Chemical Gardens at the Air–Liquid Interface Form Spirals That Transition to Fractal Fingers with Periodic Transparency
Growing a Chemical Garden at the Air−Fluid Interface

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Supporting Information

ABSTRACT: Here we grow chemical gardens using a novel, quasi two-dimensional, experimental configuration. Buoyant calcium chloride solution is pumped onto the surface of sodium silicate solution. The solutions react to form a precipitation structure on the surface. Initially, an open channel forms that grows in a spiral. This transitions to radially spreading and branching fingers, which typically oscillate in transparency as they grow. The depth of the radial spreading, and the fractal dimension of the finger growth, are surprisingly robust, being insensitive to the pumping rate. The curvature of the channel membrane and the depth of the radially spreading solution can be explained in terms of the solution densities and the interfacial tension across the semipermeable membrane. These unusually beautiful structures provide new insights into the dynamics of precipitation structures and may lead to new technologies where structures are grown instead of assembled.

INTRODUCTION

When moving fluids undergo chemical or physical changes to become solid, they can produce beautiful and intricate structures. Speleothems, lava tubes and limestone terraces are all natural, self-constructing precipitation structures whose shapes have been modeled recently. However, these are but a few of the many morphologies that precipitation structures can take, especially when they are grown in the lab under controlled conditions. Research on these systems has been revitalized recently by the possibility of technological applications, especially on nanoscales where growing is more efficient than building. Many of these precipitation structures are biomimetic in appearance and behavior, hence they have historically been dubbed "chemical gardens", however the more recent name for the field is chemobrionics.

The experiments presented here involve the chemical reaction between calcium chloride and sodium silicate solution (see Table 1). This precipitation reaction has long been studied since it is the primary reaction in the formation of Portland cement. However, the method for producing the precipitate is new; here the buoyant calcium solution flows radially out over the surface of the silicate solution (see Figure 1). This quasi-

Table 1. Solutions Used in This Experiment, and Their Relevant Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>concentration (mol/liter)</th>
<th>density (g/cm³)</th>
<th>viscosity (mPa s)</th>
<th>surface tension (mN/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>calcium chloride</td>
<td>0.50 M</td>
<td>1.0425</td>
<td>1.16</td>
<td>75 ± 5</td>
</tr>
<tr>
<td>sodium silicate</td>
<td>0.70 M</td>
<td>1.0605</td>
<td>1.43</td>
<td>50 ± 5</td>
</tr>
</tbody>
</table>

Figure 1. (a) Photograph of fully developed surface structure, from above, with blue dye added. Note the spiraling channel in the center and, for the radial spreading outside of the spiral, fingers and periodic precipitation inside the fingers. (b) Sketch of experimental setup.

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the silicate solution in the container was 20 mm. A variety of different container sizes were used, including areas of 10 cm × 10 cm, 25 cm × 25 cm, and 60 cm × 60 cm. Pumping rates from 5 mL/h to 20 mL/h were used.

The silicate solution was prepared by diluting Sigma-Aldrich, reagent grade, sodium silicate solution (density 1.39 g/mL) consisting of 13.4–14.4% NaOH and 12.0–13.0% Na2SiO3 by weight. The solution of calcium chloride was prepared using distilled water and reagent grade calcium chloride hexahydrate. The precipitate is naturally white, so, for the photographs shown in the present work, food coloring was added to the calcium chloride solution to enhance the visibility of the structure. The food coloring (predominantly water with some propylene glycol) was never more than 1 mL dye to 100 mL solution. The values given in Table 1 for the physical parameters of the solution were measured without the food coloring added. The surface tension of the two solutions were measured using the method of maximal pressure of a bubble.

The growth of the structure was video recorded from above and from the side. These images were later analyzed to quantitatively describe the growth of the structure.

RESULTS AND DISCUSSION

Formation of a Spiral Channel. There are multiple stages in the structure’s growth. The initial surface structure is approximately a horizontal tube without a top side—an open channel. The growing channel adheres to the existing structure, producing an Archimedean spiral around the center (see Figure 2a). For 45 trials studying this initial growth, there were 14 clockwise spirals, 12 counterclockwise spirals, and 19 asymmetric spiral structures (as viewed from above). The latter structures typically occur when the vertical column ruptures at more than one spot, producing multiple open channels that grow simultaneously.

A channel grows in a manner very different than a tube does in traditional chemical gardens. Membrane formation occurs where the vertical front face of the channel curves inward and meets the older, outer wall of a previously formed channel. A channel grows in length by unfold this front face outward. This unfolding compresses the outermost, vertical membrane forming small, vertical wrinkles about 0.5 mm apart; these wrinkles can be seen in Figure 2b. At the same time, this unfolding stretches the bottom, horizontal membrane causing it to tear at regular intervals. The tears are often visible as darker bands across the bottom of the channel and can been seen in Figures 1a and 2a. The dimensionless Reynolds number, the ratio of inertial to viscous forces, is about 1 for the growing channel. This suggests that there is a balance between inertial and viscous forces at the growing channel front.

There are many examples of spirals in nature, but the formation mechanism here is different than for such common examples as chemical waves or cracks, and it is different than for the spirals produced in most closed cell, Hele-Shaw experiments (see, however, ref 7). The spiral forms primarily for two reasons. First is the Coanda effect, which is that any fluid flow will tend to follow an existing wall. This occurs because the flowing fluid will drag the external fluid between the wall and the flow with it, and then the flow moves into the space thus created. The second reason is the gradient in surface tension near the structure. The concentration of the high surface tension metal salt solution will be largest at the center of the structure, so concentration gradients at the surface
will produce a gradient in surface tension with a net surface force inward. This inward force causes the membrane of a channel to curve inward at the surface, as can be seen in Figure 2b.

The curvature of a thin membrane is described by the Laplace equation for the pressure difference across the membrane,

\[ \Delta \rho g (z - z_0) = \frac{T_1}{R_1} + \frac{T_2}{R_2} \]  

(1)

The left-hand side of eq 1 is the static pressure difference due to the density difference between the two solutions, with \( z \) measured positive upward and \( z_0 \) the depth where the pressures difference vanishes. On the right-hand side, the \( R \)'s and \( T \)'s are the membrane radii and tensions. Here \( T = \gamma + \sigma_i \) with \( \gamma \) the interfacial tension of the membrane from its molecular interactions with the inner and outer fluids, \( t \) the thickness and \( \sigma_i \) the internal stress. Figures 2c and 2d show analysis of the curvature of the membrane, as viewed from the side and above. When viewed from above, the spiral channels sometimes exhibit deviations from uniform width. A narrowing of a channel is usually accompanied by a "straightening" in the channel (see Figure S1 in the Supporting Information). This behavior follows from eq 1 since, at a given depth, the curvature combination on the right-hand side is a fixed quantity. Figure 2d plots the inverse curvature in the horizontal plane versus the channel width for an intermediate part of a spiral through two oscillations in width. The linearity of the plot implies that tensions in the membrane are not too different in the different directions; however, there is insufficient information to quantitatively extract any membrane parameters. When viewed from the side, as in Figure 2b, the membrane curvatures becomes larger as the depth increases. This behavior is similar to that observed for a puddle of oil floating on water. Figure 2c shows a quantitative analysis of the curvatures for a cross-section of the membrane at two different times, where, for simplicity, it has been assumed that \( T_1 \approx T_2 \) and the subscript dropped. There is good agreement between eq 1 and the data. The difference in the model fits between the two times shows that \( z_0 \) increases with time, while the slope, \( \Delta \rho g / T \), decreases with time. These changes are consistent with the changes expected to occur from the viscous drag of fluid flowing down the channel ahead of this section of membrane. As the channel grows longer, a larger pressure difference at a fixed depth is required to drive the fluid down the channel, and this larger pressure increases the stress in the membrane. The fact that the channel width appears relatively uniform from above implies that the changes in channel width must stop a short distance behind the leading front. This may be due to a flow over the interior walls separating one channel from the next.

The initial time in Figure 2c is during the initial stages of membrane channel formation, when the membrane is not well connected at the base of the channel. Thus, the tension at this early time should be a good upper limit/estimate of the intrinsic interfacial tension, \( \gamma \). The slope of the line at this time is given in Table 1, gives

\[ \frac{60 \mu N}{m} \gtrsim \gamma \]  

(2)

This value for the membrane interfacial tension is 3 orders of magnitude less than the air–fluid surface tensions of the individual fluids. However, unlike these immiscible interfaces, the calcium-silicate membrane is well-known to be semi-permeable. The above value is similar to the transient interfacial tensions observed between miscible fluids. The interfacial tension parameter \( \gamma \) has not been included previously in
discussions of traditional chemical gardens, but it is relevant there also.

Taking a value of \( \gamma = 50 \, \mu \text{N/m} \) (see later analysis from radial spreading depth), the membrane interfacial tension parameter \( \gamma \) can be combined with other fluid parameters to determine a length scale

\[
 l = \sqrt{\frac{\gamma}{\Delta \rho g}} = 0.5 \, \text{mm} \tag{3}
\]

This is the capillary length for the inner fluid–membrane–outer fluid interactions. It is the length scale over which buoyancy effects cause the membrane to change shape.

Radial Spreading. After the growing channel has completed a few rotations (as many as four were observed), the growth transitions from spiral growth to radial growth. This transition occurs when the interior fluid starts to flow over the outermost edges of the spiral, usually at multiple locations at the same time. The flow over the edge spreads out approximately radially away from the point like breaches in the outer wall.

The transition from spiral/channel growth to radial flow is caused by a decrease in the concentrations of the reacting solutions at the outermost edges of the structure, from membrane formation and osmosis. At these lower concentrations, the precipitate does not form fast enough to create a membrane near the fluid front. Thus, (1) the flow pattern is more like a fluid spreading out on a surface and (2) the lower surface tension silicate solution is now free to flow over the metal salt solution.\(^{26}\) The latter follows from direct observations and because the dimensionless Marangoni number, the ratio of surface driving to damping forces \( \Delta \gamma d/\mu D = 10^7 \) (where \( \Delta \gamma \) is the difference in surface tensions between the two solutions, \( d \) is the thickness, \( \mu \) is the viscosity and \( D \) the diffusivity) is much larger than the critical value needed for horizontal flow. The outward flow of the buoyant metal salt solution occurs in a thin sheet under the surface of the higher surface tension silicate solution (see Figures S2 and S3). The precipitation membrane forms behind the leading edge of the fluid flow.

To study the dynamics of the radial spreading, the growth was videotaped from above (see Figure 3). From these videos, the area and perimeter of the precipitation membrane were calculated. These are shown in Figure 3b,c. Note that the data are not plotted versus time, but instead geometric measures of the structure are used. When plotted in this way, the data for different flow rates lie on top of each other. This demonstrates that the structure produced during radial spreading is independent of the rate of pumping. This implies that the relevant forces are not velocity dependent, such as from viscosity or inertia, but velocity independent, such as the surface tensions and the buoyancy.

Figure 3b plots the area viewed from above versus the volume of metal salt solution pumped since the structure reached the surface. The linearity between volume and area suggests that the average depth of the spreading flow plus membrane is approximately constant. The scale of this depth is given by the inverse of the slope of the plot

\[
 \frac{dV}{dA} = 1.1 \pm 0.1 \, \text{mm} \tag{4}
\]

This value is compatible with visual observations from the side of the container. This depth scale is much larger than the thickness of the membrane, which is on the order of 10 \( \mu \text{m} \) when removed from the structure and measured while still wet. Thus, most of this depth is due to the spreading, interior fluid. The actual depth of the fluid might be somewhat more or less than this value, depending on which effect is larger: the amount of metal salt solution that flows beyond the edges of the structure, or the amount of fluid added by osmosis.

This depth can be related to the membrane’s interfacial tension. Assuming that a membrane forms on both the upper and lower calcium–silicate solution interfaces, with the same interfacial tensions, and that the thickness of the two membranes, and also the top silicate solution layer, is small enough to be neglected, then

\[
 \gamma = \frac{1}{4} \Delta \rho g d^2 \approx 50 \frac{\mu \text{N}}{m} \tag{5}
\]

where the depth of the solution, \( d \), is taken to be given by eq 4 and the density difference is taken to be that of the original solutions. This value is consistent with the estimate/upper limit in eq 2 coming from the curvature analysis.

Fingers. The radial spreading is not axisymmetric but instead is in the form of fingers (see Figure 3a). The fingers typically have a blunt front and exhibit tip splitting.

Scaling behavior is expected to occur in a system when the structure is large compared to intrinsic length scales. For the system studied here the ratio of the maximum finger length to the depth of the calcium chloride solution (eq 4) was approximately 6.0 cm/0.1 cm = 60 while the ratio of the maximum finger length to the typical finger width was less than this. To look for scaling, the perimeters of the fingers was plotted as a function of the equivalent circumference \( 2\sqrt{\pi \times \text{Area}} \) (see Figure 3c). The black curve is the best fit power law, and its exponent is 1.7. For this way of plotting the data, this scaling exponent is also the fractal dimension.\(^{27}\) This value of the fractal dimension is similar to that found for other two-dimensional, radial systems such as viscous fingering in a Hele-Shaw cell\(^{28}\) or diffusion limited aggregation.\(^{29}\)

In a simple experiment, the calcium chloride solution was replaced with dyed sodium chloride solution of the same density. In this case, a membrane does not form. The salt solution rose to the surface and spread out axisymmetrically there in a thin layer with no finger formation. This demonstrates that the membrane formation (in the experiments using calcium) does not just record the flow pattern, instead it is crucial to the formation of the fingers. Further evidence for this is seen on microscopic examination of the sides of the fingers where a vertical membrane forms, which restricts further expansion in that direction.

Transverse Bands near the Front of Growing Membrane. At the outermost regions of the growing fingers, and transverse to the flow, there are often oscillations in the appearance of the membrane. These are visible at the ends of the largest two fingers in Figure 3a. The newly formed membrane oscillates between light-colored and transparent, in bands that span the entire width of the finger. In the light-colored regions, the membrane appears to have a white, granular surface that is opaque. In the transparent regions, there is no visual evidence that a membrane is there, but structurally there must be some membrane present to hold in place against the flow the light colored membrane that forms downstream of the transparent region. Over time, the transparent regions disappear, with light colored material replacing or growing over the transparent membrane. The light colored material grows...
into the transparent regions mostly from the downstream side. These oscillations have been observed to occur over a wide range of times during the radial spreading, from near the start of the radial spreading out to distances of several centimeters. Somewhat similar bands have been reported elsewhere.\textsuperscript{18}

There is considerable scatter in the distance from one transparent region to the next, but there appears to be a general trend for this width to grow larger with distance from the center of the structure. To see whether this change in band width was tied to changes in the velocity of the center of the structure. To see whether this change in band width and membrane growth velocity were simultaneously measured for several different pumping rates, and the data from these different runs were combined (see Figure 3d). The average width of the bands appears to be relatively independent of the velocity.

Oscillatory patterns have been observed previously in precipitation structures, but none of the previous explanations apply directly to the bands observed here. Oscillations occur in chemical gardens when closed tubes grow, but these are associated with pressure relaxation oscillations.\textsuperscript{15,16} This does not appear to be relevant here because the radial spreading motion is smooth and uniform across a wide front. It has been shown that different concentrations of the reacting solutions used here can produce different membrane transparencies.\textsuperscript{17} Thus, the bands may be an indicator that the concentration of the solution is oscillating. In that case the periodic precipitation may be similar to that observed in Liesegang rings.\textsuperscript{30–32}

However, in previous discussions of Liesegang bands, the formation process was driven purely by diffusion, whereas for the bands here both diffusion and fluid flow are relevant. More theoretical work is needed to see if chemical kinetic models can describe the band structures under the conditions observed here.

Other Features. In addition to the parts of the precipitation structure that have already been discussed (channels, fingers, and early stage transverse bands), there are other interesting features of this structure. The column leading from the bottom of the tank to the top is often irregular (see Figure 2b), and sometimes this irregularity occurs in a spiral similar to a Solomonic column. Also, there are a secondary set of light- and dark-colored transverse bands that appear at much later times inside the fingers (see Figure 1a). These bands have widths that are on the order of a centimeter or more, much larger than the previously discussed bands. Also, at the ends of the fingers there are often lines of diffuse precipitate flowing radially away (see left and bottom right sides of photos in Figure 3a). Also, there is some evidence that the radial spreading is sensitive to how the structure is illuminated. The multiple levels of complexity produced by combining two simple, inorganic solutions is quite surprising.

\section{Conclusions}

The precipitation structure described here is unusual in several ways. One unusual feature is its robustness (insensitivity to pumping rates) despite the relatively unconstrained experimental configuration. Another is that the basic elements of the structure can be so well described by simple physical principles. Certainly the most unusual aspect is that so many different, self-organized, complex patterns appear in a single system.

The complex chemical structure discussed here is made from many substructures: spirals, radial spreading, fingers, branching and transverse precipitation. One structure is built and then the building algorithm is switched. The building and sculpturing of structures on each level is made by a different group of physical processes. It is interesting to note that a similar method of construction is observed in biology; for example, a plant builds roots, stems and leaves by switching algorithms and processes. This suggests that this ‘switching of algorithms’ may be a standard way that complex systems develop.

There are several fundamental reasons for the complexity of the structure discussed here. This is a damped and driven system, with driving coming from the pumping of concentrated chemicals into the system and damping coming from the chemical reactions and diffusion that dilute these concentrations. Also, this system has positive feedback in that fluid flows shape where membranes form, which then in turn shape the flow. Besides the preceding generic sources of complexity, there is another factor that is specific to this system and may be relevant. The precipitation membrane is formed by reaction between calcium and silicate, and the compounds produced in this reaction are known to have a remarkable level of structural complexity on the microscopic level.\textsuperscript{5}\textsuperscript{20} The conditions of this experiment may be translating some of this complexity from the molecular level to the macroscopic level.

\section{Associated Content}

\section{Supporting Information}

The Supporting Information is available free of charge on the ACS Publications website at DOI: \url{10.1021/acs.langmuir.5b04196}.

Experimental details, additional photographs, and sketch of relevant interfacial forces (PDF)

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Notes

The authors declare no competing financial interest.

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\section{References}


