Hydrotextural Description of an Unsaturated Humid Granular Media: Application for Kneading, Packing and Drying Operations

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Abstract

The kneading of a powder generates a product made of three phases (solid/liquid/gas) that interact through many interfaces. The respective proportions of each phase can vary according to the process parameters and the applied stress. After the initial operation of kneading, the medium can also be subjected to other stresses such as packing and thermal stresses or mechanical drying which will induce deep modifications in the relative proportions of the three phases. According to the twin influence of process strain and the nature of the three phases, the rheological behavior of the granular material can vary from that of a rigid solid to that of a more or less deformable plastic paste. The objective of this work is to depict, on a phase diagram, the potential states of each fraction constituting an unsaturated wet granular medium and their potential connectivity. From an experimental point of view, sorption isotherms and capillary retention curves allow determination of the two fluid phases state (liquid and gas). The hydrotextural diagram can be considered as a tool for the analysis and understanding of the mechanisms occurring during the processing (kneading and packing) or drying of wet granular media.

Keywords: state diagram, humid granular media, kneading, packing, drying, transformation path

1. Introduction

The ground is the most widespread wet granular medium. Nevertheless, many processes of product processing start with the wetting of a powder bed during a kneading stage.

Whatever their nature (agglomerates, dough or hard suspension), the wet media obtained can potentially be made up of three dispersed phases: solid, liquid and gas. These phases interact through the interfaces resulting from the divided character of the solid raw material. Many other of processing operations can succeed to this first step of kneading.

They generate a mechanical stress (tapping, packing or extrusion), a thermal or hydric stress (drying, osmotic dehydration), contributing to the evolution of the granular matrix towards its final application properties. These transformations combine the textural properties of the product and the process capabilities. The identification of the respective proportions of the “product” and “process” aspects in tropisms controlling the transformation is the object of a twin analysis that requires the follow-up of the relevant description parameters of the granular medium throughout the elaboration process.

Based on the relations of volume and mass conservation between the components of a granular medium at a representative elementary volume scale, the objective of this work is to propose a global representation to enable to depict the hydric and textural state of a wet granular medium in order to follow their evolution when process stresses are applied (compaction force, mixing stress, drying speed, etc.). The work presented here is a synthesis of many works performed on powder processing. The objective is...
to focus on the hydrotextural variations of materials during the unit operation constituting the processing of powders. In this way, the use of the hydrotextural diagram permits following the transformation paths during processing from the wetting stage to drying. This representation of hydric, textural and rheological aspects corresponds to the definition of the thermodynamical approach of a system’s states starting from a phase diagram. Applied to dispersed media as granular media, this macroscopic concept of a phase diagram was initiated by Matyas and Radhakrishna\textsuperscript{1}, to describe the hydrotextural state of an unsaturated soil subjected to hydromechanical stress. These authors showed that four parameters are necessary to completely define the state of an unsaturated soil: the water content ($\omega$, which is the ratio of the liquid mass to that of the solid) and the void index ($e$ which is the ratio of the void volume to that of the solid phase) on the one hand, and the net mechanical stress and the capillary suction on the other hand. On state surfaces, which are diagrams built starting from experimental tests, it is possible to depict the “loading path.” These paths symbolize the potential “trajectories” of a soil state subjected to mechanical and/or hydric stress, and are common in geotechnics.

Furthermore, the existence of particular state transitions such as the blocking transition (jamming transitions) observable on discrete systems (colloids, macromolecules, powders) for specific concentrations, inspired Liu & Nagel\textsuperscript{2} who proposed a jamming phase diagram specific to the soft matter. This phase diagram established for “homogeneous” media is based on the temperature ($T$), the applied stress ($\mathcal{L}$) and the reverse of compactness ($1/\phi$ where $\phi$ is the ratio of the apparent volume to that of the solid phase). When the particles are large enough to be insensitive to Brownian agitation (which is the case of the dry granular media), the system is defined as a zero-temperature system. Two parameters (compactness and applied stress) can describe the state of such a system. This type of representation is then used to depict the packing or the tapping of such materials\textsuperscript{3}. When such media are composed of several components, it is necessary to supplement the description by parameters informing about the relative proportions of each component. In the case of a triphasic media such as unsaturated wet granular media, it is necessary to take into account another parameter, for example the water content. The reverse of compactness and the void index are related by a linear relation: $1/\phi = 1 + e$, and it is thus possible to note that the approaches of Matyas and Radhakrishna and Liu & Nagel are obviously isomorphous.

On this basis, we propose the development of a “hydro textual diagram”\textsuperscript{4,5}, constituting the synthesis of the previously quoted works improved by the positioning of limits describing the connectivity state of the involved phases as well as their consistency state. The tests which make it possible to locate the state transitions of the wet granular medium will be briefly described. The first test allows the plotting of the water sorption isotherms which make it possible to identify the water proportion necessary to permit formation of the saturated monolayer and the appearance of the capillary condensation phenomenon (that marks the end of the hygroscopic field). Beyond this water content, the pendular state occurs during which the interstitial water generates capillary bridges between solid particles. The second test allows plotting of capillary retention curves mainly used in geotechnics. This test makes it possible to follow the variation of the water content of a sample with respect to the values of applied capillary suction increments. The curves established here for various compactness values allow identification of (i) the residual water content that corresponds to the value beyond which it becomes funicular (thus ensuring the connectivity of the liquid phase), and (ii) the water content of air inlet. Other geotechnical tests make it possible to identify the rheological consistency limits: the liquid and the plastic limit\textsuperscript{6}. The depiction of all these limits depends on the intrinsic characteristics of the product and its affinity with the added wetting liquid phase. Stresses generated by the process (mechanical, hydric, etc.) will then lead to depiction of the produced states within the diagram. It is thus possible to anticipate and estimate the reaction of the granular medium to the stress imposed by the process. In this study, the hydrotex tural diagram is specifically plotted for tests carried out on kaolin wetted by distilled water. The phase diagram of this mixture subjected to static packing is then shown. The texturing phenomena appearing during kneading, packing and drying of such a granular medium are specified.

2. Materials and Methods

2.1 Materials

The raw material chosen for this study is a cohesive powder: kaolin. This is a clay, classified in the category of non-swelling clays thanks to its structure made of rigid layers which prevent liquid penetration\textsuperscript{7}. The true density ($\rho_s^*$) of the raw material
is measured with a helium pycnometer 1305 (Micromeritics) and is equal to 2580 kg/m$^3$. A granulometric analysis, performed with a Malvern Master Sizer (Malvern instrument), allowed determination of the $d_{50}$ which is equal to 8.8 µm for kaolin native particles. Distilled water is used as the wetting liquid.

2.2 Determination of consistency limits and fluid percolation thresholds

Consistency limits are defined as the water content corresponding to changes in the product’s mechanical behavior from solid to plastic and from plastic to pseudo-liquid. Atterberg limits$^{5,6}$ are measured according to the French standards which define liquid limit ($w_l$) as the water content of transition between the plastic and the pseudo-liquid state$^9$. The plastic limit ($w_P$) corresponds to the water content of transition between the solid and the plastic state$^{10}$.

Fluid percolation thresholds and more generally hydrotextural limits are determined on cylindrical samples of the product according to two methods. The first method consists in identifying two specific water contents ($w_{mono}$ and $w_{capil}$) on an isotherm curve established for several product samples of different initial solid volume fractions. These two values correspond to the water content allowing the saturation of the specific surface area by water molecules ($w_{mono}$) and to the outbreak of capillary condensation phenomenon ($w_{capil}$)$^{11}$. Analysis of the isotherm curves by the BET$^{12}$ and GAB$^{13}$ approach makes it possible to define these specific water contents. From an experimental point of view, isotherm curves are plotted after experiments carried out in accordance with the gravimetric method conducted in an isotherm vessel where $T=25^\circ$C and $RH$ varies between 7 and 96%. The follow-up of the sample dimensions during the experiments allows determination of the solid volume fractions relative to $w_{mono}$ and $w_{capil}$. Repetition of this experiment for various initial solid volume fractions makes it possible to obtain coordinates ($w$, $\phi$) that delineate specific zones of the hydrotextural diagram$^4$. The second test corresponds to a draining/imbibition experiment conducted on product samples over a controlled capillary suction$^{14}$. This test is carried out with a pressure plate that makes it possible to identify the water contents for which the fluid phases are connected within the sample. The capillary suction curves (volumetric water content versus capillary suction for different values of sample compactness) make it possible to identify the residual water content ($w_r$) and the inlet air water content ($w_i$). $w_i$ corresponds to the water content for which the connectivity of the liquid phase is due only to water films at the particle surface$^{14}$. The water content of the inlet air is the water content for which the gas phase is not connected anymore in the matrix. The repetition of this experiment for various initial solid volume fractions makes it possible to obtain coordinates ($w$, $\phi$) that delineate specific zones on the hydrotextural diagram which correspond to those where liquid and gas phase are connected.

2.3 Kneading, packing and drying methods

Kneading. Wet masses are processed in a planetary mixer (Kenwood Major 1200). Rotation speed and dry load are constant and fixed at 70 rpm and 200 g, respectively. The wetting liquid is added steadily during 3 min. The wet mass is then homogenized for another 3 min before draining the mixer content on a smooth and clean surface. The water content, defined by the ratio of water to dry solid mass, ranges from 0% to 77%. Wet mass samples could be in two different states: an agglomerate bed at a water content lower than the plastic limit$^5$, and a dough for higher water content values. We consider here the agglomerate state with two characteristic scales: the agglomerate scale and the bed bulk scale. Measurements of water content, compactness and saturation degree are in accordance with the methodology defined by Ruiz et al.$^9$ and Rondet et al.$^{15}$. To define these hydrotextural variables $V_b$, $V_s$ (the bed bulk and agglomerates volumes, respectively), $m_s$ and $m_w$ (water and solid masses, respectively) must be assessed.

The volume measurements are carried out by sampling the wet mass with a cylindrical metal ring ($V_s$) of 319 mm$^3$ ($\phi=7.22$ mm; $h=7.81$ mm), or by reading the displaced volume ($V_b$) after introducing weighed amounts of one or more agglomerates into paraffin, respectively. The wet masses sampled with the metal ring are weighed before and after drying in an oven ($105^\circ$C over 24 h), the water content of each sample is evaluated by means of the $m_s$ and $m_w$. Concerning the water content of the immersed agglomerates, this is evaluated on agglomerates of equivalent size taken in the same wet mass and placed in the oven ($105^\circ$C over 24 h).

Packing. The samples are subjected to an uniaxial packing. This is carried out after the kaolin is kneaded with water, 20 g of this mixture is then placed in a cylindrical metal mold (2.54 cm in diameter and 19 cm long). Measurements are carried out using an instrumented press that controls the displacement rate of the piston in the mold (1 mm/s). The packing pressure resulting from this displacement is also
measured. During the test, the air is drained, which does not generate overpressure. The piston stops as soon as the net stress is equal to the set pressure (0.4; 1; 2; 4 MPa). The water content \( w \) and compactness \( \phi \) of the sample are measured at the end of the test by weighing them before and after drying (105°C for 24h). The volume of the compact sample, necessary for calculation of its compactness, is deduced from the displacement of the piston at the end of the packing experiment.

**Drying.** The samples are dried in soft condition (constant and low temperature and immobile air). Thus, only the relative humidity (RH) of air could vary by using the saturated saline solutions method \( 7, 22, 33, 43, 63, 75, 85, 91 \) and 96\%\) at constant temperature 25°C. During the experiment, each sample (placed in different cells) was removed to measure its mass and dimensions. The samples were weighed on a balance (accuracy 0.01 milligram) to monitor the water loss, and their mean sizes were measured consecutively with a digital thickness micrometer \( 0.02 \) mm precision. Dry mass \( m_i \) is measured at the end of the experiment by placing the sample in an oven \( 105^\circ C \) for 24 hours. All these measurements do not exceed 2 minutes per manipulation and do not significantly disrupt the observed results.

### 3. Construction of the Hydrotextural Diagram

In accordance with Matyas and Radhakrishna \( 1\) and Liu and Nagel \( 2\), the phase diagram of a wet granular medium is a graph plotted in the benchmark made up of compactness \( \phi = V_s/V_b \) with \( V_s \) and \( V_b \) being respectively the solid volume and the apparent volume at the bed bulk scale or the agglomerate scale), of water content \( w = m_w/m_s \) and of the operational parameter related to the transformation undergone by the product \( (\Sigma) \). However, independently of the transformations which are applied to the triphasic medium, it is possible to note in the benchmark \( (w, \phi) \) that particular hydrotextural states can be distinguished. For example, for each water content, the saturation state represents the solid volume fraction needed so as to saturate the granular media with water (Fig. 1).

It depends only on the ratio of the solid \( (\rho_s^\ast) \) and the real density of the liquid \( (\rho_w^\ast) \). If the constitution of a phase diagram makes it possible to establish a potential cartography of the states of the system, it becomes capital to identify the trajectories that the transformation path can take during the elaboration process (wetting/kneading, packing and drying).

**Fluid phase states.** The establishment of sorption isotherms of kaolin at different compactness makes it possible to identify the extent of the hygroscopic field of the product and then the transition towards the pendular state (Fig. 2a). The equilibrium water contents are depicted according to the relative humidity (RH). These isotherms are classified as a type \( 2_{11} \) and correspond to isotherms usually obtained with nonporous or macroporous adsorbents on the surface of which the adsorbed layer gradually thickens. This is characteristic of a multi-molecular adsorption. The GAB model \( 13 \) makes it possible to identify, for each isotherm, the water content necessary for saturation of the surface of the particles by a molecular monolayer \( (w_{mon}) \) and the water content that marks entry in the capillary field \( (w_{cap}) \). The capillary state is consecutive with the establishment of capillary menisci between the adsorbed water layers. The system has a sufficient interfacial energy to ensure the establishment of capillary bridges between grains. The Laplace pressure reaches the order of magnitude of the disjunction pressure. The localization of the coordinates \( (w_{mon}, \phi_{mon}) \) and \( (w_{cap}, \phi_{cap}) \) on the hydrotextural diagram makes it possible to de-

**Fig. 1** Hydrotextural diagram of kaolin.
limit a “hydrotextural” surface corresponding to the establishment of a saturated molecular mono-layer of adsorbed water and to the appearance of capillary bridges marking the end of the hygroscopic field and the entry in the pendular field (Fig. 1).

From the experimental results, the capillary retention curves can be depicted for each compactness value on a semi-logarithmic graph: volumetric water content \( (\theta = V_w/V) \) versus capillary pressure (Fig. 2b).\(^{16}\) Let us mention that the experimental results presented are interpolated by the model of Fredlund and Xing\(^{14}\), which allows a better recognition of the specific water contents \( w_i \) and \( w_r \). The air inlet water content \( (\theta \rightarrow w_i) \) corresponds to the percolation threshold of the gas phase. When the medium is not saturated, and for water contents higher than \( w_i \), the interstitial gas phase is entrapped in bubbles disconnected from each other. Beyond \( w_i \) the water is in the funicular state and the gas phase pressure exists at the global scale of the gaseous phase. The residual water content \( (\theta \rightarrow w_r) \) is the equivalent of the inlet air water content for the liquid phase. It marks the connectivity transition of the interstitial water and corresponds to the percolation threshold of water. For lower water contents, water is in the pendular state of “disjointed” menisci and adsorbed films. For higher water contents, the water pressure is a parameter that becomes representative of the total hydric state of the liquid phase (funicular state). The application of a hydrostatic pressure induced a flow of water (Darcian flow).

The positioning of these particular water contents on the hydrotextural diagram illustrates this fact and makes it possible to locate the characteristic zones of the two interstitial liquid phases with respect to the compactness state of the solid matrix (Fig. 1). The hygroscopic limit and the “lower” limit of the pendular field are slightly dependent on the compactness state of the granular network. Contrarily, the liquid and gas percolation thresholds previously defined are extremely dependent on the value of the void volume. Between these percolation threshold curves corresponding to (i) residual water content for the liquid phase and (ii) to inlet air for the gas phase, the two fluid phases are simultaneously connected within the porous network. It is in this zone that the diphase flows can take place and the intensive parameters such as densities are representative of the macroscopic phase state. Beyond this zone of tri-connectivity, at least one of the phases manifests a local state which it is advisable to consider statistically.

**Rheological consistency limits.** The granular medium is subjected to morphological changes as a function of the increase in water content: from a more or less pulverulent powder according to its cohesive nature, to the saturated state. Conversely, liquid/solid separation carried out by draining and/or drying shift the state of the system in the opposite direction without following the same path of hydrotextural transformation. From the dry states to the saturated states (of liquid), the rheological consistency of the mixture changes markedly by successively crossing the plastic limit and the liquid limit \( w_{P} \) and \( w_{L} \) of kaolin are close to \( w_{P} = 0.66 \) and \( w_{L} = 0.29 \), respectively. We checked that solid volume fractions which correspond to these water contents are located respectively on the saturation curve. This experimental result corroborates the observations of \(^{17}\) showing that these Atterberg values correspond to a quasi-saturated state. The Atterberg limits make it possible to define three distinct fields of consistency (Fig. 1): solid, plastic and liquid. For the water contents higher than the plastic field, the medium behaves like a pseudo-liquid, creeping under its own weight.

The superposition of rheological, hydrotextural and, although not treated in this “isothermal” study, thermal aspects constitutes the hydrotextural dia-

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![Fig. 2 Desorption isotherms -a) and capillary retention curve -b) for kaolin at 25°C.](image-url)
4. Transformation Path on the Phase Diagram

The hydrotextural state of an unsaturated wet granular medium is initially characterized by its “distance” to the saturation state (dry or wet). Water content, compactness and saturation degree ($S$) (ratio of the liquid volume to that of the voids) are linked by a conservation balance:\(^{1}\)

$$\phi(w, S) = \frac{1}{1 + d_s w / S}$$  \hspace{1cm} (1)

This equation derives from the saturation curve\(^{19}\), taking into account the fact that for unsaturated states $w = S \cdot w_{sat}$ in equation (1) $d_s = \rho_s / \rho_w$. This relationship indicates that in a dry state ($w = 0$), compactness equals 1, which indicates that the solid apparent bulk density equals the real density of the solid particles. When the medium is saturated ($S = 1$), compactness depends only on the water content and the hydrotextural state is located on the saturation curve (Fig. 1). Between these two extreme states, the medium is not saturated and the relation between the saturation degree and the water content $S(w)$ is characteristic of the transformation path followed by the state of the medium during its transformation.

4.1 Kneading and wetting

At the agglomerate scale, Rondet\(^19\) suggests a power law to describe the relation between the increase in saturation degree and water content (Fig. 3a):

$$S(w) = \left( \frac{w}{w_{sat}} \right)^n$$  \hspace{1cm} (2)

where $w_{sat}$ is the water content corresponding to saturation of the agglomerate, and $n$ is an exponent relative to the hydromechanical behavior of the agglomerates. Its value is lower than 1 for deformable media and equal to 1 for rigid and non-deformable materials. We observe that $n$ is constant during agglomeration under defined process conditions. By reporting equation (2) in equation (1), we obtain the relation of compactness variation according to the water content during agglomeration morphogenesis:

$$\phi(w) = \frac{1}{1 + d_s w_{sat} / w^{1-n}}$$  \hspace{1cm} (3)

At the bulk scale, the authors proposed interpolation of the experimental dependence of the saturation degree on the water content (Fig. 3a), by means of a logistic law which corresponds to a sigmoid pattern:

$$S(w) = 1 - \frac{1}{1 + e^{w_{ws}} - w_{ws}}$$  \hspace{1cm} (4)

where $w_{ws}$ and $d$ are parameters corresponding respectively to the water content when the saturation degree equals 50% and the inverse value of the slope of the central part of the curve.

Fig. 3b depicts the hydrotextural diagram of kaolin. The texturation curves are plotted showing the variation of the solid volume fraction according to the water content at the two scales. At the bulk scale, three phases can be identified: (i) a phase of expansion during which the solid volume fraction is lower than that obtained in a dry state; (ii) a phase of gentle densification of the medium leading to a soft increase in the solid volume fraction until the water content reaches the percolation threshold previously defined\(^5\) and from which the densification is very strongly accentuated; (iii) a final phase during which the medium reaches the saturation state and the solid volume fraction decreases. This phase of dilatation is extended until the granular medium reaches a suspension state. This texturing phenomenon, taking place between the dry and the saturated state, is the result of the interactions between the three phases constituting the unsaturated mixture. More explanation of these phenomena can be found in the references\(^{5,15,19}\).

4.2 Texturation by static packing

In the case of static compaction, Ruiz et al.\(^4\) showed that the filling of the voids followed a sigmoid pattern (Fig. 4) and could be interpolated by eq. (4).
The two parameters of eq. (4) depend on the applied pressure. It is shown that a correlation between the normal compaction stress ($\sigma$) and the parameter $w_m$ exist:

$$w_m \propto \frac{1}{a\sigma + b} \quad (5)$$

where $a$ and $b$ are fitting parameters, respectively, equal to 0.3499 and 1.1892, and whose physical meaning remains to be defined.

On the hydrotextural diagram (Fig. 5), these transformation paths reveal the same texturing phenomenon as that observed during kneading due to the static compaction (0.4; 1; 2; 4 MPa).

By reporting equation 4 in equation 1, it is possible to obtain the mathematical expression of the transformation path ($w, \phi$):

$$\phi(w) = \frac{1}{1 + d^2 w [1 + e^{-\frac{w-w_m}{w}}]} \quad (6)$$

It is shown mathematically that the concomitant existence of the optima of expansion and densification implies that the $w_m/d$ ratio is strictly higher than 0.02. In addition, it has been shown that these parameters are linearly dependent. This linear correlation is true whatever the powder:

$$d = 0.2368w_m + 0.02 \quad (7)$$

The equations (5) and (7) make it possible to directly introduce the influence of the compaction stress applied in the expression of the transformation path (Eq. 6). Equation 6 describes a state surface specific to the packing of kaolin. The state surface is depicted in the phase diagram of figure 6. The transformation paths specific to the pressures applied in the experimental study (Fig. 5) correspond to projections of this surface in the plane ($w, \phi$). Fig. 6 shows that the increase in the pressure submitted to the compact respects the texturing phenomenon (expansion, densification and dilution) by shifting it towards values of increasing compactness.

On Fig. 7, all the properties obtained from the sorption, draining/imbibition and consistency tests are overlaid on the transformation path. The texturing phenomenon can then be analyzed from various angles. The hygroscopic field extends from the dry state to the water content that allows capillary condensation and the formation of the first menisci. It is for higher water content that is reached the residual...
water content, which marks the end of the pendular field and the initiation of the liquid percolation within the matrix. From this limit on, the capillary bridges, whose number increases up to this point, will be gradually drowned by the successive water additions. The two fluid phases, water and gas, are then connected: water is in a funicular state. For higher water contents, it is possible to locate the water content of the inlet air beyond which the gas phase will remain in the matrix as entrapped air bubbles. This state is obtained for water contents close to 90%. These different water contents constitute important limits marking the change of the water state within the matrix. Whereas the water contents which ensure saturation of the molecular monolayer and capillary bridges (capillary condensation) are relatively independent of the compactness state of the medium, it is not the same for the residual water content and inlet air water content, whose values increase as the compactness of the medium decreases. The medium densification does not induce a significant variation in the surface accessible to water but a reduction in pore size, caused by an increase in compactness, reduces the water quantity that is necessary to crossing the limit which marks the end of the pendular and funicular field. The superposition of these various fields on the evolution of the texturing phenomenon obtained after compaction enables us to link the succession of the three stages of the texturing phenomenon to the liquid phase state within the granular matrix (Fig. 7).

Concerning the expansion, the adsorbed water films are subjected to a disjunction pressure which counteracts the connection of grains, thus generating a reduction in compactness. Then, beyond the water content of capillary condensation, capillary menisci develop. These capillary bridges, whose number grows in the water content range corresponding to the pendular state, induce a capillary Laplace pressure and exert a traction between grains and induce a connection, or, in the case of packing, promote their local connection. The effect is all the more marked that the number of menisci increases. The densification slope is thus the more pronounced during the field where water is in the pendular state. With the increase in wetting, the antagonistic effects of the disjunction pressure and of Laplace pressure turn in favor of the capillarity, gradually extinguishing the expansion phenomenon to the detriment of densification. This phenomenon continues until the residual water content from which the connectivity of the liquid phase induces a progressive reduction.
in the number of local capillary bridges. This pore filling results in a less pronounced densification slope up to the optimum of densification. This is obtained when all the menisci disappear and when capillary traction is exerted in the periphery of the sample as is the case in the capillary field. It is important to mention that the densification optimum corresponds systematically to the inlet air water content. The gas percolation threshold in the porous network is concomitant with the densification because the result of the capillary actions then reaches its paroxysm. These water contents correspond to saturation degrees close to 90%. Menisci corresponding to the liquid and air interface are circumscribed at the sample periphery and thus exert their action synergetically on the whole system, as is the case for the action of the surface tension around a water droplet. The densification optimum thus corresponds to the definition of the Proctor Optimum described in soil science \(^\text{16}\). The progressive saturation of the medium decreases the capillary actions which will gradually disappear. Compactness thus decreases until the total saturation state beyond which it will be given by the saturation curve of the product. It is the dilution stage for which the saturated paste is comparable to a hard suspension \(^\text{20}\), then to a soft suspension when the solid phase is not connected anymore.

### 4.3 Texturation by drying

The drying of a saturated kaolin compact processed by static compaction implies shrinkage until compactness reaches its random close packing value \((\phi = 0.6)\) corresponding to the shrinkage limit. At this value, the granular medium becomes rigid and an interstitial gaseous phase appears (Fig. 8). Before this value, the medium remains in a saturated state. After this value, the saturation degree varies with water content, and follows equation (2), with \(n = 1\). The drying continues until the hygroscopic equilibrium is reached. Relative humidity had no influence on the drying paths (Fig. 8b), except on the equilibrium water content given by the desorption isotherm. Texturing due to drying in soft conditions is easy to model, and the phase diagram is reduced to a single curve (Fig. 8b).

### 5. Conclusion

This experimental work is classified within the theoretical framework of establishing a state diagram for this particular soft matter class, i.e. the wet granular materials. The proposed diagram makes it possible to depict the hydric, textural and rheological states of a wet granular medium. Thanks to specific tests borrowed from multiple sciences treating the granular media, the hydrotextural diagram of kaolin is experimentally built. This voluntary multi-field approach is only a reflection of the phenomenological richness of the wet granular media. More pragmatically, this representation makes it possible to identify the repartition of the three dispersed phases within the mixture and its densification capacity during packing.

This phase diagram is thus a cognitive tool to enable the transformation path of a granular product during its processing to be followed. This work mentions, for example, the similarity between the effects of drying and draining on the evolution of the medium compactness. It finally makes it possible to understand, on a continuous medium scale, the succession of the various stages of the texturing phenomenon induced by the increase in water content. The experimental results make it possible to conclude that the succession of these various stages is linked with the water state within the matrix. Under the modulated effect of the capillary forces, the cohesion of the wet granular medium evolves, enabling it to adopt more or less compact configurations.

The state diagram of a wet granular media appears
that follows the example of its remote cousin the state diagram of “molecular” bodies, (i) like a tool for identification of the impact of the product and of the process on the transformation of a system, (ii) as the support of a twin product/process analysis for the processing of products with defined functionalities.

Nomenclature

\[ d \] inverse value of the slope of the central part of the curve (S=f(w))

\[ d^* \] ratio of the density of the solid to that of the liquid [-]

\[ d_{50} \] median diameter [mm]

\[ e \] void index [-]

\[ m_w \] mass of water [g]

\[ m_s \] dry mass [g]

\[ n \] exponent relative to the hydromechanical behavior of agglomerates [-]

\[ S \] Saturation degree, ratio of the liquid to voids volume [-]

\[ T \] temperature [°C]

\[ V_a \] volume of agglomerates [cm³]

\[ V_s \] volume of the agglomerates’ bulk [cm³]

\[ V_c \] solid volume [cm³]

\[ V_o \] volume of water [cm³]

\[ w \] water content [-]

\[ w_{capil} \] water content allowing initiation of capillary condensation phenomenon [-]

\[ w_i \] inlet air water content [-]

\[ w_m \] liquid limit [-]

\[ w_{sat} \] water content when the saturation degree equals 50% [-]

\[ w_{smax} \] water content of saturation of the specific surface area by water molecules [-]

\[ w_r \] plastic limit [-]

\[ w_{r} \] residual water content [-]

\[ w_{sat} \] water content corresponding to saturation of the agglomerate [-]

Greek letters

\[ \theta \] volumetric water content [-]

\[ \rho_s^* \] density of the solid [g/cm³]

\[ \rho_w \] density of the liquid [g/cm³]

\[ \Sigma \] applied stress [Pa]

\[ \sigma \] normal compaction stress [Pa]

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Author’s short biography

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After a university course focused on health and industrial formulation of health products, Eric Rondet obtained in 2005 a master's degree in process engineering. He prepared a PhD thesis on the capillary texturing of wet granular media in the Process Engineering - Water and Bioproducts Laboratory (UMR CIRAD 016) of Montpellier, and obtained his doctor’s degree in 2008 from the University of Montpellier 2 (France). He then integrated the laboratory of Agropolymer and Emerging Technologies (UMR IATE - Montpellier SupAgro - INRA) for a study related to the agglomeration of cereal powders. Eric Rondet is currently an assistant professor in the Process Engineering - Water and Bioproducts Laboratory (UMR CIRAD 016).

Montana Rungsiyopas
Montana Rungsiyopas obtained her master’s degree in Mechanical Engineering (Energy Technology) in 2001 from KMUTT (Thailand). She then worked as a lecturer in the mechanical engineering department, Burapha University (Thailand). She is now studying for her Ph.D. in the Process Engineering - Water and Bioproducts Laboratory (UMR CIRAD 016), at the University of Montpellier 2 (France). Her thesis is related to the theoretical analysis of mass and energy transfer connected with the deformation during the drying process of granular media. She will return to work in the mechanical engineering department of Burapha University as soon as she obtains her doctor’s degree.

Thierry Ruiz
The path in the scientific world of Thierry Ruiz began with a mathematical course in the Science Faculty of Montpellier, followed by a Ph.D. which deals with non-equilibrium thermodynamics applied to the modeling of reactive mass transfer in porous media (Mechanic and Civil Engineering Laboratory of Montpellier). Assistant professor in the Process Engineering - Water and Bioproducts Laboratory (UMR CIRAD 016) since 1999, his works are focused on mass and energy transfers coupled with the morphogenesis of heterogeneous materials elaborated with soft matter (granular media, residual sludges, clay), where capillary interaction corresponds to the main texturing action.

Michèle Delalonde
Michèle Delalonde is a pharmacist from the pharmacy school at the University of Montpellier 1 (1983). She first specialized in writing Common Technical Documents (CTD) on novel drugs for different industrial partners. Afterwards, she obtained a master’s degree in polymers for therapeutic applications and a PhD thesis focused on the rheological properties of wet masses. She obtained her doctor’s degree in chemical and biological sciences for health in 1998. Currently, she works as an assistant professor in the Process Engineering - Water and Bioproducts Laboratory (UMR CIRAD 016). Her research works are actually focused on granular media and on the optimization of elaboration processes.
Jean-Pierre

Jean-Pierre Desfours began his career at the University of Montpellier 2 where he obtained his PhD on the electrical properties of magnetic semiconductors. An assistant professor at this university until 1987, he worked as a full professor in Marseille up to 1997. Since returning to the University of Montpellier, he has coordinated the Process Engineering, Water and Bioproducts Laboratory (UMR CIRAD 016). During his career, he has conducted research work and theses on different subjects in a large area of physics ranging from high-frequency electronic circuits, microchemical sensors and other devices, and his focus now lies on process engineering for the elaboration of materials from granular media.