

Swelling pressure development and inter-aggregate porosity evolution upon hydration of a compacted swelling clay

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1 Swelling pressure development and inter-aggregate porosity evolution

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Abstract

A specific oedometer cell has been set up to measure the swelling pressure of compacted montmorillonites at constant volume and to concomitantly visualize the evolution, upon wetting, of how the microstructure is organised through X-ray microtomography. The swelling pressure experiments were conducted with solvents of various natures. In addition to conventionally used water and saline solutions, we used an organic solvent (methyl methacrylate – MMA). We chose this to explore the effect of its different physical and chemical properties, and to differentiate the respective roles of crystalline and osmotic pressures on macroscopic swelling behaviour.

The results, which combined both swelling pressure measurements and quantification of microstructure evolution upon hydration for the two different solutes, give sound understanding on the development of osmotic and/or crystalline swelling and their relative impact both on the microstructure and on the magnitude of the macroscopic swelling pressure of compacted montmorillonites.

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1 Introduction

Clays are of importance for many geo-mechanical environments: they are ubiquitous on Earth's surface, where they play an important role in soil stability. They are also commonly used as engineered barriers or backfill materials in the design of waste disposal repositories (Kaufhold et al., 2015). The main properties that swelling clays such as smectites offer to limit pollutant transfer and ensure the mechanical stability of engineered constructions include ion adsorption capacity, sealing ability, and low permeability. Depending on the context, fluids of different natures (e.g. alkaline, acid, salty) may interact with clay materials. We need to understand the driving force responsible for the underlying clay swelling to optimize engineered barrier behaviour. Therefore, to assess performance, we have to understand swelling pressure development in situations close to field conditions. Swelling behaviour in bentonites is mainly related to the presence of montmorillonites, a clay mineral made of 2:1 layer structure in which one octahedral sheet is sandwiched between two tetrahedral layers (Figure 1). Due to isomorphous substitutions involving either the tetrahedral or the octahedral sheet, the clay unit layer bears a structural negative charge, which is balanced by cations adsorbed on layer surfaces in the interlamellar spaces. The particular behaviour of clay with respect to water or aqueous solutions results from cation hydration, but is also influenced by how the sheets are turbostratically stacked to form particles (Bergaya and Lagaly, 2013). For a clay system in contact with an aqueous solution or a humid atmosphere, two main processes contribute jointly to control the overall swelling in the materials: crystalline swelling and osmotic swelling (Laird et al., 1995; Madsen and Müller-Vonmoos, 1989; Norrish, 1954). Crystalline swelling happens at the nanometric level for the lowest water contents (undersaturated systems). From an initially dry state, hydration occurs on the most energetic sites, i.e. on unit layer surfaces (both on particles' external interfaces and in interlayer spaces) and on interlayer cations (Bérend et al., 1995; Cases et al., 1992; Rinnert et al., 2005). This latter phenomenon of cation solvation results in the successive adsorption of several water layers in the interlamellar spaces and leads to separation of clay unit layers that can be followed by the measurement of the basal spacing (d_{001}) using X-ray diffraction (XRD).

Several authors, for instance Lloret et al. (2003), Ferrage et al. (2005), Likos and Wayllace (2010), 62 Holmboe et al. (2012) and Villar et al. (2012), have shown that for Na-montmorillonites the basal 63 spacing d_{001} evolves from 9.7 Å in the dry state to 12.6 Å, 15.6 Å and 18.6 Å corresponding to one, two, 64 or three water layers, respectively, as the relative humidity increases. Crystalline swelling is influenced 65 by different parameters such as interlayer cation nature, relative humidity or water activity, dry density 66 and swelling conditions (free or confined) (Di Maio, 1996; Di Maio et al., 2004; Imbert and Villar, 2006; 67 68 Karnland et al., 2011; Karnland et al., 2008; Karnland et al., 2006; Karnland et al., 2007; Kaufhold et al., 2015; Komine and Ogata, 1994, 1996, 2003; Komine et al., 2009; Lloret et al., 2003; Pusch, 1982; 69 70 Schanz and Tripathy, 2009; Sridharan et al., 1986; Studds et al., 1998; Villar et al., 2012; Villar and 71 Lloret, 2008). 72 In addition to crystalline swelling, the other process that comes into play during hydration is osmotic 73 swelling. This occurs for higher water contents (water activities above 0.8-0.9 and in saturated systems) 74 and corresponds to a further ingress of water in the materials (Madsen and Müller-Vonmoos, 1989). The 75 driving force for osmotic swelling is the repulsion between the electrical diffuse double-layers that form 76 on platelet surfaces (Chapman, 1913; Gouy, 1917; Gouy, 1910; Stern, 1924). For smectites exchanged 77 with monovalent cations, osmotic swelling manifests itself by clay platelet separation distances larger 78 than 40 Å and that can progress continuously towards infinity for very dilute suspensions (Meleshyn 79 and Bunnenberg, 2005; Michot et al., 2004; Norrish, 1954). For divalent smectites (Ca- or Mg-80 montmorillonite), osmotic swelling seems to be prohibited in the interlayer spaces due to strong ion-ion 81 correlation forces that reduce double-layer repulsion (Kjellander et al., 1988; Wang et al., 2011). For divalent montmorillonite, the greatest basal spacing measured does not exceed 19 Å (Holmboe et al., 82 2012; Michot et al., 2013; Norrish, 1954). Even if basal distances are limited to 19 Å, Ca-83 84 montmorillonite may continue to accommodate additional water that cannot enter the interlamellar 85 spaces and that is found outside particles. This phenomenon is called "inter-particle osmotic swelling" and is linked to osmotic forces that may exist on the particles' outer surfaces (Madsen and Müller-86 87 Vonmoos, 1989; Segad et al., 2010), meaning that the interlamellar spaces are not the only places that 88 play an important role in the swelling behaviour of clay materials but particles' external surfaces have also to be taken into account (Laird, 2006; Liu, 2013; Madsen and Müller-Vonmoos, 1989). 89

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From this we conclude that regardless of the swelling mechanism and whatever the cation nature, hydration will induce major reorganization in both the clay fabric and the associated porosity. That is why we must refer to porosity when we speak of swelling. Many studies (Bihannic et al., 2009; Bihannic et al., 2001; Cases et al., 1992; Keller et al., 2013; Likos and Wayllace, 2010) have focused on the porosity description. They used various investigative techniques (XRD, SAXS/SANS, FIB/SEM, MIP), and from those results, we can schematically consider the total porosity to be composed of pores of different sizes (Figure 1) such as the interlayer space, the porosity between particles (inter-particle porosity) and the porosity between aggregates (inter-aggregate porosity). The effect of hydration on microstructure has been described (Delage et al., 2006; Devineau et al., 2006; Tang et al., 2011; Van Geet et al., 2005) but often only considering one or two porosity levels, e.g. inter-aggregate and/or interlayer porosity. Globally, for sodium-dominated clays, hydration leads to widening of interlayer spaces with an associated decrease in inter-aggregate porosity. Some authors (Kozaki et al., 2001; Pusch and Yong, 2006; Tomioka et al., 2010) explain this process by the formation of gel structure on the outer part of the particle/aggregate and/or by exfoliation of the particles (Cui et al., 2002; Pusch, 1982). Indeed it has been observed that hydration leads to a decrease in the number of layers per particle (Bérend et al., 1995; Perdrial and Warr, 2011; Saiyouri et al., 2004). Hydration has consequences on clay microstructure organisation and pore distribution, and consequently it also impacts materials' mechanical properties, especially in confined or compacted conditions. In that case, as macroscopic swelling is prevented, swelling pressure develops in the materials. Its amplitude is again related to the nature of the exchangeable counterions and the ionic strength of the solutes, but also to the material's dry density. Some authors (Brackley, 1973; Gens et al., 2011; Imbert and Villar, 2006; Pusch, 1982; Schanz and Tripathy, 2009) have shown that for samples with dry density of between 1.2 and 2.0 Mg/m³, swelling pressure behaviour upon wetting is non-monotonic. It reaches a peak, then falls significantly and rises to a value that remains stable over time. Push (1982) suggested that this behaviour could be related to the clay fabric being modified upon hydration. Validating this hypothesis remains difficult as most of the microstructural studies are conducted either on samples submitted to a specific preparation procedure (freeze drying, solvent exchange, etc.) that may have altered their fabric (Delage et al., 2006; Holzer et al., 2010), or without any concomitant determination of materials' macroscopic

mechanical properties (Van Geet et al., 2005). Most of the time microstructures are only observed once the sample reached the final steady state, without intermediate observations between the beginning of wetting and the final stage. These kinds of experimental conditions limit the understanding of the relationships between fabric modifications upon wetting and swelling pressure development but it has been established that this mechanical behaviour is influenced by water uptake (Harjupatana et al., 2015) and induced physicochemical phenomena occurring at different porosity scales: (1) interlayer, (2) inter-particle and (3) inter-aggregate (Bérend et al., 1995; Laird, 2006; Madsen and Müller-Vonmoos, 1989; Perdrial and Warr, 2011; Saiyouri et al., 2004). In this context, the main objective of our study was to analyse the relationship between swelling pressure development and the associated microstructure evolution induced by wetting. A new oedometer cell, transparent to X-ray, was designed both to monitor swelling pressure over time and to visualise interaggregate porosity changes through X-ray micro-computed tomography (µCT), on a unique specimen. During µCT, the mechanical constraint was kept on the sample, thus limiting disturbance related to its preparation (e.g. sample decompaction, or sample dehydration). A commercially purified montmorillonite was used to perform the experiments. Homo-ionic water solutions with two ionic strengths and a polar organic solvent were considered to analyse the relative impact of osmotic and crystalline swellings on the clay fabric and to tentatively relate microstructural changes to swelling pressure development.

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2 Material and methods

2.1 Kunipia-G, Japanese swelling clay

A smectite provided by Kunimine Industries was used for this study (Table 1). This material, available as Kunipia-G grade, is a highly pure montmorillonite (>95%) (Fukushima, 1984; Kozaki et al., 1999; Sato, 2008; Sato et al., 1992; Wilson et al., 2004) and has among others the advantage of avoiding long purification steps to remove secondary mineral phases. Powder X-ray diffraction (XRD) patterns indicate traces of quartz and carbonates (Figure 2). Examination of the 060 band at 1.49 Å indicates that

145 Kunipia-G is a dioctahedral smectite. XRD patterns obtained on oriented preparations recorded in air-146 dried conditions after ethylene glycol solvation or after temperature increase (550°C) show that (i) the 147 basal spacing recorded in the air-dried state is compatible with a Na interlayer counterion, (ii) a rationality of the 001 reflections (Figure 2a) proving the absence of illite/smectite mixed layered 148 149 minerals. The cation exchange capacity (CEC) determined by the chloride cobaltihexamine 150 displacement method (Orsini and Rémy, 1976) is 115 mequiv/100g with the following distribution of 151 exchangeable cations: Na 91%, Ca 8%, K 1.0%. The chemical formula, 152 $Na_{0.41}K_{0.01}Ca_{0.04}(Si_{3.92}Al_{0.08})(Al_{1.51}Mg_{0.37}Fe_{0.12})0_{10}(OH)_2, nH_2O$, derived from X-ray fluorescence 153 (XRF), is compatible with previous studies (Fukushima, 1984; Sato, 2008; Sato et al., 1992; Wilson et 154 al., 2004). The dry particle density of Kunipia-G is 2.71 Mg/m³. 155 The specific surface area determined from a nitrogen adsorption experiment using the BET equation 156 (Brunauer et al., 1938) is 42 m²/g, similar to the specific surface area (SSA) founded by Kozaki et al. 157 (1999). The water sorption isotherms (data not shown) have a typical shape for swelling clays and particularly for Na-exchanged smectites, with two steps on the water adsorption curve (Cases et al., 158 159 1992). Considering the desorption branch of the water isotherm, and assuming that in this state all the 160 interlayers are accessible, applying BET formalism gives an estimated total surface area of around 524-660 m²/g. This estimation agrees with the ethyleneglycolmonoethylether (EGME) measurement (Kozaki 161 162 et al., 1999).

2.2 Experimental strategy: new tomographic oedometer to follow both

swelling pressure and inter-aggregate pore evolution

2.2.1 Tomographic oedometer cell features

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A new oedometer device has been developed to continuously monitor swelling pressure during the hydration process, and to image, at selected swelling stages, the specimen structure using X-ray microcomputed tomography (μ CT) (Figure 3). The designed cell has been built with polyether ether ketone (PEEK), which is a material with limited X-ray attenuation and that can sustain high swelling pressure with very low deformation. TECAPEEK CF 30 grade, provided by Ensinger®, was used due to its improved mechanical strength with 30% carbon fibre (Young's modulus: 18.5 GPa, yield stress:

215 MPa). The cell is composed of three parts: a ring and two pistons. Compared to standard oedometer
cells, the sample diameter was reduced to 10 mm in order to obtain the best possible resolution taking
into account the shape and size constraints (distance of the sample relative to the X-ray source and to
the charge coupled device (CCD)). The initial sample height was set at 10 mm. The dimensions of the
complete device were adapted to the available space in the X-ray tomograph (Phoenix Nanotom®).
Under these conditions, μCT images were recorded with a voxel size of 5 micrometres.
2.2.2 Simultaneous in situ measurement of both swelling pressure and sample
microstructure at the X-ray tomography scale
The cell was placed on a load frame to monitor sample swelling pressure. The solution was injected (50
kPa) at the lower side of the sample with a pressure-volume controller. All the tests were performed
under constant volume conditions. A closed-loop control kept the sample height constant, i.e. we had
constant volume conditions, by adjusting the vertical load exerted on the sample during the wetting. All
the experiments were conducted at a temperature of 20 ± 1.5 °C. Vacuum was imposed inside the pistons
before the beginning each test to avoid air bubbles being trapped at the base of the sample, or in the
lower piston.
An experimental protocol was defined to remove the cell from the loading frame to perform X-ray
tomography acquisition. It consisted in stopping fluid injection, screwing the cell to prevent any
volumetric sample deformation and placing the whole in the tomograph. The entire scanning process
lasted between 3 and 4 hours. In total, five points were selected at specific times on the swelling curve.
The impact of that protocol on material behaviour has been assessed and is discussed later in this paper.
2.2.3 Image processing and inter-aggregate porosity (at a 5 μ m resolution scale)
extraction
Images were recorded using a Phoenix Nanotom® tomography system and its 180 kV/20 W nanofocus
X-ray tube. Scans were performed at 80 kV and 75 μA with 2880 projections to cover 360° (angle step
of 0.125°). During X-ray tomography scans, the Coupled Charge Device (CCD) recorded the intensity I
of the X-ray beam passing through the specimen to reconstruct a 3D-volume after mathematical
reconstruction based on back-projection.

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200 greyscale from 0 (black) to 255 (white), which is linked to the X-ray attenuation by the specimen: the 201 higher the attenuation, the higher the intensity, i.e. a solid medium (such as our Kunipia-G) has a higher 202 grey value than macropores. For each sample, a sub-volume of the same size (450 x 1400 x 1800 pixel³) 203 was extracted from the same position (Figure 4a). The aim was to reduce the amount of data we had to 204 analyse and to optimize the volume of interest (VOI). The VOIs are 9 mm tall (1800 pixels) excluding 205 0.5 mm at both ends of the sample because the conical shape of the beam means these parts are not 206 illuminated similarly to the rest of the sample. 207 The inter-aggregate porosity was quantified along the height of the specimen (z-profile) using an image 208 analysis procedure that was adapted to extract the pores from the solid skeleton of the 3D computed 209 volumes. Image quality was first enhanced by applying (i) a contrast and brightness adjustment 210 spreading the histogram and (ii) a classic Gaussian Blur 3D filter with a radius of 2 pixels to reduce 211 noise. To separate these pores from the surrounding clay matrix, the maximum gradient magnitude, 212 which is equivalent to the inflection point of the smooth intensity profile across the interface (due to the 213 insufficient resolution), was enhanced by optimizing the edge of the transition between pores and solid 214 grains. The sharp transition of the greyscale profile across the solid/pore interface was restored from the 215 actual smooth profile by using a local weighted filter. This sharpening filter does not transform the edge 216 position of the object but improves sharpness by increasing acutance (Sheppard et al., 2004). A 217 watershed algorithm (Vincent and Soille, 1991) was then used to separate the pore from the solid in the 218 gradient greyscale images. The watershed separations (markers belonging to the pores and solid) were 219 selected by identifying the slope change of the grey level histogram on its first derivative (Gaboreau et 220 al., 2016; Prêt et al., 2010a; Prêt et al., 2010b). The result of this segmentation at the initial dry state is 221 illustrated in Figure 4. 222 In addition, a morphological characterisation of the pore space distribution with pore size distribution 223 (PSD) was performed using a public domain software iMorph (http://imorph.fr/). The characterization 224 was done in five regions of interest (ROI) of same height (1.8 mm) along the z-profile from bottom to 225 top (ROI1 being close to the solvent inlet at the specimen bottom and, ROI5 at the top).

Each voxel of the reconstructed volume (8-bit) is characterized by its intensity value ranging on a

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2.2.4 Comparison with standard constant volume oedometers

In order to validate the results obtained with the new tomographic oedometer cell, constant volume oedometers were used to characterize the swelling behaviour of Kunipia-G specimens in standard conditions. The basic principle of these devices is to allow sample hydration and to maintain the sample at constant volume while measuring swelling pressure. On the lower side of the specimen, hydration occurs by diffusion during the entire test duration, and the solution is renewed with a peristaltic pump. The height of the sample in these devices was set at 10 mm for diameters of 50 mm or 34 mm. More details on these standard oedometer cells are available in Cuisinier (2002).

2.3 Experimental procedure

2.3.1 Sample preparation and compaction

- The dry density of the specimens compacted in the tomographic cell was set to $1.40 \pm 0.02 \,\mathrm{Mg/m^3}$,
- 237 corresponding to a theoretical total porosity ø of 48% according to the following equation:

$$\emptyset = 1 - \frac{\rho_d}{\rho_s}$$

- where ρ_d is the dry density (Mg/m³) and ρ_s is the particle density (Mg/m³).
- 239 The specimens were statically compacted from a crushed and sieved dry Kunipia-G powder (~1 mm)
- 240 (oven-dried at 105 °C) at a speed of 1.14 mm/min, to the desired dry density.

241 **2.3.2 Solvent selection**

- To assess the effect of the solvents on swelling pressure, two aqueous solutions (NaCl) at two different
- 243 ionic strengths (10⁻¹ and 10⁻⁴ M) and an organic solvent (methyl methacrylate, MMA) were used.
- 244 Saturation with NaCl solutions was to evaluate the coupled development of crystalline and osmotic
- swelling. In our case, at full saturation, considering the chosen dry density (1.4 Mg/m³), the intercalation
- of two to three-water layers in the interlayer spaces is estimated (Holmboe et al., 2012; Villar et al.,
- 247 2012), regardless of the ionic strength of the solution. Salt concentration is mainly expected to affect
- 248 osmotic phenomena.
- 249 MMA was also selected for its physical properties close to those of water (Table 2). MMA is widely
- used to impregnate finely divided solids (Gaboreau et al., 2012; Gaboreau et al., 2011; Gaboreau et al.,
- 251 2016; Prêt et al., 2010a; Prêt et al., 2010b; Prêt et al., 2004; Pusch and Schomburg, 1999; Sardini et al.,

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2009). Given its properties, impregnated MMA samples are described as mimicking a hydrated microstructure (Prêt et al., 2010b; Pusch, 1999; Sammartino et al., 2002) with the intercalation of MMA molecules in clay interlayer spaces (Prêt, 2003; Prêt et al., 2010b). Such behaviour is mainly due to MMA's low viscosity and its dipolar moment close to that of water. Indeed, MMA, like water, is a polar molecule, so apparently leads to interlayer hydration (Blumstein et al., 1970; Tabtiang et al., 2000). A smectite powder saturated with MMA displays basal spacing d_{001} of 17.2 Å (Blumstein, 1965; Prêt, 2003), characteristic of two layers of MMA in the interlayer, mainly though electrostatic dipole-ion interaction with the ester functional group. This was confirmed by powder X-ray diffraction patterns of Kunipia-G samples saturated with MMA (Figure 2b), where d_{001} was found to be 17.1 Å. This d_{001} value is equivalent to a hydration state between two and three water layers when hydration is performed with water solutions. Moreover, no osmotic swelling is detected with MMA, while in the same XRD acquisition conditions (free swelling in a huge solution volume) with a 10⁻³M NaCl solution, large basal d_{001} spacings have been measured, corresponding to osmotic swelling leading to around 21 Å, equal to four layers of water molecules (Holmboe et al., 2012; Michot et al., 2004). Further experiments undertaken at the macroscopic scale showed that the interaction of MMA molecules with clay induced swelling pressure in compacted clay specimens (Pusch, 1999). Therefore, using MMA was a good means of assessing the swelling pressure and the porosity evolution mostly controlled by the influence of the crystalline swelling component, as the osmotic pressure was hindered.

2.3.3 Measurement approach

First of all, experiments were conducted to validate the new oedometer tomographic cell. This was based on comparing results obtained with standard oedometer cells, and literature data. The impact of sample size and the tomography procedure were assessed. These experiments were conducted using NaCl 10⁻⁴ M solution.

Once the cell was validated, experiments were performed to characterise the impact of fluid features on swelling pressure development and on the associated porosity reorganisation. Five experiments were undertaken with compacted Kunipia-G specimens at dry density of 1.4 ± 0.02 Mg/m³ using the tomographic cells. Two experiments were conducted with NaCl 10^{-4} M solutions and two others used NaCl 10^{-1} M, the last run being acquired with MMA. For each run, X-ray tomography scans were

performed at the initial and final states. Intermediate scans were only performed for one specimen of each NaCl ionic strength. In those cases, a first acquisition (t0) was performed just after compaction. Four different scans (t1, t2, t3, t4) were performed to obtain intermediate hydrated states at particular specific times on the swelling pressure curve. The last scan (t5) was performed once steady state conditions were reached. Intermediate scans with MMA as wetting fluid were not conducted because of the high kinetics of hydration process.

3 Results

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3.1 Assessment of the tomographic cell measurements

3.1.1 Comparison with standard oedometers

The swelling pressure measured over time and swelling pressure values at steady state for both the standard oedometer cells and the new tomographic cell were compared. In this sub-section, all the experiments were performed with NaCl 10⁻⁴ M solutions. Swelling pressure first developed a peak reached after a few days (Table 3) and then a plateau (Figure 5a). After the peak, the swelling pressure fell to around 10% of the peak value. Steady state conditions (second maximum value) were then reached. Typically the first peak was obtained between 7.7 and 10.2 days while the steady state occurred after 38 and 48 days. The first maximum was comprised between approximately 1.9 and 2.2 MPa while the steady state values are comprised between 2.7 and 3.5 MPa. The first maximum typically occurred at around 20% of the time needed to reach the steady state and corresponded to about 60% of the stable swelling pressure value. In all cases, the swelling pressure curves obtained with the Kunipia-G hydrated with NaCl 10⁻⁴ M solutions were typical of those described in the literature (Gens et al., 2011; Imbert and Villar, 2006; Komine and Ogata, 2003; Pusch, 1982; Schanz and Tripathy, 2009). The steady state values, i.e. at final stage of the test, were compared to existing literature data obtained with two other types of clays, and to data obtained on Kunipia-G for densities ranging between 1.2 and 1.75 Mg/m³ (Table 3 and Figure 5b). At a dry density of 1.40 Mg/m³, the difference between swelling pressure at peak and at steady state is limited whatever the specimen size (10, 34, 50 mm diameter with tomographic, pressure and injection cell respectively). These results are in line with the study of Gens et al. (2011), Komine et al. (2009), Imbert and Villar (2006) or Volckaert et al. (1996) working with

oedometer cells at different sample sizes. They demonstrated that the size of the sample, diameter rather than height, modifies the kinetics of swelling pressure upon hydration (slower for longer specimens), but does not significantly impact the magnitude of swelling pressure (difference at peak and at final state). Based on these conclusions, a dimensionless representation of the curve displaying the swelling pressure versus time has been used previously to facilitate sample comparison. The y-axis corresponds to the ratio of swelling pressure to swelling pressure at the plateau and the x-axis is the ratio between time to the time of peak occurrence.

3.1.2 Effect of intermediate tomography scans

The impact of intermediate tomography scans was assessed by comparing swelling pressure curves determined in the new oedometer cell of specimens hydrated by 10⁻⁴M and 10⁻¹M NaCl with and without intermediate scans (Figure 6 and Table 3). Swelling pressure curves of samples subjected to tomography scans fit well to the swelling pressure evolution of the test undertaken without tomography acquisition. As described previously, swelling pressure evolution is non-monotonic: the peak swelling pressure reached around 65% of the swelling pressure at steady state with or without intermediate scans. Slight differences over time are observed for the specimen hydrated by NaCl 10⁻¹ M solution. The kinetics of swelling pressure over time of this specimen subjected to intermediate tomography scans were slightly impacted by the intermediate scans, but the peak appearance was at 20% of the total time to reach the plateau as it was with the other tests and the swelling pressure value at the peak is comparable (68% of the final value).

Thus, the experimental procedure used to assess both swelling pressure and porosity with intermediate scans has limited impacts on swelling pressure development in the compacted samples as a function of time from the beginning of hydration.

3.2 Effect of fluid features on swelling pressure

3.2.1 NaCl hydration at various ionic strengths

The shapes of the swelling pressure curves for specimens hydrated with 10⁻¹ M NaCl solutions (Figure 6) are similar to those recorded with 10⁻⁴ M NaCl solutions. The non-monotonic behaviour is also observed, with a peak before reaching a stable plateau. The swelling pressure peak was observed at a

time equivalent to 20% of the time needed to reach the maximum, and the value corresponded to about 66% of the final pressure irrespective of ionic strength (Table 3). Nonetheless, we see (Figure 7) that the higher the ionic strength, the lower the swelling pressure at peak and at steady state (30% lower with Na 10⁻¹ M than Na 10⁻⁴ M). These results, in accordance with previous studies (Karnland et al., 2006; Karnland et al., 2007; Pusch, 1982), are related to the development of repulsion between the electrical double layers whose thickness is reduced at higher ionic strength (Norrish, 1954; Santamarina et al., 2002). Consequently, the osmotic pressure also falls at higher ionic strength.

3.2.2 MMA hydration

With MMA injections, swelling pressure increases sharply over time, almost instantaneously, to reach a plateau within a few minutes (Figure 7). The maximum swelling pressure value is significantly higher (3.10 MPa) with MMA as hydrating fluid than those measured with 10^{-4} or 10^{-1} M NaCl solutions. The experiment was stopped sooner than for the samples hydrated with NaCl solutions since the steady state was reached after 15 days. The slight variations observed in steady state can be explained by the sensitivity of MMA fluidity to slight temperature variations in the room (20° C± 1° C).

3.3 Tomography results

The X-ray tomography images recorded for the Na 10⁻⁴ M specimen are displayed in Figure 8a. For clarity, only four times were selected. The fabric observed in the initial state before the beginning of hydration is an entangled multi-layered structure, characterized by darker zones that may be assigned to pores. The pores are anisometric and ellipsoidal and the largest are some hundreds of microns long and a few tens of microns wide. Pores are oriented with their biggest size perpendicular to the compaction axis. This type of layered structure is uniformly distributed throughout the entire specimen. For the first point visualized during hydration, which is in the rise of the curve before the peak (t1), some changes are observed in the lower part of the image. The contrast between pores and the particles that separate them is greatly reduced, giving an impression of a homogeneous structure. This lowest part of the specimen is the one that is first hydrated by water. As hydration and swelling progress, this homogeneous zone extends on the image, with some tenuous remaining traces of the initial status in the

upper part of the images recorded at t3 (minimum position after the peak) and then complete
homogenisation on the plateau (t5).
While the same porosity modification trends can be observed for the sample hydrated with the second
ionic strength (Figure 8b), the evolution is different with MMA. With MMA, due to the rapid increase
in swelling pressure, only the final state was imaged (Figure 8c). Wetting with MMA does not lead to
the homogenization observed with water. Contrasting zones remain, with a shape and orientation that
seem more isotropic than in the initial state. The distribution along the vertical axis is uniform, without
the gradients that were observed in the intermediate steps during water hydration.
To analyse μCT pictures further, an image pre-processing step (see section 2.2.3) was applied for
binarizing the images and extracting inter-aggregate porosity. The porosity as defined corresponds to
the areas that have sufficient contrast with respect to the clay matrix to be distinguished from it, and
have spatial resolution greater than 5 microns. For the initial states after compaction, the μCT porosity
calculated in this manner corresponds to 38-39% of the total volume of the specimen whose total
theoretical porosity is 48%. These results are very comparable to other swelling clay like the case of
MX-80 as shown by Gens et al. (2011) at the same dry density from MIP data (inter-aggregate porosity:
37%, total porosity: 48%). This means that the thresholding procedure is valid for estimating the inter-
aggregate porosity, in agreement with results found in the literature and derived using other techniques
(MIP, nitrogen adsorption) on different swelling clays.
In addition, we deduce the inter-aggregate porosity evolution versus specimen height (Figure 9a and
Table 4). Initially, a slight inter-aggregate porosity gradient is observed along the vertical axis inside the
specimen. The inter-aggregate porosity increased from about 37% on the top up to more than 45% on
the bottom. Both ends are also slightly over-compacted. This is related to the compaction procedure,
and this effect has been well described in the case of compacted soils (Eslami, 2014; Tisot, 1974; Winter
and Clarke, 2002). These effects of the compaction procedure were comparable for all the samples
prepared in the context of that study. From morphological analysis (Table 5), the gradient is also
noticeable with a pore size reduction in the upper part of the sample (ROI 3 to 5). In this initial state, the
mean aperture radius is of 15.6 μm.

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The µCT inter-aggregate porosity profiles derived at the intermediate stages of hydration with Na 10⁻⁴ M solution show that the swelling pressure development is associated with reduced inter-aggregate porosity. For t1 and t2, this porosity decrease is not uniform along the specimen z-axis; the reduction is much greater in the lower part of the specimen, i.e. close to the water inlet (from 45% in the initial state to a few percent in the hydrated state), whereas less uniform inter-aggregate porosity reduction occurred in the upper part of the sample (porosity is reduced by half for distances greater than 6 mm from the inlet). Between these two zones a gradient was observed. On average, more than 75% of the interaggregate porosity volume was reduced when the first peak of swelling pressure was reached. At t3 the inter-aggregate porosity distinguishable with µCT was lower than 3%, and this time corresponded to the minimum swelling pressure reached after the first peak. The swelling pressure increased between t3 and the final stage occurred without any major change to porosity profile except a slight decrease in the mean value: the profiles display similar shapes at t3 and at the end of the test. The decrease of the detected porosity is also combined to a reduction of the inter-aggregate pore size (Table 5). At t1 and t2, the reduction of the inter-aggregate pore size is greater in the lower part of the specimen (mean aperture radius around 8.0 µm) than in the upper part (mean aperture radius around 12.0 µm). At t3, no difference is observed between lower and upper part with a mean aperture size of 8.0 µm. After t3, a slight decrease of pore size is noticed (mean aperture size of 7.5 μm). The impact of ionic strength is less obvious on the µCT porosity profiles (Figure 9b and Table 4) and the pore morphology (data not shown) than on the swelling pressure values. In the case of the sample hydrated with MMA, only the scans before and at the end of the tests were performed. At the end, some macropores defined by a size larger than 5 µm and a contrast different from the clay matrix, still remained, all over the specimen height (Figure 9c). A slight gradient was observed, probably resulting from sample preparation. The average porosity was about 8%; this value was significantly higher than the one derived after water hydration (Table 4). At this final state, the pore morphology (Table 5) shows also the gradient with bigger pore size in the lower part (ROI1) than in the upper part of the specimen (ROI5). The final state of the specimens hydrated by MMA is associated with larger pores at 8.1 µm.

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4 Discussion

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Kunipia-G's swelling pressure was monitored for two different solvents (sodium chloride and MMA). 416 417 In the case of NaCl, the ionic strength has been varied from 10⁻⁴ to 10⁻¹ M. During swelling pressure 418 development, changes in the structure (inter-aggregate pores) were visualised using micro-tomography. 419 The main experimental observations are the following (Figure 10): 420 • in the case of MMA, the swelling pressure abruptly increases before levelling off. On the contrary, 421 for hydration with a NaCl solution, the swelling pressure first increases, reaches a local maximum, 422 then decreases and rises until reaching a plateau (Figure 7); 423 for NaCl, the maximum value reached at the plateau is lower for the highest ionic strength, whereas 424 the shape of the swelling pressure curve does not depend on the salt concentration (Figure 7); 425 a correlation exists between the fabric heterogeneities observed in the sample at the resolution of 426 tomographic scans (inter-aggregate pores) and the macroscopic evolution of the swelling pressure; 427 although in the case of MMA it is still possible to detect some inter-aggregate porosity by X-ray 428 tomography at the apparatus' resolution (5 µm) even on the steady state, for NaCl, whatever the ionic 429 strength, the inter-aggregate porosity has disappeared at the dip that appears after the swelling 430 pressure decreases and before it increases again (Figure 9). Nevertheless, in all the cases, the decrease 431 of inter-aggregate porosity is linked to an evolution of the initial anisotropic pore distribution with 432 the obvious development of pores with size lower than the resolution. Some of these differences observed between samples hydrated by water solution or by MMA can be 433 434 explained by MMA's properties. In particular its low viscosity and low surface tension (Table 2) increase the wettability of the solvent injection in the sample and consequently the swelling pressure 435 436 kinetics. 437 The following discussion focused on the experimental results summarised above, aims at understanding 438 (i) the inter-aggregate porosity changes and (ii) the non-monotonic swelling pressure evolution with 439 peak occurrence.

4.1 Processes responsible for inter-aggregate porosity decrease

As already discussed in the introduction, the main processes that generally operate in concert to control bentonite swelling in aqueous systems are crystalline (interlayer) swelling and osmotic swelling (both double-layer at the inter-particle and the inter-aggregate level); the second process leading to break-up the initial dry particles into thinner ones. Based on the work of Liu (2013), these two contributions can be evaluated from its model for the Kunipia-G material used in this study (Figure 11a). Whereas the crystalline pressure is empirically related by an exponential law (see equation 26 and the related one in Liu (2013)) to the length of the diffuse double layer (DDL) between two montmorillonite particles (reflecting the decay of the hydration forces as the distance increases), the osmotic pressure can be derived by applying the Gouy-Chapman theory according to the following equation issued from Liu (2013).

$$P_{DDL} = 2cRT(\cosh y^{m}-1)$$

Where c is the ionic concentration of the pore solution in mol/m³, R is the gas constant, T is the absolute temperature in Kelvin and y^m is the scaled midplane potential at the midpoint between unit layers. In this approach, an important parameter, the Deybe length, which can be considered as an estimate of the double layer thickness, has to be used. The Debye length is square root dependent on the relative dielectric constant of the pore solution. Considering that MMA's relative dielectric constant is about 12 times lower than water's (6.32 versus 78.54, see Table 2), calculation shows (Figure 11b) that for a dry density of 1.4 Mg/m³, the osmotic pressure developed with MMA is one order of magnitude lower than that obtained with water (NaCl, both 10⁻⁴ and 10⁻¹ M), reaching a negligible pressure (0.4 MPa) compared to the total pressure measured (3 MPa).

The first conclusion that can be derived from this simple calculation is that in the case of MMA the main process that operates is crystalline swelling. The second is that, in the case of sodium chloride solution, the calculated osmotic pressure is approximately 2.65 MPa for ionic strength of 10⁻⁴ M and 2.16 for 10⁻¹ M. These values are very close to the values that are measured during our experiment after reaching a steady state (Figure 7 and Figure 11b). Introducing crystalline pressure into the calculations, the main

contribution at the working density is given by osmotic processes (Figure 11a and b). In the case of MMA, crystalline pressure cannot be calculated because no isotherm data are available with MMA but it contributes mainly to the total swelling pressure as the osmotic component is negligeable (Figure 11b). Hydration of Kunipia-G specimens by saline solutions induces particle breakup due to osmotic component with major aggregate reorganisation. This could explain partly the inter-aggregate porosity reduction seen by μ CT (Figure 8a and b). In contrast, for specimens hydrated by MMA, only crystalline swelling occurs which does not lead to particle breakup, probably explaining the slighter inter-aggregate porosity decrease observed by μ CT (Figure 8c). The assumption made concerning particle breakup leading to inter-aggregate filling is confirmed by literature results (Perdrial and Warr, 2011; Saiyouri et al., 2004), nevertheless further investigations at lower scale (FIB/SEM, TEM) may ensure that (currently conducted).

4.2 Explanation of peak occurrence

Several assumptions have been made to describe the non-monotonic swelling behaviour of smectiterich material related to inter-aggregate pore evolution. For instance, Pusch (1982) related the swelling pressure peak to the formation of gel structures upon wetting that modify the mechanical characteristics of aggregates/particles (shear strength) and decrease the swelling pressure. This has been integrated by Alonso et al. (1999) in the Barcelona Expansive Model (BExM), with the progressive reorganisation of the internal structure of samples upon wetting. Progressive filling of the macrostructure (inter-aggregate void ratio decrease) occurred. Gens et al. (2011) modelled this process, based on tests performed on FoCa clay compacted at 1.45 Mg/m³. They showed that the modelled non-monotonic swelling pressure is linked to the modelled reorganisation of inter-aggregate porosity. This reorganisation is progressive upon wetting with remaining inter-aggregate porosity of 25% at the end of the test. Figure 12 shows that the kinetics of observed inter-aggregate porosity decrease of our Kunipia-G's specimen wetted by NaCl 10⁻⁴ M agree with the evolution of the FoCa clay at different specimen heights (lower, middle and upper part). Nevertheless the extent of the porosity decrease is different, with almost total filling of the interaggregate porosity with the Kunipia-G sample. A possible explanation for this difference may be linked

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to the difference in mineralogy of both materials. FoCa is only made of 45% swelling clay, the remaining mineral being kaolinite, whereas Kunipia-G contains 95% of smectite. Another explanation could be relied to the BBM definition with the interaction function between microstructure elastic deformation and macrostructure plastic deformation. Thus, from our results and the above comparison with BEXM model, we can suppose the non-monotonic behaviour with peak occurrence is related to the progressive inter-aggregate porosity reorganisation. This may be linked directly to the particle-solvent interaction introduced previously in the discussion, in other words to the crystalline and osmotic swellings. Regarding hydration processes, Wang et al. (2013) conducted wetting experiments on a specimen composed of a 7/3 MX80/quartz dry mass mixture to assess the evolution of the relative humidity versus specimen height. They concluded that specimens hydrated by aqueous solutions are not subject to the same water transfer between the lower part in contact with fluid and the upper part. Liquid water transfer occurs in the lower part whereas above the hydration front vapour water transfer prevails (Pusch and Yong, 2003). Moreover, Ichikawa et al. (2004) have followed the change in d spacing with an in situ XRD apparatus called a 1-D consolidometer for a dry density of 1.4 Mg/m³ and loading of 1.9 MPa (close to the measured swelling pressure in our experiment). They have described two consolidation stages. Firstly, external pore water is drained, and the state of three water layers' hydration causes a large displacement; secondly two water layers of hydration are detected, increasing with time; and finally in the final stage the water layers of hydration remain constant while the displacement is still increasing. In this latter stage the interlayer water is drained. In the case of MMA the intercalated layers are always limited to two, leading to basal spacing mimicking 2-3 water layers. Like vapour water hydration (Tang et al., 2011), the intercalation of two MMA molecule layers into the interlayer spacing (Figure 2b) leads to swelling of particles filling up the inter-particle porosity with limited closure of inter-aggregate porosity. Such swelling development without the momentary decrease of swelling pressure over time has been also observed under RH regimes when particle swells without total interaggregate porosity filling (Likos and Wayllace, 2010; Tang et al., 2011). Instead of microstructure reorganisation in between the aggregates, the intercalation of water layers inside and between particles leads to their swelling, which fills up the inter-aggregate pores. Depending on the ionic strength this

particle reorganisation can be described as gel formation with the exfoliation of particles situated on the outer surface of the aggregates (Kozaki et al., 2001; Pusch and Yong, 2006; Tomioka et al., 2010). We should note that this explanation only stands for monovalent cations, and solutions with low ionic strength.

Considering these data, osmotic component (P_{DDL}) is mainly the physical driving force leading to the reorganization of the microstructure and cumulative mechanisms are responsible for the non-monotonic swelling pressure evolution upon hydration. Visualising the structure by tomography corroborates the assumption of reorganization already made, mainly when osmotic phenomena may develop. Unfortunately, the spatial resolution of this technique does not allow qualifying or quantifying this new arrangement at a smaller scale.

5 Conclusion

In this study, the specific experimental procedure conducted with a newly designed innovative oedometer allowed us to assess the evolution of swelling pressure and inter-aggregate porosity upon hydration at the same time (and for the first time as far as we know). From X-ray tomography scans and image post-processing, we can correlate between both parameters. The inter-aggregate porosity diminished from the start of the test until the minimum after the peak is reached. Then, water redistribution inside the structure leads to reaching a stable swelling pressure. Moreover, controlling the swelling pressure at a particle scale via the use of various fluids (NaCl at two ionic strengths and MMA) aimed to differentiate between the impact of crystalline swelling and osmotic swelling on swelling pressure development. Two behaviours of swelling pressure developments were observed according to the different solvents with non-monotonic and monotonic evolutions according to saline solutions and MMA inlets, respectively. Because this non-monotonic behaviour is not seen with MMA, where calculation has shown that the osmotic pressure is negligible (crystalline contribution), the non-monotonic swelling pressure development was found to be due to the osmotic pressure under the hydration front of the compacted sample, leading to reorganisation of the microstructure with filling of part of the inter-aggregate porosity; combined phenomena could be both responsible for the drop in

548	swelling pressure. A comparison with the BExM model shows a similar correlation between swelling
549	pressure and inter-aggregate porosity reorganisation upon wetting.
550	Further investigations performed on a smaller scale (from μm to nm) will allow assessment of the inter-
551	aggregate pores of size smaller than 5 μm and the number of layers per particle at full saturation in
552	compacted samples and will lead both to improvement in how we understand our system and to
553	connections across the different scales.
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1 TABLES

2

5

3 Table 1. Relevant features of Kunipia-G

Sodium smectite
95%
1-2% carbonates
2-3% quartz
2.71
115.0
91% Na, 8% Ca, 1% K
524-660
321 000
42

6 $\,$ Table 2. Physical features of water and methyl methacrylate (MMA) at 20 $^{\circ}\mathrm{C}$ (Blumstein,

7 1965; Prêt, 2003; Prêt et al., 2004; Siitari-Kauppi, 2002)

8

Water	(MMA)
1.85	1.7
2.65	3.8
1.002	0.584
0.998	0.94
80	6.32
72.10 ⁻³	28.10 ⁻³
	1.002 0.998 80

Table 3. Swelling pressure and normalized swelling pressure of various specimens at dry density 1.40 ± 0.02 Mg/m³ at peak and at steady state of the conducted tests

			Т	ime	Swe	elling	Normalised	Nor	malised
		Ionic	•	mic	pre	ssure	time	swellin	g pressure
		strength	Peak	Steady state	Peak	Steady state	Peak	Peak	Steady state
		mol/L	day	day	МРа	МРа	-	-	-
Standard cell	(ø 34 mm)	Na 10 ⁻⁴	7.7	43.2	2.18	3.45	0.18	0.63	1
Standard cell	(ø 50 mm)	Na 10 ⁻⁴	8.0	48.0	1.87	3.07	0.17	0.61	1
	No intermediate scan	Na 10 ⁻⁴	10.2	38.8	1.89	2.68	0.26	0.71	1
Tomographic	Intermediate	Na 10 ⁻⁴	8.1	34.0	1.75	2.73	0.24	0.64	1
cell	No intermediate scan	Na 10 ⁻¹	11.2	45.0	1.19	1.91	0.25	0.62	1
	Intermediate	Na 10 ⁻¹	6.4	27.7	1.34	1.96	0.23	0.68	1

Table 4. Mean inter-aggregate porosity (%) of specimens at dry density 1.40 ± 0.02 Mg/m³ hydrated with NaCl 10^{-4} M, NaCl 10^{-1} M and MMA using tomographic cell in the different hydration states.

=		Na 10 ⁻⁴			Na 10 ⁻¹		MMA
-	Time	Normalised	Mean	Time	Normalised	Mean	Mean
-	day	time	porosity %	day	time	porosity %	porosity %
t0	0	0.0	38	0	0.0	38	38
t1	7.1	0.2	14	4	0.1	19	
t2	8.8	0.3	10	7.2	0.3	9	
t3	15.8	0.5	3	14.1	0.5	2	
t4	19.7	0.6	1	23.8	0.9	0	
t5	39.8	1.2	0	38.8	1.4	1.4 0	

Table 5 Mean aperture radius of the inter-aggregate pores calculated from PSD of the specimens hydrated by NaCl 10⁻⁴ M and MMA. Calculations are performed in five ROIs across the specimen height (Z-location: ROI1 0.5-2.3 mm, ROI2 2.3-4.1 mm, ROI3 4.1-5.9 mm, ROI4 5.9-7.7 mm, ROI5 7.7-9.5 mm). Only the data from the tomography stages t0, t1, t3 and t5 related to the images of the Figure 8 are given.

		Na10-4				
t0	ROI1	ROI2	ROI3	ROI4	ROI5	Mean
Mean aperture radius (μm)	17.2	16.0	14.8	15.0	14.9	15.6
t1	ROI1	ROI2	ROI3	ROI4	ROI5	Mean
Mean aperture radius (μm)	8.0	9.6	10.9	11.8	11.9	10.4
<i>t</i> 3	ROI1	ROI2	ROI3	ROI4	ROI5	Mean
Mean aperture radius (μm)	7.9	7.8	7.8	8.1	8.2	8.0
<i>t</i> 5	ROI1	ROI2	ROI3	ROI4	ROI5	Mean
Mean aperture radius (μm)	0	0	0	0	0	0
		MMA				
t5	ROI1	ROI2	ROI3	ROI4	ROI5	Mean
Mean aperture radius (μm)	8.3	8.2	8.0	8.0	7.8	8.1

Figure Captions

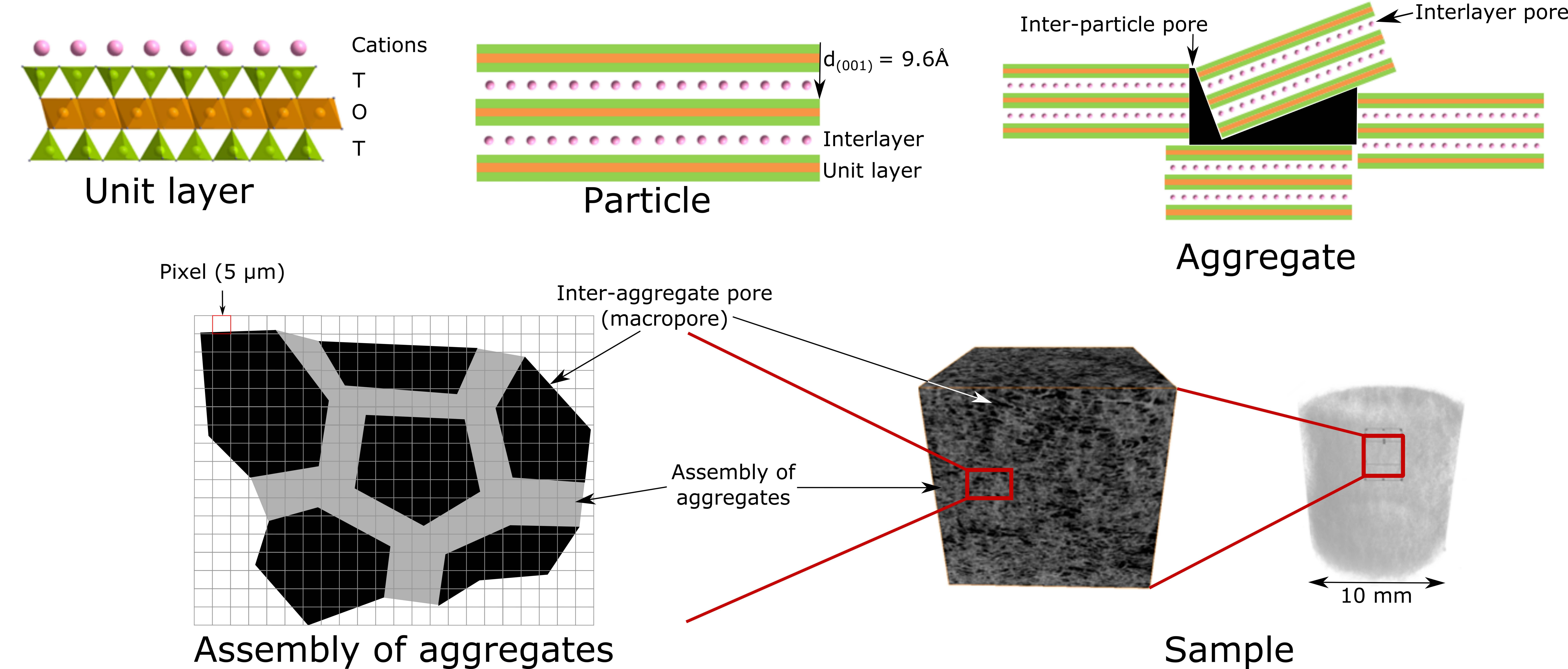
2	
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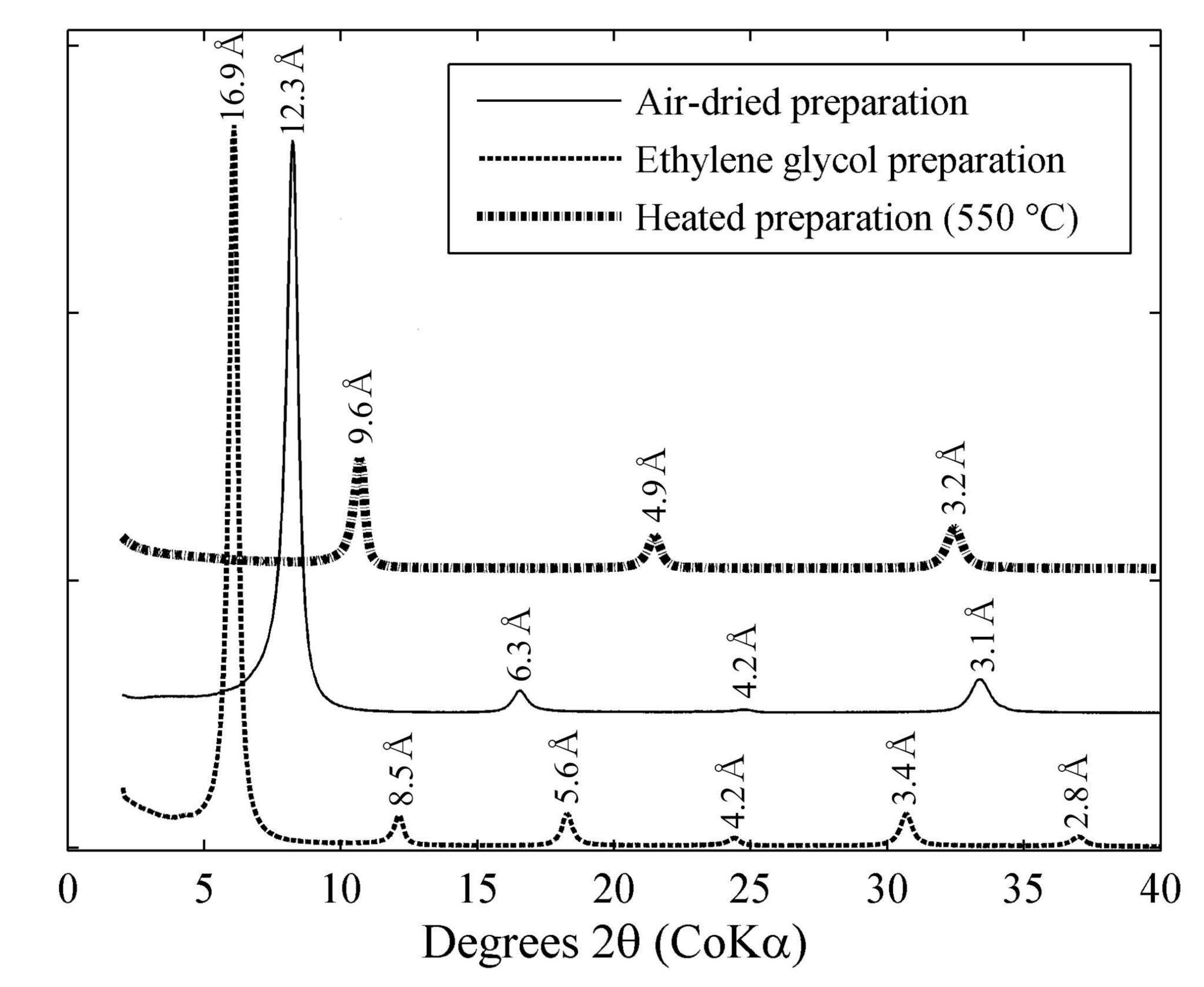
1

3	Figure 1. Organisation of Kunipia-G across the different scales (from unit layer up to
4	centimetre scale)
5	Figure 2. X-ray diffraction patterns of Kunipia-G: (a) oriented X-ray diffraction patterns
6	recorded under air-dried conditions, ethylene glycol hydration and heated at 550°C, (b)
7	capillary preparations in air-dried conditions and hydrated by MMA.
8	Figure 3. Representation of the new designed oedometer cell at constant volume: (a)
9	schematic layout, (b) cell with upper piston unscrewed into load frame and (c) cell with
10	upper piston screwed and installed into X-ray tomograph.
11	Figure 4. (a) VOI location inside the sample, (b) visualisation of sample porosity, (c)
12	threshold value identified after the slope change of the first derivative of the grey-scale
13	histogram, and comparison between raw and threshold images (d) in the vertical plane
14	(YZ) and (e) in the horizontal plane (XY).
15	Figure 5. (a) Dimensionless evolution of swelling pressure in Kunipia-G specimens at the
16	same dry density using standard cells and tomographic cell at dry density 1.40 ± 0.02
17	Mg/m3, (b) Swelling pressure at equilibrium versus Kunipia-G dry density compared to
18	other swelling clay materials (MX-80, FEBEX bentonite).
19	Figure 6. Dimensionless evolution of swelling pressure of four specimens at dry density 1.40
20	$\pm~0.02~Mg/m3$ subjected to NaCl 10-4 M or 10-1 M hydration for comparison between
21	oedometer tests with or without tomography scans.

Figure 7. Swelling pressure evolution of specimens at dry density 1.40 ± 0.02 Mg/m³ 22 subjected to various fluid features using a tomographic cell. 23

24	Figure 8. Inter-aggregate porosity evolution of specimens wetted with NaCl 10-4M, NaCl 10-
25	1M solutions or MMA at specific stages using tomographic cells: X-ray tomography
26	picture, scan time after hydration start, mean porosity.
27	Figure 9. Evolution of inter-aggregate porosity volume during hydration with (a) Na 10-4 M
28	and (b) Na 10-1 M, and comparison of porosity profiles of specimens hydrated by NaCl
29	solution and MMA at initial states and final state.
30	Figure 10. Schematic evolution of inter-aggregate porosity and swelling pressure upon sample
31	hydration with (a) aqueous solution and (b) MMA.
32	Figure 11. (a) Crystalline swelling (PCSS), electrostatic (PDDL) molecular (PvdW)
33	components and total swelling pressure modified from Liu (2013). Input parameters are
34	modified with the Kunipia-G available data. (b) Electrostatic component based on
35	Gouy-Chapman theory calculated for different NaCl ionic strength and MMA
36	considering dilute ionic concentration. The coloured markers represent the experimental
37	data acquired in this work.
38	Figure 12. Inter-aggregate porosity decrease versus time after wetting start at different height
39	positions on the sample from experimental data (Kunipia-G) and computed data (FoCa)
40	by Gens et al. (2011).





Counts

