Flow velocity-dependent transition of anisotropic crack patterns in CaCO$_3$ pastes

Yuri Akiba$^1$ and Hiroyuki Shima$^1$$^\ast$

$^1$Department of Environmental Sciences, University of Yamanashi, 4-4-37, Takeda, Kofu, Yamanashi 400-8510, Japan
(Dated: September 8, 2018)

We investigate the desiccation crack patterns on the surface of a drying paste made of calcium carbonate powder and distilled water. The forced vibration of the paste prior to drying results in an anisotropic crack pattern after drying. We found the preferred direction along which many long cracks develop. We reveal that the preferred direction changes from vertical to parallel with respect to the vibration direction at the threshold velocity of vibration. The transition is attributed to the reorientation of constituent particles subjected to the forced oscillatory flow of fluid in the paste.

PACS numbers:

I. INTRODUCTION

Desiccation cracks are widely observed on the surfaces of granular pastes. A paste is a mixture of liquid and insoluble grains; as such, upon drying, the liquid content evaporates from the air-exposed surface, causing volume shrinkage of the grain-liquid mixture followed by surface cracking. The fractured surface often exhibits an isotropic polygonal pattern similar to those developed on the dried surfaces of mud and paint. The patterns are characterized by cracks with different lengths and directions, splitting the entire surface of the fractured media into many polygonal cells.

Although desiccation cracks are widely studied, it is difficult to predict the direction or the position of crack advancement on the drying surface from actual experiments, not even from a statistical viewpoint. The difficulty stems partly from the fact that the crack phenomenon is governed by complex interaction between microscopic particles. In fact, the internal structure of granular pastes is spatially inhomogeneous because of the wide dispersion both in the spatial distribution of constituent particles and in their particle size distribution as well as because of the spatial inhomogeneity in the drying rate of the paste. In addition, as a crack progresses through a paste, the local stress field in the vicinity of the crack changes with time. On the other hand, it has been reported that the desiccation crack pattern in some pastes can be controlled to some extent by applying an oscillatory fluid flow. The transition to the anisotropic crack pattern is clearly different from an ordinary random, isotropic crack pattern.

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A paste of calcium carbonate (CaCO$_3$) is a typical example exhibiting the memory effect. Figure 1 shows experimental results of CaCO$_3$ pastes dried completely. It is known that CaCO$_3$ pastes exhibit two types of memory effects, one of which is the memory effect of “shaking.” This effect is characterized by many long surface cracks propagating in a direction perpendicular to the vibration direction of a thin container in which the paste is poured; see Fig. 1(a). The other effect is called the memory effect of “flow.” This effect is manifested by many long cracks that propagate parallel to the direction of flow induced by the horizontal vibration of the container; see Fig. 1(b). Here, the term flow implies the vibration-induced solvent flow that occurs around the constituent particles of the paste. The two types of memory effects result in an anisotropic crack pattern, which is clearly different from an ordinary random, isotropic crack pattern demonstrated in Fig. 1(c). The memory effects have academic significance in the apparently counterintuitive fact that the global geometry of desiccation crack patterns can be altered only by imposing a horizontal vibration.

In an earlier study, the mechanism of memory effect of shaking has been explained using elastoplastic theories. The theory suggests that the memory effect of shaking results from the anisotropy in the residual stresses due to the plastic deformation of a paste. In addition, a nonlinear analysis, wherein the nonlinear effect is introduced into the elastoplastic model, has been proposed. These theories are consistent with experimental observations, thus making them suitable to describe the memory effect.
of shaking. In contrast, the mechanism of the memory effect of flow has not been fully explained. A plausible idea is based on flow-induced anisotropy in particle configuration. When a solvent flow through the gap between constituent particles of a paste, the particles are believed to form a network structure because of the hydrodynamic attractive interaction. As the flow continues, the network structure is elongated overall, thereby orienting many chains of the particles in the flow direction. In fact, a numerical simulation showed that the hydrodynamic interaction may lead to an anisotropic chain structure of the particles in colloidal suspensions. If the constituent particles in the paste form a chain-like network structure, it is expected that the flow velocity around the particles driven by the horizontal vibration of the container is responsible for the degree of elongation in the network. Intuitively, a strong flow will enhance the elongation and thus promote the occurrence of the memory effect of flow. However, there has been no experimental observation that supports this plausible idea.

The present work is aimed at verifying the conjecture that the flow velocity governs the mechanism of the memory effect of flow in pastes. We conduct drying crack experiments on CaCO₃ pastes to examine the correlation between the flow velocity and the degree of anisotropy in the crack pattern as a manifestation of the memory effect. The systematic tuning of the flow velocity shows that the memory effect enhances with the increase in the flow velocity, thus supporting the aforementioned theoretical scenario.

II. MATERIALS AND METHODS

A. Sample preparation

We used a paste of calcium carbonate (CaCO₃) as the experimental material to investigate the memory effect of flow. Calcium carbonate is composed of white, micrometer-sized particles, which are insoluble in water. In our actual experiments, we mixed 95.65 g of CaCO₃ powder (Hayashi Pure Chemical Industries) and 104.35 g of distilled water in a container. The solid volume fraction of the paste was set to 25 %, at which the paste has been reported to exhibit the memory effect of flow. It should be noted that CaCO₃ powder is composed of electrically-charged particles. Thus, we added sodium chloride (Nihonkaisui) to the CaCO₃ paste to eliminate the Coulombic repulsive interaction between the charged particles, as the interparticle repulsive interaction is thought to hinder the effect of vibration on network structure formation. Sodium chloride was selected as the electrolyte to generate chloride ions in water. Hence, the calcium carbonate paste is neutralized by chloride ions. The additive amount of sodium chloride was set to 0.61 g (0.1 mol/L for the paste), which was sufficient to neutralize the calcium carbonate.

B. Measurement method

The paste was poured into a plastic, rectangular-shaped container. The longer side, narrow side, and depth of the container were 215, 153, and 39 mm, respectively. The container was fixed on a horizontal plate on a shaker (TOKYO RIKAKIKAI, MMS3010). Thereafter, the container was vibrated horizontally for 60 s. Figure 2 shows the schematic of the experimental setup.

The vibration direction is parallel to the longer side of the container. The flow velocity is tuned by controlling the amplitude and frequency of the vibration in a separate manner; the two quantities were set as 10, 20, and 30 mm and 80, 130, and 180 rpm, respectively. After the vibration, the samples were left to rest and dried completely for 24 h in a room maintained at 28 °C. We analyzed the images of the polygonal cracks after drying using the image processing software ArcGIS, which is a geographic information system tool employed to analyze geographic data.

The flow velocity was controlled by varying the amplitude (r) and frequency (f) of the horizontal vibration of the container. The vibration was in the form of a simple harmonic oscillation. Accordingly, the velocity of vibration V is given by

\[ V = r \omega \cos \omega t, \]

where \( \omega \) is the angular velocity, and \( t \) is the duration for which the oscillation is applied. Hence, the maximum velocity of oscillation \( V_{\text{max}} \) is represented by \( V_{\text{max}} = r \omega \).

C. Order parameter

The geographic data of crack pattern was quantified using the orientation order parameter defined as follows. We assume that a completely dried surface of colloidal suspension is divided into many polygonal cells by N cracks with different crack lengths and orientations. In the following equations, \( l_i \) represents the length of the \( i \)th crack \( 1 \leq i \leq N \), and \( \theta_i \) denotes the angle between the direction of the \( i \)th crack and the direction along which the sample is vibrated. Figure 3 shows schematic of \( l_i \).
and \( \theta_i \). In particular, if a crack orients in the vibration direction, we have \( \theta_i = 0 \); otherwise, if a crack is perpendicular to the vibration direction, we have \( \theta_i = \pi/2 \). In general, \( \theta_i \) takes an intermediate value ranging from 0 to \( \pi \). Now, we define the order parameter \( O \) of the system as follows.

\[
O \equiv 2C - 1, \quad C = \frac{\sum_{i=1}^{N} \ell_i \cos^2 \theta_i}{\sum_{i=1}^{N} \ell_i}.
\]

Alternatively, \( O \), expressed in Eq. (2), can be rewritten by the sum of \( \cos^2 \theta_i \) with a weight of \( w_i \) as follows.

\[
O \equiv 2 \left( \sum_{i=1}^{N} w_i \cos^2 \theta_i \right) - 1, \quad w_i = \frac{\ell_i}{N} \sum_{i=1}^{N} \ell_i.
\]

Following are the values of \( O \) for three extreme cases:

i) When all the cracks orient in the vibration direction, we have \( \theta_i = 0 \) for arbitrary \( i \). Substituting this into Eq. (2), we obtain \( C = 1 \) and \( O = 1 \). This case corresponds to the perfect realization of the memory effect of flow.

ii) When all the cracks are oriented in a direction vertical to the vibration direction, we have \( \theta_i = \pi/2 \) for arbitrary \( i \). Substituting this into Eq. (2), we obtain \( C = 0 \) and \( O = -1 \). This case corresponds to the perfect realization of the memory effect of shaking.

iii) If we assume that all the cracks are randomly oriented but have an identical length denoted by \( \ell_0 \), \( C \) can be obtained as follows.

\[
C = \frac{\ell_0 \sum_{i=1}^{N} \cos^2 \theta_i}{N\ell_0} = \frac{1}{N} \sum_{i=1}^{N} \cos^2 \theta_i.
\]

For a sufficiently large \( N \), the sum in the rightmost side of Eq. (4) can be replaced by an integral; thus, \( C \) is approximated as follows.

\[
C \approx \frac{1}{\pi} \int_{0}^{\pi} \cos^2 \theta \, d\theta = \frac{1}{2}.
\]

This leads to the following conclusion for a randomly oriented case: \( O = 0 \).

Consequently, when the order parameter takes a positive value, it indicates the occurrence of the memory effect of flow. On the other hand, when the order parameter takes a negative value, it indicates the occurrence of the memory effect of shaking.

**III. RESULTS**

We anticipated that the flow velocity would govern the mechanism of the memory effect of flow in the paste, because of two reasons. One is reorientation of constituent particles with the solvent flow in the paste. We believe that the higher flow velocity, the easier it is to form a network structure. The other reason is the frequency of particle collisions with the increase in the vibration amplitude. The amplitude and frequency are the two parameters that can change the flow velocity. With regard to the shaking amplitude, the number of colliding particles increase because of the expansion in the range of particle movement.

Figure 4 shows the dependence of the order parameter on the flow velocity. The horizontal and vertical axes represent the maximum velocity of vibration \( V_{\text{max}} (= r\omega) \) and the order parameter, respectively. The number of samples is three for each data plot. The upper and lower ends of the error bar represent the maximum and minimum values of the order parameter, respectively. The sign of the order parameter shifts at \( V_{\text{max}} \approx 0.3 \text{ m/s} \). Thus, the value of 0.3 m/s represents the transition point from the memory effect of shaking to the memory effect of flow. We fitted the data points onto a straight line defined by \( O = 1.54V_{\text{max}} - 0.50 \), and the R-square value was found to be 0.83. This shows a positive correlation between the flow velocity and the orientation order under the present experimental condition.

It is worthy to note, however, if a significantly lower flow velocity is imposed on the paste, the data points will deviate from the linearly fitted line and converge to the origin with the decrease in the flow velocity. This is because the anisotropic crack pattern is non-existent if the vibration strength is insufficient. Specifically, at the zero velocity, the system clearly exhibits an isotropic crack pattern as confirmed from the experiments (as shown in Fig. 1c). In contrast, if a higher flow velocity is imposed on the paste, the order parameter is expected to be a constant, representing the memory effect of flow. Additionally, if the flow velocity becomes significantly greater...
than the flow velocity described above, the data points will converge to the origin. This is because it is difficult to constitute particle network structure under strong currents.

It follows from Fig. 4 that the absolute value of the order parameter obtained from the experiment is lower than the extreme value of 1. This fact is attributed to the energy release process in the desiccation crack formation. It is unlikely that all the cracks would orient in the parallel or vertical directions, because the parallel or vertically aligned cracks, which are induced in the initial stages of desiccation, are not enough to release the internal stress. As a result, the subsequent cracks, the directions of which are perpendicular to those induced in the initial stages, exhibit a ladder-type pattern.

Figure 5 shows the phase diagram of the order parameter distribution in the amplitude-frequency plane. The data points with circles (colored in red) indicate the positive values of the order parameter, representing the occurrence of the memory effect of flow at a given amplitude and frequency. The negative values are indicated by black squares, representing the occurrence of the memory effect of shaking. In either case, the magnitude of the order parameter is represented using different symbols (solid or open) depending on whether the absolute value is greater or lower than 0.1. It follows from the diagram that the memory effect of flow tends to occur in the upper-right region, whereas the memory effect of shaking occurs in the lower-left region. The curves depicted in the diagram are the contours along which the maximum vibration velocity \( V_{\text{max}} = r\omega \) is kept constant, as listed in the legend. The contour line of 0.3 m/s serves as the threshold, beyond which the memory effect changes from the shaking-type (below the threshold) to the flow-type (above the threshold). In addition, it is inferred from the contour map that the vibration amplitude and frequency mutually contribute to the determination of which type of memory effect, i.e., flow or shaking, occurs at the given parameter values. The product of the two parameters (i.e., the maximum flow velocity) uniquely determines the type of memory effect to be observed.

**IV. DISCUSSION**

Our experimental results clearly show the positive correlation between the flow velocity and the orientation order in the anisotropic crack patterns induced by the memory effect of flow. With the increase in the flow velocity, the drying crack pattern undergoes a transition from a shaking phase to a flow phase, each of which exhibits completely different patterns with respect to the preferred direction of the crack formation. To elucidate the physical origin of the flow velocity-induced transition in the crack pattern, we study how the fluid flow penetrating through the gap between the particles affects their configuration from a microscopic viewpoint.

In hydrodynamics, under conditions of sufficiently low fluid velocity and uniform flow around the particles, the fluid force acting on a particle can be represented by the following equation:

\[
F = 6\pi\mu L V. \tag{6}
\]

Here, \( \mu \) represents the coefficient of viscosity of water, \( L \) is the radius of the particle, and \( V \) denotes the flow velocity. This equation shows that the fluid force increases linearly with the increase in the flow velocity. It is expected that Eq. (6) can be applied to the colloid particles of the paste employed in this study, as the space within which particles can move freely is large enough when the solid volume fraction of the paste is 25%. Consequently, the fluid velocity in the vicinity of the particles becomes lower than the vibration velocity of the container because of the viscosity of the fluid contained in the paste.

![Figure 4](image_url)  
*FIG. 4: Almost linearly increasing behavior of the order parameter with the flow velocity.*

![Figure 5](image_url)  
*FIG. 5: Phase diagram of the order parameter, amplitude, and frequency. The data points with circles (colored in red) indicate the positive values of the order parameter, representing the occurrence of the memory effect of flow. The negative values are indicated by black squares, representing the occurrence of the memory effect of shaking.*
Assuming that a fluid force, expressed using Eq. (6), acts on a particle, it is plausible that the high fluid velocity enhances the anisotropy in the particle configuration, thus generating a chain-like structure that orients in the vibration direction. Figures 6(a) and (b) show a nucleation of such a flow-induced chain. If the direction of the particle pair does not coincide with that of the flow [e.g., perpendicular to each other, as shown in Fig. 6 (a)], the oscillatory flow of the fluid exerts a force on the pair such that it reorients in a direction parallel to the flow direction [Fig. 6 (b)]. The same reorientation due to the oscillatory flow will occur even in small-sized aggregates having more than two particles, resulting in elongated short chains of the constituent particles. Once the chains are bonded to each other via repeated displacement and collision by flow, a large-scale anisotropic network structure of particles is formed, in which the gap between adjacent chains is mechanically fragile and is likely to fracture under drying.

V. CONCLUSION

In this work, we experimentally obtained evidence of a positive correlation between the flow velocity and the orientation order with regard to anisotropic crack patterns in CaCO$_3$ pastes. We presented a phase diagram with respect to the type of memory effect in the vibration amplitude-frequency plane. Furthermore, we demonstrated that the transition between the two types of memory effects occurs at a threshold flow velocity of approximately 0.3 m/s. The experimental findings support the plausible scenario that the memory effect of flow in pastes is attributed to the flow-induced formation of anisotropic chain-like structures.

Acknowledgment

The research was supported by the Sasakawa Scientific Research Grant from The Japan Science Society and by JSPS KAKENHI (Grant Nos. 16K00810 and 18H03818)