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Spatially resolved analysis of calcium–silica tubes in reverse chemical gardens

Fredy S. Pratama, Hannah F. Robinson, Jason J. Pagano*

Department of Chemistry, Saginaw Valley State University, University Center, MI 48710, USA

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ABSTRACT

Reverse chemical gardens consist of hollow tubular structures that form in a downward direction from a mechanically held silicate crystal immersed in a metal salt solution. As a model case for this reaction–precipitation system, we investigate the composition, morphology, and microstructure of these tubes in the framework of an experimental model based on preselected reactant concentrations and flow rates. In these experiments, the heavier waterglass solution is being injected downward into large volumes of lighter calcium chloride solution. The resulting hollow precipitation tubes have diameters that range from 0.5 to 3.0 mm. The tube walls have a typical width measurement of 40 μm and are gradient materials. Scanning electron microscopy along with energy-dispersive X-ray spectral data identify calcium and silicon as the major components within the exterior and interior surfaces, respectively. Finally, we compare the behavior, chemical composition, and morphology of tubular precipitation structures created upon the hydrodynamic injection of calcium chloride into a large volume of sodium silicate solution carried out in the upward direction.

1. Introduction

Self-assembled hollow tubular structures are prevalent in nature. Their emergence often relies upon complex physicochemical mechanisms which involve some form of aggregation, precipitation or mineralization within a chemical gradient field. Some examples include corrosion of metals [1–3], soda–straw speleothems [4], black smoker chimneys located on the ocean floor [5], biomineralized shells of algae [6], and the hydration of Portland cement [7,8].

Chemical gardens or silica gardens are the gravity-opposing tree-like structures that form when metal salt crystals are placed in silicate solution. This process is an ideal target laboratory reaction–precipitation system used to create permanent tubular structures. Specifically, the silica garden reaction is capable of yielding hollow precipitation tubes with outer diameters that can range from 500 μm to 1.5 mm that rise to decimeter length. The growth velocities of the fibers vary on the magnitude of mm/day to mm/s depending on the seed metal crystal. A wide variety of inorganic metal salts can be utilized as seed crystals that include the d-block elements [9–11] and Group 2 elements [12–14]. The formation of precipitation tubes is not always limited to waterglass solutions. Tubes may indeed grow in solutions containing anions such as phosphate [15] or carbonate [16].

The first reference to chemical gardens was asserted three centuries ago by Glauber [17]. In modern times, the study of silica gardens has experienced a renewed interest in the scientific community. For instance, tube growth has been investigated under microgravity conditions on the space shuttle [18–20]. Collins et al. [21] identified that tubular precipitates produced from the aluminum silicate system are hierarchical nanostructures. Duan et al. [22] studied the formation of chiral tubes in the presence of magnetic fields. Cronin et al. [23] showed that microtube growth from polyoxometalate-based grains can be controlled by externally applied fields. Recently, Makki et al. [24] developed a procedure for producing hollow metal-silicate microshells and microtubes from reactant-loaded agarose beads.

The well known mechanism responsible for tube growth in silica gardens involves the formation of a semipermeable, colloidal membrane surrounding the dissolving seed crystal [25]. A concentration gradient is created across the membrane allowing for the passage of water molecules through it. As the ionic concentration of the metal salt increases, an increase of osmotic pressure occurs and the inflow of water across the membrane causes it to rupture. From the site of rupture a lighter buoyant solution is ejected into the ambient heavier waterglass. This solution has a different pH from that of the alkaline external sodium silicate solution indicating that a pH gradient is responsible for differences in chemical composition. In conjunction with subsequent polymerization and precipitation reactions this process templates hollow, vertical tubular precipitation structures of amorphous silica and metal hydroxides (oxides). Reverse chemical gardens are produced during the hydration of

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* Corresponding author. Tel.: +1 989 964 2638; fax: +1 989 964 2796.
E-mail address: jpagano@svsu.edu (J.J. Pagano).

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cement. Cement is a ternary mixture composed of tricalcium silicate, dicalcium silicate, and tricalcium aluminate. As water is added to the mixture, silicate particles become surrounded by a colloidal membrane from which micrometer-scale tubes form. This growth process is analogous to silica gardens, but in cement the reactants are rearranged where silicate crystals are employed as the seed.

The silica garden reaction presents several obstacles toward quantification studies. Some of the major difficulties include differences in the size of the seed crystals, slope or shape of the seed crystal, multiple rupturing of the membrane at numerous sites, tubular growth led by air-bubbles [26], and the interaction of neighboring tubes. The flow-controlled method developed by Thouvenel-Romans et al. [27–31] circumvents these problems by replacing a seed crystal with a “seed solution” which is injected at constant flow rates into a large volume of silicate solution. This approach allows for the identification of three regimes of tubular growth namely jetting, popping, and budding. The regimes are all dependent on the density difference between the waterglass in the reservoir and the injected seed solution.

It is important to note that earlier reports using the latter method all consider a lighter seed metal solution being injected into a heavier waterglass solution in an upward direction. Pagano et al. [32] modified this method which involves reversing the density differences. The authors identified four different regimes (reverse jetting, reverse popping, reverse budding, and fracturing) for the downward injection of denser waterglass into lighter cupric sulfate solution. Other experiments revealed that the growth dynamics of the fracturing regime can be described quantitatively by log-normal distributions. Furthermore, the authors did not report spatial-resolved compositional analyses of tubular precipitates originating in the reverse copper–silicate system.

In this article, four regimes of tube growth are identified for the downward injection of denser waterglass into lighter calcium chloride solution. The existence of the four growth regimes is dependent on the variation of experimental parameters. These data are obtained by optical micrographs taken during the experiment. We found that reverse calcium–silica precipitation tubes exhibit similar morphology to that of tubes generated from the reverse copper–silicate system. Moreover, we analyze the microstructure and chemical composition of tube walls for fracturing precipitation tubes by scanning electron microscopy with energy-dispersive spectroscopy. Finally, we compared our findings from the reverse approach to the conventional flow control method, specifically, the upward injection of calcium chloride into sodium silicate.

2. Experimental

2.1. Synthesis

Solutions of 1.0 M sodium silicate ($Na_2SiO_3{\cdot}5H_2O$, Fisher) are prepared and then injected into a vessel of calcium chloride solution ($CaCl_2{\cdot}2H_2O$, Fisher). The injection is carried out in a downward direction through a vertical glass capillary (length = 4.4 cm, inner diameter ≈ 1.0 mm). The injection rate is controlled and predetermined using a syringe pump (KD Scientific 200). A large cylindrical glass vessel (height = 23 cm, inner diameter = 3.5 cm) serves as the container for the calcium chloride solution. The conventional synthesis is performed by upward injection of 0.25 M calcium chloride solution through a glass capillary (length = 4.8 cm, inner diameter ≈ 1.0 mm) into a container (height = 23 cm, inner diameter = 2.2 cm) holding the 1.0 M sodium silicate solution. All solutions are prepared by dissolving the analytical grade salts in distilled water. The experiments were performed at a temperature of $(23 \pm 1)\,^{\circ}$C. Optical micrographs are acquired with a monochrome charged-coupled device camera (CCD; Matrix Vision mvBlueFOX-120G, 640 × 480 pixels at 8 bit/pixel). Image sequences are captured using Matrix Vision Impact (mvIMPACT) software at a typical rate of 10 frame/s.

The density of the calcium chloride solution has an essentially linear dependence on calcium chloride concentration at constant temperature. Accordingly, the density difference $\Delta\rho$ between the sodium silicate solution (waterglass) and the calcium chloride solutions obeys a linear relation $\Delta\rho = \rho_{\mathrm{WG}} - (\rho_{\mathrm{H_2O}} + \xi[\mathrm{CaCl_2}])$ where the density of waterglass and the density of water equal $\rho_{\mathrm{WG}} = 1124\ \mathrm{kg/m^3}$ and $\rho_{\mathrm{H_2O}} = 998\ \mathrm{kg/m^3}$, respectively. The proportionality constant ξ has been measured at 0.10 kg/mol [33].

2.2. Microscopy

Tubular precipitates are synthesized for $[\mathrm{CaCl_2}] = 0.25$ M, $[\mathrm{Na_2SiO_3}] = 1.0$ M, and pump rate of $Q = 2.0$ mL/h. The tubes are collected in a Petri dish filled with distilled water. The tubes and tube fragments are rinsed three times. Excess water is removed and the tubes are air-dried at room temperature. The specimens are either carbon coated or gold sputtered prior to elemental analysis/micrograph acquisition. The latter analyses employ a JEOL JSM-5400 scanning electron microscope (SEM) with an energy-dispersive X-ray (EDS; Oxford Instruments INCA 250) attachment operating at 15 kV.

3. Results and discussion

The conventional or typical silica garden experiment involves the placement of a soluble metal salt crystal in waterglass. The heavy seed crystal sinks to the bottom of the container holding the silicate solution resulting in the formation of hollow tree-like structures. However, the reactants can be rearranged or reversed. For instance, a silicate crystal serves as the seed crystal and then is placed in an aqueous metal salt solution. The key behind this particular experiment is to mechanically hold the particle in the salt solution. When silica gardens are grown under reverse conditions, the tube surface facing the outer excess electrolyte solution is expected to produce the precipitation of cation hydroxide/oxide and the internal face of the wall produces the precipitation of amorphous and/or colloidal silicate. Note that no tubes are observed for the case of a silicate particle that sinks to the bottom of the container.

Fig. 1 shows a snapshot sequence of a typical reverse silica garden produced from a silicate seed crystal glued to a wooden applicator stick and placed in a dilute calcium chloride solution. As mentioned in Section 1, many disadvantages are present during the formation of precipitation tubes. First, the interaction of three neighboring tubes is observed on the left side of the crystal (Fig. 1a). Second, notice the presence of a newly formed tube located on the right side of the crystal that is growing at a faster rate than the other previously formed tubes (Fig. 1b and c). Fig. 1d shows the rapidly growing tube connecting to a “stalagmite-like” pile thus completing the “column”. The experiment given in Fig. 1 clearly does not allow for reproducibility. Specifically, the tubes may grow at different rates, radii of the tubes may vary, and tubes may not resemble one another upon visual inspection. For this purpose we implement the flow controlled method described in Section 2 of this article. This method allows for more control over system parameters (e.g., reactant concentrations, flow rates, densities, and viscosities) and the identification of four regimes.

In Fig. 2, we show examples of the four different regimes observed. The first set of the image sequences shows reverse jetting behavior (Fig. 2a). The tube forms around a descending jet of injected waterglass. Reverse jetting growth is observed for conditions of high flow rate (35–200 mL/h) and high density differences