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Effect of the crystallization of a solute on the cohesion in granular materials

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We study experimentally the macroscopic cohesion of wet granular materials during water evaporation and progressive crystallization of a solute between grains. The samples are wetted granular columns of cylindrical shape subjected to vertical compression tests. The compressive strength allows us to follow the evolution of the material from the capillary cohesion regime to the cemented cohesion regime. Surprisingly, we find that this transition is governed by a control parameter defined as the ratio of the crystallized solute mass to the total mass of the solute present in the sample rather than the absolute amount of the crystallized solute.

Keywords: Capillarity; Cementation; Evaporation; Compression test

1. Introduction

The study of the phenomena initiated by the presence of an interstitial liquid in granular materials is of major interest for understanding the mechanisms of cohesion within these materials. These phenomena are of primary importance to many fields such as powder technology or the formation and transformations of rocks, concretes, etc. In pharmaceutical industry, for example, the process of “wet granulation” is widely used to manufacture tablets. The principle is to introduce a liquid, composed of solvent(s) and solute(s), into a sheared bed of several granular materials in order to obtain a homogeneous mixture that otherwise would present a strong tendency to segregation. The formation of aggregates in this process has been a subject of extensive investigation [1–3]. The solid tablets are then obtained by drying: the solvent evaporates and solid bridges are formed between grains, thus ensuring the macroscopic cohesion of the tablets. Also in the field of civil engineering, the interstitial liquid plays a significant role in the mechanical behaviour of many geomaterials. The liquid is

generally water containing various impurities and/or dissolved minerals. As a result of reactive transfers or phase changes, the liquid may generate damage in masonry works by dissolution of cemented joints or crystallization of solutes [4–6]. In the case of granular soils such as sands, the liquid can also be at the origin of the macroscopic cohesion of material. At low liquid contents, liquid bridges are formed between grains. The hydrous field corresponding to this range of liquid contents is often described as “pendular”. The attractive capillary forces in the presence of liquid bridges between grains endows the material with a macroscopic cohesion of basically weak intensity [7]. Under the action of the surrounding hygrothermic conditions, water can evaporate, thus modifying the solute concentration. In the case of extreme concentration, the solutes crystallize to form solid bonds between grains. This phenomenon leads to enhanced cohesion at the macroscopic scale.

Capillary forces and the formation of liquid bridges have been extensively studied in the past, and several models of capillary cohesion have been proposed [7–9]. The scale-up of capillary forces to the macroscopic mechanical cohesion of granular media has been investigated by means of both experiments and discrete element numerical simulations [10–13]. The case of cohesion by cementation has been studied by many authors. Delenne et al. [14] proposed models for the mechanical behavior of solid

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bonds and studied the influence of this local cohesion on the macroscopic mechanical behavior.

The objective of this work is to consider cohesive bonds whose nature, and thus the mechanical behavior, evolves according to environmental conditions. If it is possible to follow, at a local scale, the evolution of a cohesive bond from liquid to a solid state during gradual evaporation of a solvent [15], it is particularly difficult to study at the same time the evolution of its mechanical behavior. In this study, we focus on the evolution of the macroscopic cohesion of a wet granular material during the evaporation of a solvent (water) and thus crystallization of the solute (sodium chloride). The cohesion will be characterized by the compressive strength of cylindrical granular samples.

2. Experiments: sample preparation and testing protocol

We prepared two types of samples with glass beads and Ventoux sand, respectively. In each case, the granular material was first washed and dried, then it was sieved to keep only grains with diameters in the range 0.4 mm to 0.8 mm (Fig. 1a). The resulting materials were homogeneously mixed with an aqueous solution of a solute that can crystallize during the evaporation of water. We used sodium chloride (NaCl), and the solution was thus simply a *saturated brine* containing 35.6 g of NaCl for 100 g of water. This maximum concentration depends very slightly on the temperature [16,17]. The initial gravimetric content of granular samples in saturated brine (brine content) was obtained by mixing in a tight box suitable amounts of saturated brine and dry granular material. The samples (diameter 25 mm and height 17 mm) were prepared in a cylindrical mould.

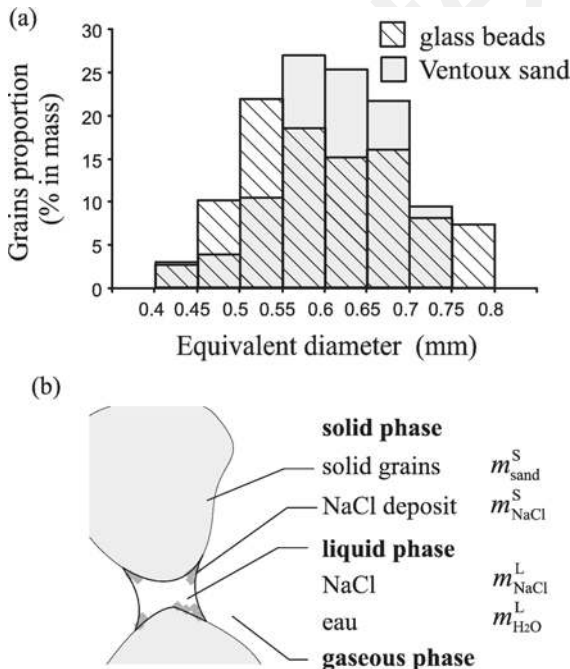


Fig. 1. (a) Particle size distribution of the solid phase, (b) A schema of the three-phase character of the granular material.

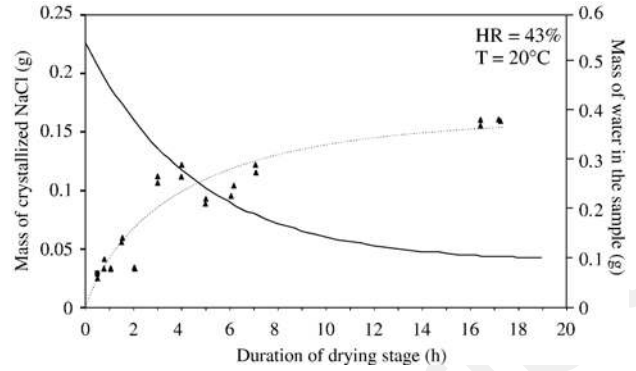


Fig. 2. Example of the kinetics of NaCl crystallization for glass beads samples with an initial brine content of 5% (dashed line). The solid line represents the evolution of the mass of water in the sample.

Hence, each sample is initially a three-phase material including (Fig. 1b):

- a solid phase (denoted by S) composed of grains (glass beads or sand) with a total mass m_{grains}^S ,
- a liquid phase (denoted by L) composed of water of mass $m_{\text{H}_2\text{O}}^L$ and dissolved NaCl of mass m_{NaCl}^L .
- a gaseous phase composed of air and water vapor with negligible mass compared to the two other phases.

At this initial state, the samples are particularly delicate to handle since their cohesion and mechanical strength are solely ensured by weak capillary forces between grains. Because of this brittleness, particular experimental precautions were necessary in order to avoid damage to the samples.

According to hygrothermic conditions of the atmosphere, water can evaporate. This leads to a thermodynamic disequilibrium of the solution that results in an excess of NaCl in an already saturated solution. Thermodynamic equilibrium is recovered through the crystallization of NaCl and thus the formation of solid NaCl deposits of a total mass m_{NaCl}^S .

Three series of samples were prepared with three different levels of the liquid content: 3%, 5% and 7%. These values are selected in the hydrous field corresponding to the “pendular state”, for which liquid bridges between grains ensure the mechanical

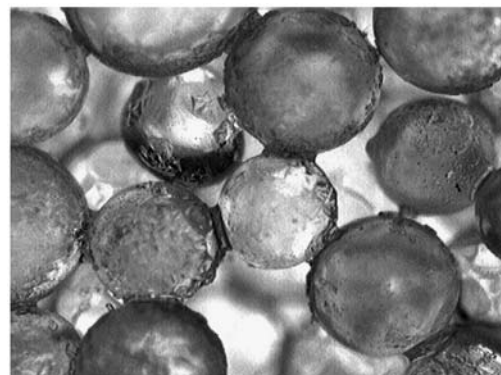


Fig. 3. Formation of deposits of crystallized NaCl as a result of the evaporation of the water contained in the saturated brine.

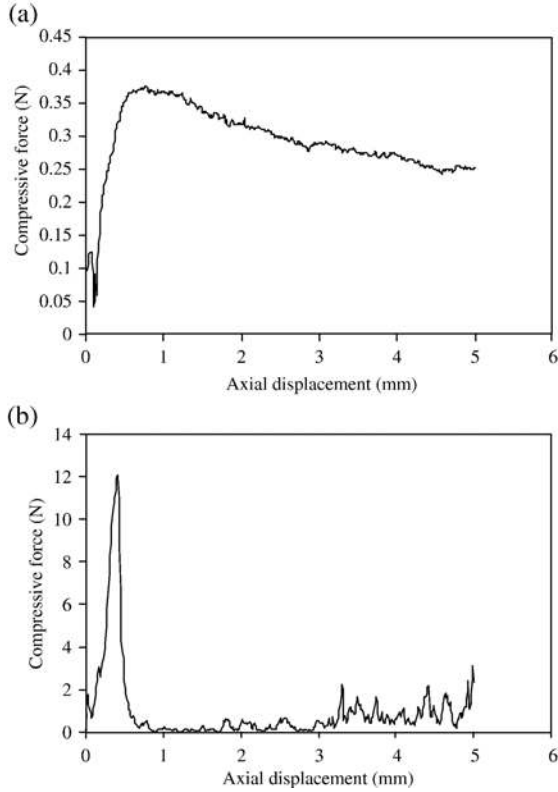


Fig. 4. Compressive force versus axial displacement for glass bead samples with an initial brine content of 5%. Duration of drying: (a) 0 h 30 min, (b) 17 h 15 min.

integrity of the sample. The samples were weighed just after preparation (the corresponding mass denoted by m_i), and left to dry at a fixed temperature ($T=20\text{ }^\circ\text{C}$) and Relative Humidity ($\text{RH}=43\%$) for durations varying from 15 min to 18 h.

At regular intervals of time, the samples were weighed (mass m_f), and then subjected to unconfined vertical compression up to rupture. The difference $m_f - m_i$ gives access to the mass of the evaporated water and thus that of the crystallized fraction of NaCl. Since all samples are prepared under similar conditions, they are assumed to follow the same evolution in time. This allows us to reconstitute the kinetics of NaCl crystallization. Unconfined compression tests were carried out by means of a “low capacity”

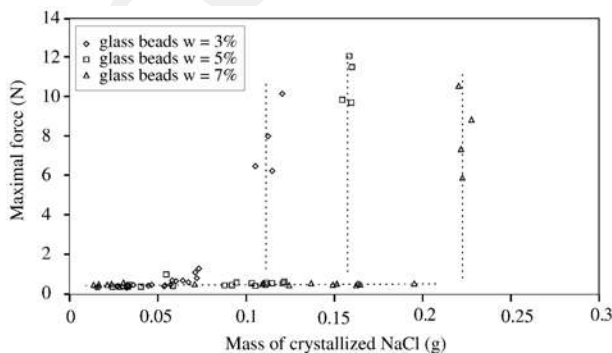


Fig. 5. Maximal compressive force as a function of the mass of crystallized NaCl for three initial brine contents in the case of glass beads. The dashed lines are drawn as a guide to the eyes.

press allowing to test samples with low dimensions and forces up to 50 N with an accuracy of 0.01 N.

3. Results and discussion — case of glass beads

We obtain a classical kinetics for the crystallization of NaCl as shown in Fig. 2. The trend remains basically the same independently of the initial brine contents. The crystallization is fast in the initial stage, and then slows down considerably. The mass of “retained” water in the sample, even for a long drying, is proportional to the initial mass of saturated brine, and thus to the initial mass of water. For all the three initial brine contents, only 88% of the mass of water can evaporate. The rest is “trapped” during crystallization.

The NaCl deposits are located at three different places in the samples:

- At the surface of the samples, corresponding to the phenomenon of efflorescence [18];
- At the surface of the grains, in the form of isolated crystals which are not directly involved in the creation of cohesive bonds between grains (Fig. 3);
- At the contacts between grains, in the form of solid bridges contributing to intergranular cohesion (Fig. 3).

Compression tests were carried out on 82 samples. The “low capacity” press allows us to follow the evolution of the compressive force as a function of the axial displacement.

Fig. 4 displays typical plots of the compressive force as a function of axial displacement for glass bead samples with an initial brine content of 5% for short (0 h 30 min) and long (17 h 15 min) drying times. The plot for short drying times represents a continuous evolution of the compressive force with axial displacement. The sample deforms continuously during the test, and the behavior appears to be of ductile plastic type. The recorded levels of the compressive force are relatively low reflecting cohesion of capillary type. In the long drying case, we observe a force peak of significant amplitude at a small axial displacement. We observe a sharply defined rupture of the sample occurring at the peak force. This brittle behavior reflects

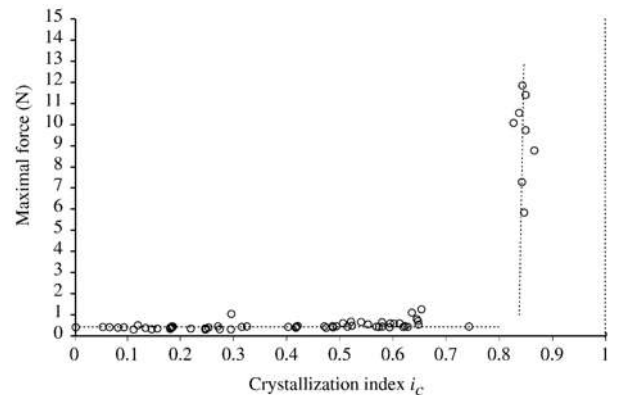


Fig. 6. Maximal compressive force as a function of the crystallization index in the case of glass bead samples for three initial brine contents ($w=3\%$, 5% et 7%).

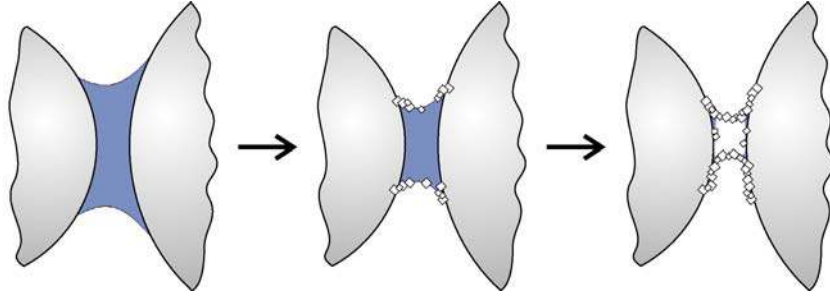


Fig. 7. Schematic representation of the evolution of a saturated brine bridge.

cohesion due to cementation between grains. In both cases, the maximum compressive force is unambiguously defined. It is noteworthy that all the samples have the same dimensions so that the maximum compressive force characterizes the mechanical strength of our granular materials.

Fig. 5 shows the evolution of the maximal force as a function of the mass of crystallized NaCl for the 82 tests carried out at 3%, 5%, and 7% of saturated brine. All plots have the same feature whatever the initial brine content. During the first stages of evolution, capillary cohesion prevails and the yield strength is pretty low as a result. In all cases, the yield strength is independent of the mass of crystallized NaCl up to a limit where crystallization slows down. In this limit, the mechanical strength is 20 to 30 times higher than the initial strength.

It is interesting to note that the strength of the granular samples is not controlled by the quantity of crystallized NaCl. In fact, as Fig. 5 shows, for the same mass of crystallized NaCl, the maximal compressive force varies in different samples depending on the initial brine content.

In order to account for the influence of the initial brine content, we define a “crystallization index” i_c :

$$i_c = \frac{m_{\text{NaCl}}^{\text{S}}}{m_{\text{NaCl}}} \quad (1)$$

Where m_{NaCl} is the NaCl mass present in the sample ($m_{\text{NaCl}} = m_{\text{NaCl}}^{\text{S}} + m_{\text{NaCl}}^{\text{L}}$). This index represents a control parameter that varies from $i_c = 0$, corresponding to full dissolution of

NaCl, to $i_c = 1$, corresponding to full crystallization of NaCl. Fig. 6 shows the maximal compressive force as a function of i_c for the three initial brine contents. Remarkably, all the data points, independently of the initial brine content, collapse nicely on the same plot that comprises two distinct parts:

- The range $i_c < 0.8$ where the maximal force is nearly constant and thus independent of the mass of crystallized NaCl;
- The range $i_c > 0.8$ where the maximal force rises sharply with i_c .

Physically, the two parts correspond to the capillary cohesion regime and the cementation cohesion regime, respectively. It is also interesting to note that the limit $i_c = 1$ is never reached. This is related to the maximum capacity of water evaporation which is 88% of the total mass of water injected into the sample.

Locally, the transition of intergranular cohesive bridges from liquid to solid is a slow and complex process. NaCl crystal fragments form initially at the liquid–gas interface on the grains. These fragments then grow wider and sustain the growth of other crystals. This leads to the formation of a crystalline area growing preferentially along the liquid–gas interface. This evolution of cohesive bridges is illustrated in Fig. 7. This process was also observed with other aqueous solutions frequently used in pharmaceutical industry [15]. Solid cohesion is effective only when the connectivity of the crystallized deposit is fully established between the two grains. This explains the importance of the capillary zone (first zone in the Fig. 6), which is also

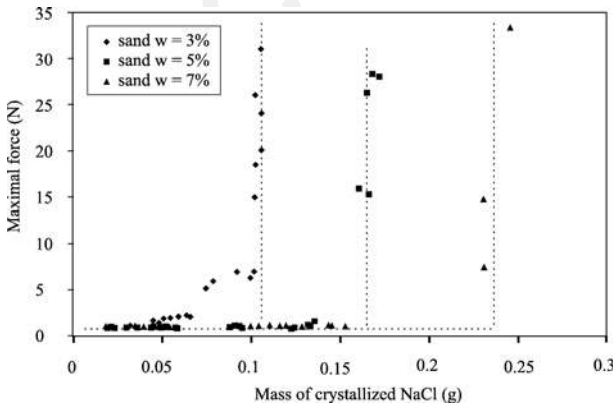


Fig. 8. Maximal compressive force as a function of the mass of crystallized NaCl for three initial brine contents in the case of Ventoux sand. The dashed lines are drawn as a guide to the eyes.

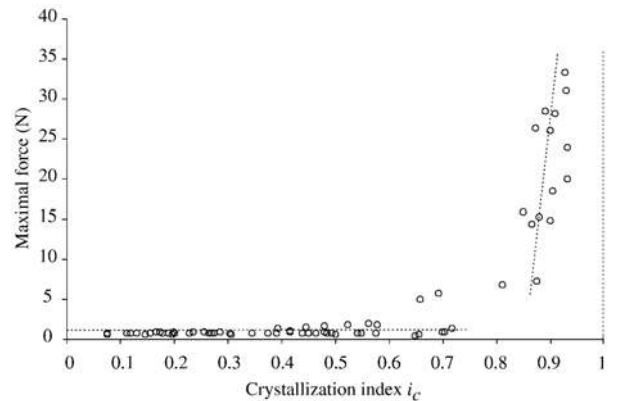


Fig. 9. Maximal compressive force as a function of the crystallization index for samples of Ventoux sand and three initial brine contents ($w = 3\%$, 5% et 7%).

involved in the phenomena of efflorescence and isolated crystallization giving rise to deposits of crystallized NaCl not contributing to intergranular cohesion.

4. Validation on a natural material — case of Ventoux sand

A similar experimental investigation was carried out on a natural granular material, namely the Ventoux sand. Sixty experiments were performed following the experimental protocol described in Section 2. The results are presented in Fig. 8.

As in the case of glass beads, our results indicate the existence of the two cohesion regimes for all initial brine contents. The crystallization index appears again as the main control parameter for the yield stress; see Fig. 9. In the case of sand, the transition occurs at $i_c=0.9$. This limit can also be related to the amount of water “trapped” in NaCl at the end of crystallization ($\approx 93\%$ for sand). These findings indicate that the maximal force is not only a function of the nature of the granular material, but also more significantly on the evolution of cohesive bonds from liquid to solid that is controlled by the crystallization index i_c .

5. Conclusion

The experimental investigations presented in this paper made it possible to estimate the effect of the crystallization of a solute (NaCl) on the mechanical strength of a granular material. Our findings, both for a model material (glass beads) and a natural material (Ventoux sand), provide clear evidence for two markedly distinct regimes: a capillary regime and a cementation regime. A crystallization index, defined as the amount of crystallized solute normalized by the total available amount of solute, appears to be the key parameter governing the evolution of the yield strength.

In extension of this work, we currently elaborate a model based on a thermodynamic approach (phase change of water and diffusion of the water vapor) in the framework of a discrete element method. The latter is a particularly promising approach that enables the scale-up from the physical phenomena at the microscopic scale to the observable behavior at the macroscopic scale. The central idea is to generalize the methodologies employed in the cases of capillarity [9,7] and cementation [14,19] to a unified representation of the cohesive bond interpolating between these two limits with internal variables that evolve according to environmental conditions.

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