig. 14(b)), confirming the necessity of
 365 combining the MIP and μ CT techniques.



366

367 Fig. 14. Corrected pore size distributions of bentonite pellets at suctions 82, 38, 4.2 and 2.5 MPa
 368 from a combined MIP/ μ CT method: (a) cumulative curves; (b) density function curves.

369 5. Conclusions

370 The porosimetry study on MX80 bentonite pellets under various suctions from 262 to 1.5 MPa was
 371 conducted by MIP and μ CT techniques. The Stanford segmentation that applies the automatic
 372 thresholding together with the manual thresholding was used in image segmentation. The pores with
 373 overlapping pore size range (with the void ratio e_{18-344}) for both MIP and μ CT were analysed for
 374 comparison, allowing a combined MIP and μ CT method to be proposed for a large range PSD
 375 determination.

376 The MIP-detection e_{18-344} nearly overlapped with the μ CT-detection one at $s \geq 57$ MPa, indicating
 377 the reliability of both MIP and μ CT results in this high suction range. However, the μ CT-detection
 378 e_{18-344} became larger than the MIP-detection one at $9 \text{ MPa} \leq s \leq 38 \text{ MPa}$. This is due to the difficulty
 379 in the thresholding process while applying the μ CT technique. Indeed, such process is user-
 380 dependent, which might result in inaccurate structural characterisation. On the contrary, the MIP
 381 technique was found to be appropriate at $s \geq 9$ MPa because the problems related to the closed pores
 382 and restricted pores appear to be insignificant. Therefore, the segmentation of μ CT images was
 383 suggested to be corrected based on the MIP results by making the μ CT-detection e_{18-344} equal to the
 384 MIP-detection one.

385 The hydration and exfoliation effects resulted in a significant MIP test data scatter at low suctions

386 (1.5 MPa $\leq s \leq$ 4.2 MPa). The large MIP data scatter was explained by the difficulty in dealing with
387 fragile samples after hydration and freeze-drying, as well as the possibility of underestimating the
388 pore volume because some sampling may be done along large cracks. This could also explain the
389 large difference between the MIP-detection e_{18-344} of this study and the results of Molinero-Guerra
390 et al. [19] at $s \leq$ 4.2 MPa. The μ CT-detection e_{18-344} decreased with suction decreasing, as opposed
391 to the MIP-detection e_{18-344} . Considering the difficulty of determining the μ CT attenuation
392 coefficient at varying suctions and the reliability of MIP results as mentioned above, it was proposed
393 to use the MIP-detection e_{18-344} of Molinero-Guerra et al. [19] as a reference for selecting the
394 thresholds at 1.5 MPa $\leq s \leq$ 4.2 MPa. For pores larger than 344 μ m, as the μ CT-detection PSD is
395 appropriate, it could be used to extend the upper limit of MIP-detection pore sizes.

396 The PSDs of bentonite pellets were thus obtained in a wide range for different suctions, which
397 can be used in further hydro-mechanical analyses.

398 **Acknowledgments**

399 The authors would like to thank the China Scholarship Council (CSC). The supports provided by
400 Ecole des Ponts ParisTech (ENPC) and Institut de Radioprotection et de Sûreté Nucléaire (IRSN)
401 are also greatly acknowledged.

402 **Data availability**

403 Data can be available from the authors upon request.

404 **6. References**

- 405 1. Ait-Mokhtar A, Amiri O, Dumargue P, Bouguerra A (2004) On the applicability of Washburn
406 law: Study of mercury and water flow properties in cement-based materials. *Mater Struct*
407 *Constr* 37(266):107–113. <https://doi.org/10.1617/13857>
- 408 2. Alonso EE, Romero E, Hoffmann C (2011) Hydromechanical behaviour of compacted granular
409 expansive mixtures: Experimental and constitutive study. *Geotechnique* 61(4):329–344.

- 410 <https://doi.org/10.1680/geot.2011.61.4.329>
- 411 3. Andrä H, Combaret N, Dvorkin J, Glatt E, Han J, Kabel M, Keehm Y, Krzikalla F, Lee M,
412 Madonna C, Marsh M, Mukerji T, Saenger EH, Sain R, Saxena N, Ricker S, Wiegmann A,
413 Zhan X (2013) Digital rock physics benchmarks-Part I: Imaging and segmentation. *Comput*
414 *Geosci* 50:25–32. <https://doi.org/10.1016/j.cageo.2012.09.005>
- 415 4. Bevilacqua V, Mastronardi G, Marinelli M (2006) A neural network approach to medical
416 image segmentation and three-dimensional reconstruction. *Lect Notes Comput Sci* 4113:22–31.
417 https://doi.org/10.1007/11816157_3
- 418 5. Cui YJ, Tang AM, Qian LX, Ye WM, Chen B (2011) Thermal-mechanical behavior of
419 compacted GMZ bentonite. *Soils Found* 51(6):1065–1074.
420 <https://doi.org/10.3208/sandf.51.1065>
- 421 6. Delage P, Marcial D, Cui YJ, Ruiz X (2006) Ageing effects in a compacted bentonite: A
422 microstructure approach. *Geotechnique* 56(5):291–304.
423 <https://doi.org/10.1680/geot.2006.56.5.291>
- 424 7. Delage P (2007) *Microstructure Features in the Behaviour of Engineered Barriers for Nuclear*
425 *Waste Disposal*. Springer Berlin Heidelberg New York, Weimar
- 426 8. Diwakar M, Kumar M (2018) A review on CT image noise and its denoising. *Biomed Signal*
427 *Process Control* 42:73–88. <https://doi.org/10.1016/j.bspc.2018.01.010>
- 428 9. Fan JL, Lei B (2012) A modified valley-emphasis method for automatic thresholding. *Pattern*
429 *Recognit Lett* 33(6):703–708. <https://doi.org/10.1016/j.patrec.2011.12.009>
- 430 10. Van Geet M, Volckaert G, Roels S (2005) The use of microfocus X-ray computed tomography
431 in characterising the hydration of a clay pellet/powder mixture. *Appl Clay Sci* 29(2):73–87.
432 <https://doi.org/10.1016/j.clay.2004.12.007>
- 433 11. Gens A, Olivella S (2001) Clay barriers in radioactive waste disposal. *Rev Française Génie Civ*
434 5(6):845–856. <https://doi.org/10.1080/12795119.2001.9692329>

- 435 12. Hashemi MA, Massart TJ, Salager S, Herrier G, François B (2015) Pore scale characterization
436 of lime-treated sand-bentonite mixtures. *Appl Clay Sci* 111:50–60.
437 <https://doi.org/10.1016/j.clay.2015.04.001>
- 438 13. Haugen HJ, Bertoldi S (2017) Characterization of morphology-3D and porous structure.
439 *Charact Polym Biomater* :21–53. <https://doi.org/10.1016/B978-0-08-100737-2.00002-9>
- 440 14. Hoffmann C, Alonso EE, Romero E (2007) Hydro-mechanical behaviour of bentonite pellet
441 mixtures. *Phys Chem Earth* 32(8–14):832–849. <https://doi.org/10.1016/j.pce.2006.04.037>
- 442 15. Jacinto AC, Villar M V., Ledesma A (2012) Influence of water density on the water-retention
443 curve of expansive clays. *Geotechnique* 62(8):657–667. <https://doi.org/10.1680/geot.7.00127>
- 444 16. Karmazyn B, Liang Y, Klahr P, Jennings SG (2013) Effect of tube voltage on ct noise levels in
445 different phantom sizes. *Am J Roentgenol* 200(5):1001–1005.
446 <https://doi.org/10.2214/AJR.12.9828>
- 447 17. Li P, Shao S (2020) Can X-ray computed tomography (CT) be used to determine the pore-size
448 distribution of intact loess? *Environ Earth Sci* 79(1):1–12. [https://doi.org/10.1007/s12665-019-](https://doi.org/10.1007/s12665-019-8777-z)
449 [8777-z](https://doi.org/10.1007/s12665-019-8777-z)
- 450 18. Mokni N, Molinero-Guerra A, Cui YJ, Delage P, Aïmediou P, Bornert M, Tang AM (2020)
451 Modelling the long-term hydro-mechanical behaviour of a bentonite pellet/powder mixture
452 with consideration of initial structural heterogeneities. *Geotechnique* 70(7):563–580
- 453 19. Molinero-Guerra A, Delage P, Cui YJ, Mokni N, Tang AM, Aïmediou P, Bernier F, Bornert M
454 (2020) Water-retention properties and microstructure changes of a bentonite pellet upon
455 wetting/drying; application to radioactive waste disposal. *Geotechnique* 70(3):199–209.
456 <https://doi.org/10.1680/jgeot.17.P.291>
- 457 20. Molinero-Guerra A, Mokni N, Delage P, Cui YJ, Tang AM, Aïmediou P, Bernier F, Bornert M
458 (2017) In-depth characterisation of a mixture composed of powder/pellets MX80 bentonite.
459 *Appl Clay Sci* 135:538–546. <https://doi.org/10.1016/j.clay.2016.10.030>

- 460 21. Ng HP, Ong SH, Foong KWC, Goh PS, Nowinski WL (2006) Medical image segmentation
461 using k-means clustering and improved watershed algorithm. Proc IEEE Southwest Symp
462 Image Anal Interpret 2006(April 2014):61–65. <https://doi.org/10.1109/ssiai.2006.1633722>
- 463 22. Otsu N, Smith PL, Reid DB, Environment C, Palo L, Alto P, Smith PL (1979) A Threshold
464 Selection Method from Gray-Level Histograms. IEEE Trans Syst Man Cybern C(1):62–66
- 465 23. Romero E, Simms PH (2008) Microstructure investigation in unsaturated soils: A review with
466 special attention to contribution of mercury intrusion porosimetry and environmental scanning
467 electron microscopy. Geotech Geol Eng 26(6):705–727. [https://doi.org/10.1007/s10706-008-](https://doi.org/10.1007/s10706-008-9204-5)
468 9204-5
- 469 24. Saiyouri N, Tessier D, Hicher P (2004) Experimental study of swelling in unsaturated
470 compacted clays. Clay Miner 39(4):469–479
- 471 25. Saxena N, Hofmann R, Alpak FO, Dietderich J, Hunter S, Day-Stirrat RJ (2017) Effect of
472 image segmentation & voxel size on micro-CT computed effective transport & elastic
473 properties. Mar Pet Geol 86:972–990. <https://doi.org/10.1016/j.marpetgeo.2017.07.004>
- 474 26. Stavropoulou E, Andò E, Roubin E, Lenoir N, Tengattini A, Briffaut M, Bésuelle P (2020)
475 Dynamics of Water Absorption in Callovo-Oxfordian Claystone Revealed With Multimodal X-
476 Ray and Neutron Tomography. Front Earth Sci 8(March).
477 <https://doi.org/10.3389/feart.2020.00006>
- 478 27. Sun H, Mašín D, Najser J, Nedela V, Navrátilová E (2019) Bentonite microstructure and
479 saturation evolution in wetting-drying cycles evaluated using ESEM, MIP and WRC
480 measurements. Geotechnique 69(8):713–726. <https://doi.org/10.1680/jgeot.17.P.253>
- 481 28. Tang AM, Cui YJ (2005) Controlling suction by the vapour equilibrium technique at different
482 temperatures and its application in determining the water retention properties of MX80 clay.
483 Can Geotech J 42(1):287–296. <https://doi.org/10.1139/t04-082>
- 484 29. Tugwell-Allsup JR, Morris RWYN, Thomas K, Hibbs R, England A (2022) Neonatal digital
485 chest radiography– should we be using additional copper filtration? Br J Radiol 95(1130).

- 486 <https://doi.org/10.1259/bjr.20211026>
- 487 30. Wang H (2021) Delayed and Swelling Behaviour of Damaged/Fractured Callovo-Oxfordian
488 Claystone. (Doctoral dissertation, Ecole des Ponts Paristech)
- 489 31. Wang Q, Cui YJ, Tang AM, Barnichon JD, Saba S, Ye WM (2013) Hydraulic conductivity and
490 microstructure changes of compacted bentonite/sand mixture during hydration. *Eng Geol*
491 164:67–76. <https://doi.org/10.1016/j.enggeo.2013.06.013>
- 492 32. Washburn EW (1921) The dynamics of capillary flow. *Phys Rev* 17(3):273–283.
493 <https://doi.org/10.1103/PhysRev.18.206>
- 494 33. Ying Z, Cui YJ, Benahmed N, Duc M (2023) Drying effect on the microstructure of compacted
495 salted silt. *Geotechnique* 73(1):62–70. <https://doi.org/10.1680/jgeot.20.P.319>
- 496 34. Yuan S, Liu X, Wang Y, Delage P, Aïmediou P, Buzzi O (2022) Applied Clay Science X-Ray
497 microtomography of mercury intruded compacted clay : An insight into the geometry of
498 macropores. 227(June)
- 499 35. Zeng Q, Chen S, Yang P, Peng Y, Wang J, Zhou C, Wang Z, Yan D (2020) Reassessment of
500 mercury intrusion porosimetry for characterizing the pore structure of cement-based porous
501 materials by monitoring the mercury entrapments with X-ray computed tomography. *Cem*
502 *Concr Compos* 113:1–16. <https://doi.org/10.1016/j.cemconcomp.2020.103726>
- 503 36. Zeng Q, Wang X, Yang P, Wang J, Zhou C (2019) Tracing mercury entrapment in porous
504 cement paste after mercury intrusion test by X-ray computed tomography and implications for
505 pore structure characterization. *Mater Charact* 151:203–215.
506 <https://doi.org/10.1016/j.matchar.2019.02.014>
- 507 37. Zeng Z (2021) Investigation of the hydro-mechanical behaviour of compacted
508 bentonite/claystone mixture. (Doctoral dissertation, Ecole des Ponts Paristech)
- 509 38. Zeng Z, Cui YJ, Talandier J (2022) Evaluation of swelling pressure of bentonite/claystone
510 mixtures from pore size distribution. *Acta Geotech* 5:1–9. <https://doi.org/10.1007/s11440-022->

511 01676-5

512 39. Zong Y, Yu X, Zhu M, Lu S (2015) Characterizing soil pore structure using nitrogen
513 adsorption, mercury intrusion porosimetry, and synchrotron-radiation-based X-ray computed
514 microtomography techniques. *J Soils Sediments* 15(2):302–312.
515 <https://doi.org/10.1007/s11368-014-0995-0>

516