

Article

Direct Observation of Transient Flow Kinematics of Environment-Friendly Silica-Based Alcogel at Instantaneous Gelation

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Abstract: This study was intended to exploit the possibility of using the quick gelation of alcogel that is induced by adding catalytic imidazole into a silicate-oligomer-based solution. For this purpose, the experimental viability of the direct observation of the gelation behavior was actually examined. The silicate oligomer, derived from tetraethyl orthosilicate hydrolyzed under an acidic condition (pH ~ 5), was used as the quickly gelling mother solution. The capability of the oligomer solution to form a non-flowable matter in only a few seconds when triggered by the addition of the catalytic solution of imidazole is promising, for example, for stabilizing a sandy ground surface, due to its simplicity. From the practical viewpoint, how long the gelation could take (=gel time) is a crucial parameter when the choice of an appropriate gelling chemical species needs to be made. Thus, this study focused its interest on as simple an experimental method as possible for evaluating the gel time of the gelling systems that actually underwent instantaneous gelation. The silicate oligomer solution was an appropriate material both in its quick gelling behavior and environmental friendliness. For such quick gelation, rheological approaches are not applicable for detecting the boundary in the mechanical properties that delineate the regime of “gel”. In this study, instead, direct observation was employed to capture the short interval during which the gelation was completed. The silicate-oligomer-based gelling solution was observed to lose its flowability within only 0.2 s, as it was seen to come off the bottom of the shaken cylinder at 5 Hz. For a more quantitative estimation, the same gelling solution was observed by high-speed motion picture. The high-speed motion picture could clearly capture the instantaneous gelation as a sudden arrest of the flow. The sub-millisecond direct observation of the gelation behavior revealed that the timescale of the instantaneous termination of the flow was as quick as 1 ms in order of magnitude. Such instantaneous gelation in the sub-millisecond-order timescale could not be forecasted from the observable megascopic gelation, which appeared to last from 10² ms to 10³ ms in our naked-eye observation. The noteworthy gap between the timescale of the naked-eye-observed gelation and that of the true gel time at a localized spot determined by the high-speed motion picture should be noted to avoid excess agitation, which can result in total collapse into gel fragments of the just solidifying or already solidified gel under strong deformational influence by mechanical agitation, for example.

Keywords: instantaneous gelation; gel time; direct observation; high-speed motion picture; silicate oligomer; flow arrest time scale



Citation: Kurumada, K.; Ue, H.; Sato, J. Direct Observation of Transient Flow Kinematics of Environment-Friendly Silica-Based Alcogel at Instantaneous Gelation. *Sustainability* **2023**, *15*, 14460. <https://doi.org/10.3390/su151914460>

Academic Editor: Kai Wu

Received: 23 August 2023

Revised: 23 September 2023

Accepted: 27 September 2023

Published: 3 October 2023



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1. Introduction

Civil engineering frequently encounters situations in which excessively flowable objects need to be stabilized in construction or for mitigating disasters. A sandy ground surface is one of the examples with these excessively and riskily flowable properties. Particularly, a sandy layer whose interparticle gap is filled with water is highly likely to undergo a sudden liquefaction or avalanche in the case of even subtle oscillation. Since

the lubricative effect of the interparticle water causes the excessive flowability, filling the interparticle gap with immobile matrices can be a viable approach to effective and lasting suppression of the risky flowability of sandy ground surface layers. Gelation induced in such excessively flowable granular locations can be a technological candidate to mitigate the likelihood of the occurrence of troubles due to their mechanical weakness. More specifically, the possibility of using silica-based gel for the above purpose is to be thoroughly examined to provide fundamentals in applying that to various actual situations. Since silica is the dominant chemical moiety that constitutes sand, it is superior in its surface chemical affinity and compatibility. Hence, the use of a silica-based immobilization medium is practically promising, both in that it can function well in stabilizing sandy grounds and that the environmental alteration due to artificially introduced chemical components in the sandy layer can be minimized. Furthermore, the extreme chemical stability of silica as an inorganic solid species is an advantage considering that silica is not involved in chemical reactions under common moderate conditions. Actually, Remzova et al. succeeded in enhancing the mechanical strength of sandy stones by mixing a silicate oligomer, followed by its polycondensation [1]. Zarzuela et al. proposed a method to enhance the performance of porous portlandite-based solid as a cementation material by filling the pores inside, which the silica oligomer polycondensed to a firm solid filler [2]. The irreversibility in the solidification of silicate oligomer to silica-based solids or non-flowable matrices can be regarded as an advantage in applying these materials to stabilizing sandy ground surface layers. In general, incorporating silica into construction materials can be regarded as a useful and effective prescription for enhancing the strength and resilience of those materials [3,4].

In the present study, the main subject was how to deal with the relatively quick gelation of silica-based materials. More specifically, the timescale for the gelation in those chemical systems should be elucidated since operations that can take more time than the gelation itself are not supposed to help us to finish the fabrication or construction works with the quickly gelling materials. Generally, the state transition from liquids to materials with no mobility is classified as gelation. In considering bringing stabilization due to the gelation into practical use, how much time the gelation requires to be completed is an experimentally obtained parameter of pragmatic importance. Obviously, the required timescale for the completion of gelation (gel time) that is long enough to guarantee the utilitarian stability crucially depends on the chemical species of the gelling objects. The authors are particularly interested in experimental evaluation of the gel time in quickly gelling systems that begin to have the outside appearance of non-flowable gels within only 10 s or so. Such quick gelation can be detected or perceived through direct observation of the kinematic behavior. For the purposes of suppressing the excess flowability of undesirably unstable objects such as sandy layers, we have had the prospect of applying the gelation of silica-based alcogel, since its gelation can be triggered and controlled through the addition of proper catalytic agents. As an indispensable fundamental parameter, we need to estimate the gel time of the silica-based gelling materials. To fulfill this purpose, developing a viable and reliable experimental method to identify the gel time is absolutely necessary. Therefore, establishing reliable measurement methods for evaluating the gel time of silica-based alcogel as a stabilizing matrix is of fundamental use. The authors implemented a preliminary observational experiment by means of high-speed motion pictures to show the possibility to directly capture the instant of gelation in silica-based alcogel [5].

Intuitively, the direct observation of the instant of the prompt gelation by high-speed visualization tends to be considered a simple experimental task. However, unexpected difficulties are found because the vanishing flowability is invisible itself, and we can never perceive it only by observing the gelation in a static manner. In other words, the visual capture of the vanishing flowability needs to be made possible while the object in flow is being “frozen” during its kinematic motion. For example, capturing the process of gelation by tube inversion is impossible, although it is often employed in order to obtain tangible

evidence of the absence of macroscopic flowability due to its simplicity [6,7]. Although the tube inversion is a quite versatile method in checking whether the observed object ought to be classified as gel or not, it cannot be applied to investigating the transient gelation process. Direct observation with naked eyes is obviously the most straightforward method for taking a view of the vanishing flowability and was used even in recent studies [8–11]. Furthermore, an auxiliary procedure of dispersing tiny particles in the gelling solution for enhancing the observability was revealed to work effectively in helping the observers to trace the in situ gelation process [12–14]. This method is particularly helpful in observing the gelling objects whose transient behavior toward the completion of the gelation occurs relatively quickly. Krause et al. succeeded in tracing the fading flowability in a system where the sol–gel transition was induced and recorded the result of the particle image velocimetry (PIV) [14].

As is stated in the following sections, the gelation occurred much more instantaneously than the above case. Thus, a different experimental approach to capturing the moment of the gelation was required.

In previous laboratory-scale studies, rheological methods have been conventionally and popularly employed for the determination of the gel time. Among them, the criterion concerning the storage and loss modulus, which was proposed by Winter and Chambon [15], has been predominantly adopted as the most reliably established experimental scale [16–62]. This criterion has a noteworthy content for the justification that tells us the view that the dominance of the storage modules to the loss modules corresponds to the marked appearance of the elastic properties versus their behavior as a viscous liquid. This physically intelligible picture can support the criterion by Winter and Chambon and enable us to regard it as sound experimental evidence of actual gelation. A technically serious complication is found in the fact that a rheological measurement for checking the satisfaction of the abovementioned criterion for gelation requires a timescale at least as long as 10^1 s in order of magnitude. In the previous studies, there were examples in which the completion of gelation was demonstrated based on the results of the rheological measurements [19,36,51,60]. For example, Huang et al. determined the gel time as a few a few thousands of seconds for a polypropylene melt mixed with carbon black particles. Obviously, in that study, the applicability of the rheological measurements was guaranteed because the required timescale for the individual rheological measurement was negligible compared to the gel time [51].

On the other hand, the set of established measurements are not applicable to materials that undergo quick gelation in a blink. For such quick gels, the only realistic method to capture the moment of gelation was anticipated to be straightforward high-speed motion picture. Therefore, the objectives of the present study were to take as clear a view of the instantaneous gelation of silica-based alcogel as possible in a high-speed motion picture at a frame rate of thousands per second and to create a viable method for the evaluation of such a very short gel time [63].

The authors were also interested in the gap between how long the quick gel lost the observable macroscopic flowability and how instantly the local gelation (=termination of the flow) occurred, as determined from the analysis of the time-series high-speed motion pictures. The abovementioned gap between the timescales of the megascopic “apparent” gelation and spotted “true” gelation was expected to provide, for example, how quickly the agitation to facilitate the quick gelation should be switched off to avoid a detrimental effect due to the vigorous agitation in trying to stabilize a sandy layer with silica-based alcogel. Therefore, the quite fundamental approach for evaluating the timescale required for effective stabilization of sandy ground is expected to help us to choose a proper method for reinforcing sand or soil. How quickly the stabilization remedy should be carried out in actual and practical situations can be linked to our knowledge of the gel time in various quickly gelling systems. Thus, this research report presents our straightforward trials to capture the instant of the gelation in simply derived silica-based materials from silicate oligomer. The gelation is characterized by its extreme rapidity when catalyzed

with basic additives. Visual presentations of the rapidity and the experimental techniques for determining the quantitative gel time applied to such a quickly gelling system were introduced with the obtained gel time, which showed non-negligible discrepancy from our anticipation based on our common naked-eye observation.

2. Materials and Methods

2.1. Materials

Tetraethyl orthosilicate ($\text{Si}(\text{O}-\text{C}_2\text{H}_5)_4$) was purchased from Tama Chemical Co., Ltd. (Kawasaki, Japan). Imidazole ($\text{C}_3\text{H}_4\text{N}_2$) (>99%), ethanol (>95%) and hydrochloric acid (1M) were purchased from FUJIFILM WAKO Chemicals (Osaka, Japan). The water for preparing all the samples was purified by ion exchange followed by distillation. All the above purchased reagents were used as provided without further purification.

2.2. Preparation of Gelling Solution and Induction of Its Gelation

The gelling solution containing silicate oligomer was prepared by mixing tetraethyl orthosilicate (156 g), water (54 g) and 1M HCl (0.3 g) with vigorous stirring at 298 K. The stirring rate was set at approximately 2000 rpm. Tetraethyl orthosilicate was hydrolyzed at $\text{pH} \approx 5$ within an hour, which was shown to be completed by the termination of the moderate emission of heat from the hydrolytic reaction. The obtained mother solution containing silicate oligomer was found to undergo immediate gelation when it was mixed with 20 mL of 40 wt% imidazole solution in ethanol (Video S1), where imidazole functioned as an effective Lewis basic catalyst to trigger the polycondensation reaction amongst the linear oligomeric silicate molecules. At room temperature, the entire gelation was proven to be induced within 8 to 10 s.

2.3. Direct Observation of Gelation in a Shaken Transparent Cylinder

Approximately 170 mL of the silicate oligomer mother solution prepared by the method described in Section 2.2. was transferred into a transparent polypropylene cylinder (inner diameter: 60 mm, height: 120 mm), which was fixed with its side facing a high-speed camera (Photron FASTCAM, MC2. 1, Yonezawa, Japan) and a normal digital camera. A thin nozzle (inner diameter: 2 mm) was attached at the upper center of the side to supply 16 mL of the 40 wt% ethanol solution of imidazole to induce the prompt gelation, whose duration timescale was only a few seconds, as observed in Video S1. The horizontally placed cylinder began to be shaken at a constant amplitude of 6 cm and frequency of 5 Hz, which was immediately followed by supplying the ethanol solution of imidazole by manual injection. The vigorous mixing by the 5-Hz shaking was continued for approximately 10 s so that the gelation was completed inside the shaken cylinder, as seen in Video S2. The alteration of the appearance of the mother gelling solution containing silicate oligomer inside the shaken cylinder was recorded using a high-speed camera at 1000 and 5000 fps.

2.4. Direct Observation of Gelation in a Stirred Container

Approximately 150 mL of the mother gelling solution containing silicate oligomer prepared by the method described in Section 2.2. was transferred into a transparent polypropylene cubic container (inner width: 60 mm, depth: 60 mm, height: 60 mm) and vigorously stirred at approximately 1500 rpm. Then, 14 mL of the 40 wt% ethanol solution of imidazole was instantaneously added by manual injection into the silicate oligomer mother solution to induce the prompt gelation, as shown in Video S3. Primarily, the scene of the gelation process was visually recorded using a high-speed camera (Photron FASTCAM, MC2. 1, Yonezawa, Japan) at 1000 fps, at first, where the completion of the gelation was observed with the whole distortion and destruction into fragments as a result of the elimination of flowability under the influence of the continuous forced agitation. Secondly, for a more quantitative and precise visual evaluation of the gel time, the gelation at a more localized spot was recorded at 5000 fps.

2.5. Image Analysis for Determination of Gel Time

The moment of gelation in the shaken cylinder was determined as the instant at which the gelling mother solution was observed to come off the bottom of the shaken cylinder. Such kinematic behavior was expected to be observed at either end of the 5-Hz oscillation where the translational velocity of the cylinder was instantaneously reversed. The moment of gelation was estimated to be in the time interval between the two adjoining ends of the oscillation at which the contained gelling mother solution was seen to “flow” at the last occasion and, subsequently, to behave as a non-flowable lump-like object at the first occasion. Therefore, the temporal resolution of this method in determining the gel time was 200 ms corresponding to the reciprocal number of 5 Hz.

The moment of gelation in the stirred cubic container was determined directly from the instant of the arrest of the translational motion of the observed part in the vigorously stirred gelling mother solution. In this direct observation, tiny bubbles generated by the vigorous stirring worked as the visual markers for tracing the translational motion of the flowing gelling solution driven by the forced stirring. Primarily, the moment of the instantaneous gelation was crudely estimated by naked-eye observation of the high-speed motion picture, where the spot for the observation was selected so that the influence due to the forced stirring on the translational motion could be minimized. Second, Image J version 1.54f was used for the image analysis to present the temporal profile of the time series of the images taken at the interval of sub-milliseconds [64,65], where the arrest of the translational motion of the bubbles was recorded as the termination of the translational motion. The number of frames required from the capture of the instant of the onset of the termination of the flow to its completion was employed as the measure to evaluate the gel time.

3. Results and Discussion

3.1. Direct Observation of Gelation in a Shaken Cylinder

Figure 1 presents the snapshots of the gelling mother solution of the silicate oligomer. The supplementary high-speed motion picture was given in Video S4. In the pre-gelation period (Figure 1A–C), the solution maintained a liquid state, as seen in the snapshots and motion pictures, where the turbulence on the impingement against the right-hand bottom of the cylinder was characteristic of highly flowable objects. In the gelling period, on the other hand, the kinematic characteristics obviously altered as the oscillatory cycle progressed at every 0.2 s, as observed in Video S4. The most prominent symptom that showed the irreversible loss of the flowability of the gelling solution was found in the kinematic behavior when it was detached from the right-hand bottom. At a frame number in the vicinity of 4405, a slit-like gap was seen to form between the gelling mother solution and the right-hand bottom (Figure 1E). Such a solid-like morphology did not appear even only one cycle prior ($=0.2$ s prior) to the abovementioned clear detachment, as seen at a frame number of approximately 4194 (Figure 1D). It should be noted that the gelling mother solution before the solid-like behavior began to stand out exhibited characteristic stretch-like kinematics, which indicated the rapidly increasing viscoelastic properties toward the vanishment of the flowability. Furthermore, once the detachment of the gelling mother solution from the cylinder bottom occurred in the slit-like manner, the liquid-like turbulent impingement onto the right-hand bottom was never observed again (Figure 1F), and the slit-like detachment from the bottom became more dominant, as observed in Video S4. The appearance of the gelling mother solution was altered to a visible extent at each oscillatory cycle, and finally, it behaved much like a bouncing ball in the collision with both the bottoms of the shaken cylinder. After gelation was completed, the gel immediately broke into smaller solid grains whose size was as small as a few millimeters. Once the gel fragmented during the post-gelation period, it stayed unchanged, although it was repeatedly hit by the bottoms of the shaken cylinder (Figure 1G–I).

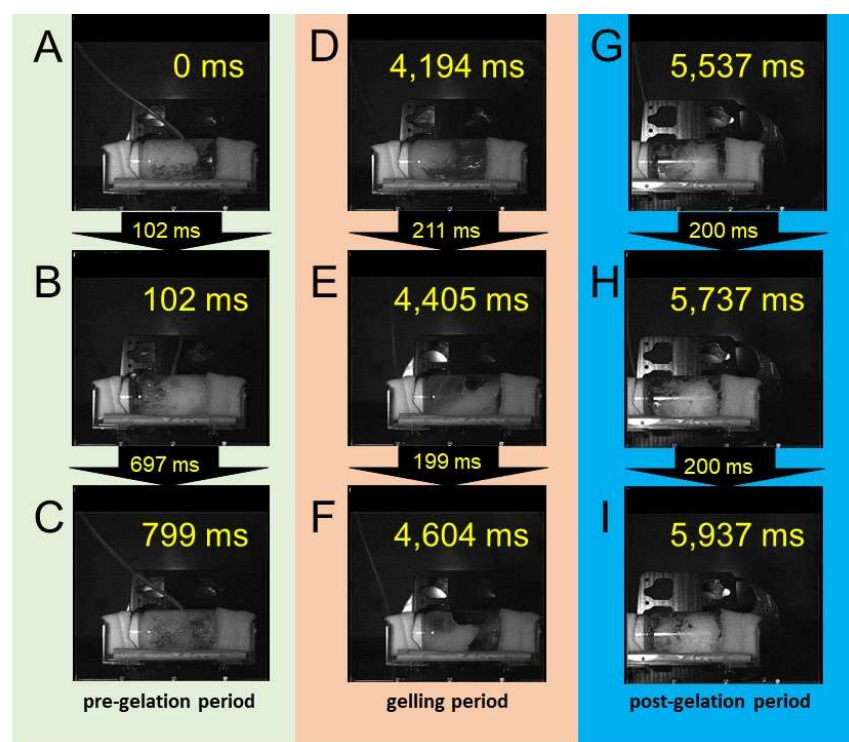


Figure 1. Nine representative snapshots of the gelling solution contained inside the transparent polypropylene cylinder shaken at 5 Hz. (left: A–C) show the pre-gelation morphology before gelation. (middle: D–F) captured the time intervals during which the morphological alteration of the gelling mother solution was the most drastic. (right: G–I) present the constancy in the appearance of the object that already went through gelation.

Considering the visible morphological alteration at every oscillatory cycle at 5 Hz in the gelling period, as mentioned above, the gel time, which means the timescale required for gelation (=loss of the flowability), should be considered significantly smaller than 0.2 s. Since a couple of the cycles corresponding to 0.4 s were sufficient for the visible transition from flowable liquid to entirely non-flowable gel, the gel time of the megascopic object was in the order of 10^{-1} s when gelation was induced by the polycondensation reaction in the mother solution of silicate oligomer, being catalyzed with imidazole as a Lewis base.

3.2. Direct Observation of Gelation in a Stirred Container

Figure 2 presents the five sequential snapshots of the gelling mother solution of silicate oligomer from the moment of the injection of the catalytic 40 wt% imidazole solution in ethanol to the thorough collapse of the solidified gel due to the incessant vigorous stirring. Video S3 is the corresponding motion picture that contains the series of the above five snapshots. Video S3 is displayed in real time by displaying 1000 serial pictures per second, where the motion picture was originally taken at 1000 fps. On the addition of the catalytic imidazole, the mother solution was still in a completely liquid state, as indicated by the pattern formed on the frontal side by the turbulent agitation (Figure 2A). The incipient symptoms of gelation appeared at a frame number of approximately 3749 with the overall sudden darkening of the image (Figure 2B), followed by surface undulation, which became more prominent after the frame number of 3791 (Figure 2C). The total distortion of the object implying the rapid progress of the gelation was clearly seen after the frame number of 4000 (Figure 2D). The detachment of the gelling mother solution from the inner wall was seen to begin on the right-hand side at the frame number of 4041 (Figure 2D), which continued thereafter. The gelation was completed no later than the frame number of 4500, after which the completed gel no longer behaved like a flowable object. At this stage, the

gel was collapsed by the forced stirring and oscillated at the cycle of the rotating stirring blades (Figure 2E).

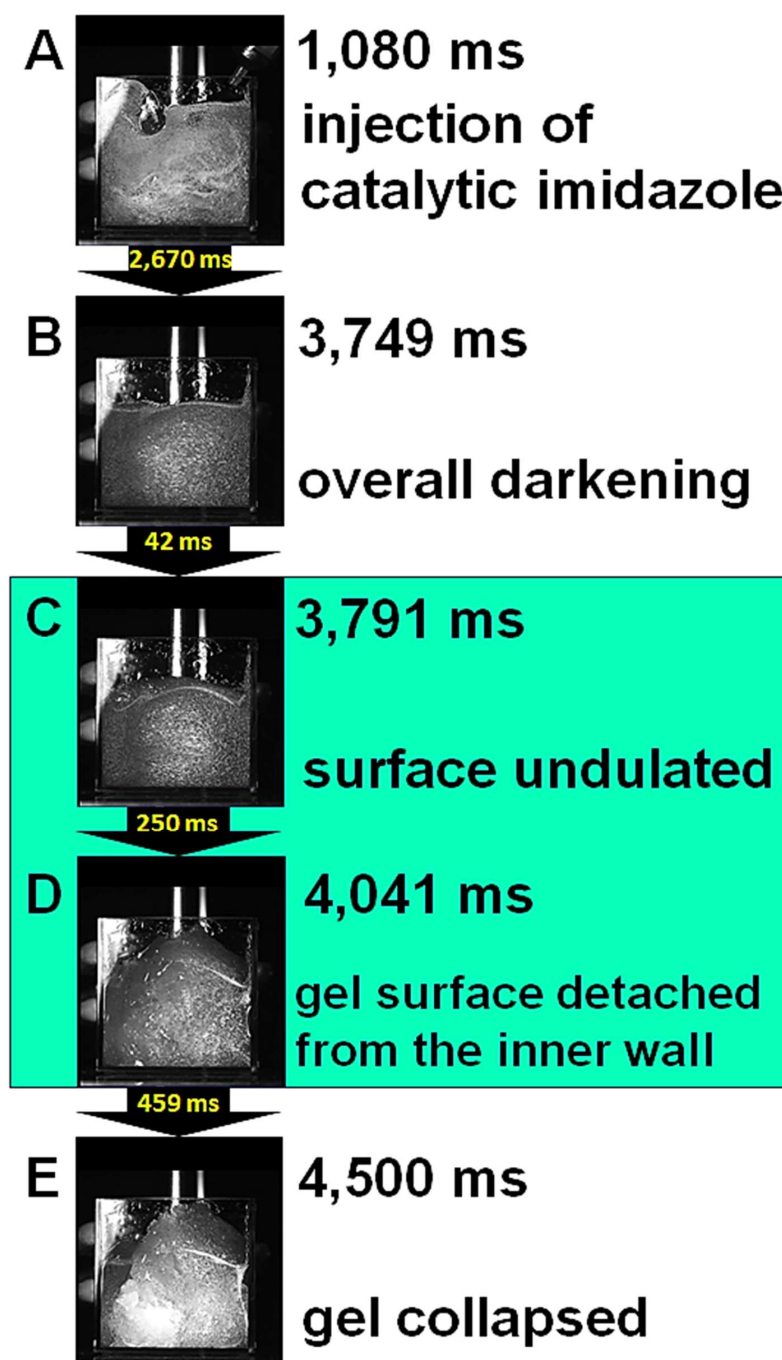


Figure 2. Five representative snapshots (A–E) of the gelling solution contained in a transparent polypropylene cube (60 mm × 60 mm × 60 mm) and being incessantly stirred with blades at 1500 rpm. The frame number is shown beside each snapshot with the time interval to the following one.

Assuming that the gel time corresponds to the time interval from the moment of the first faint symptom of the vanishment of the flowability to that when the object no longer behaved as a flowable matter, the time interval (0.250 s) between the two instants (Figure 2C,D) must have included the process of overall gelation in the present megascopically agitated system, as captured in Video S3. The abovementioned timescale for the gelation to occur is roughly in agreement with the fact that the loss of the flowability of the gelling mother solution in the shaken cylinder at 5 Hz was clearly observed.

3.3. Direct Observation of Gelation near the Inner Wall of the Stirred Container

In order to minimize the disruptive influence of the forced stirring on the capture of the short instant of gelation, a spot near the left inner walls was selected, as shown in Figure 3. The zoomed area was selected so that the motion picture would not be affected by the vertically undulating upper surface of the gelling mother solution. The focused area for direct observation was chosen as shown by a rectangle fixed along the left-hand inner wall of the cube whose thickness was 2 mm, as seen in Figure 3. Video S5 presents the zoomed motion picture that captured the whole process of the gelation until the entire termination of the upward unidirectional flow along the left-hand wall. Obviously, gelation was observed as the irreversible arrest in the flow. Video S6 shows the zoomed motion picture of the selected area in the near-gelation temporal range in Figure 3, displayed at 10 fps, where the original frame rate was 5000 fps.

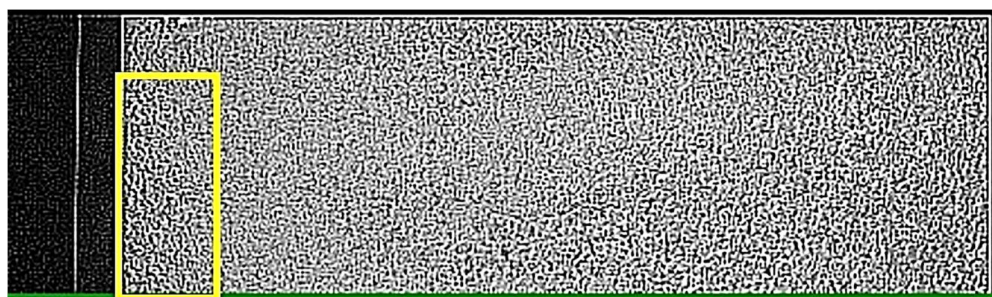


Figure 3. Zoomed snapshot of the gelling mother solution near the left-hand inner wall of the transparent polypropylene cube. The part in the yellow box in Figure 3 was selected to analyze the kinematics of the instant of the gelation, (Video S5 is helpful to observe the gelation where the constant upward translation of the liquid terminated).

Figure 4 shows a snapshot in Video S6. The middle horizontal red line showed the viewing position of the time dependence of the black-and-white profile, which was used in analyzing the temporal variation of the above black-and-white profile.

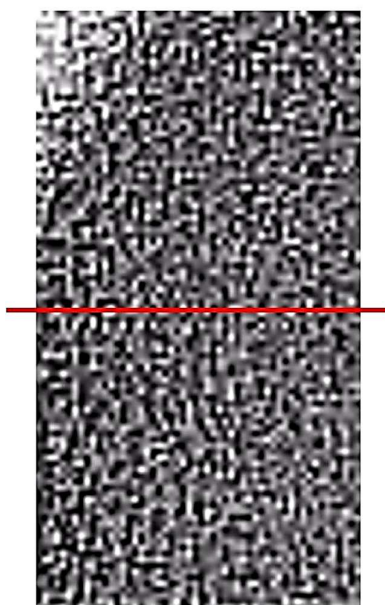


Figure 4. Zoomed snapshot of the gelling mother solution in the rectangle in Figure 3 for selecting the area suitable for the direct observation of the gelation. The projected temporal profile at 5000 fps was taken on the red horizontal line shown thereon.

Figure 5 shows the 3D representation of the 0.2-s profile of the selected area for the direct observation of instantaneous gelation. The arrest of the flow seen in Videos S5 and S6 correspond to the transition of the flow curve to the time-independent plateau as seen in the yellow circle in Figure 5. Since the upward slant of the flow curve vanished within a timescale much shorter than 0.2 s, the estimate of the gel time from the megascopic direct observation of the gelation in the shaken cylinder at 5 Hz or the stirred cubic container should be considered much longer than the true timescale of gelation at localized spots.

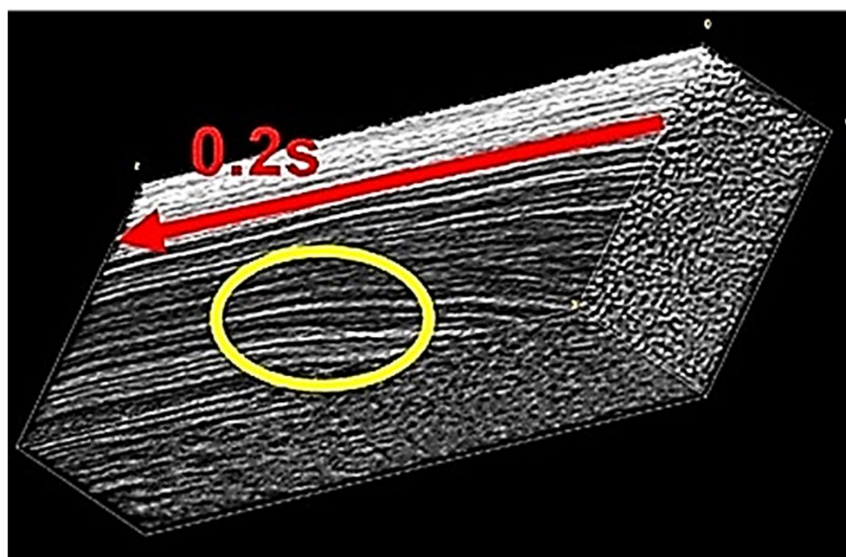


Figure 5. Three-dimensional representation of the 0.2-s temporal profile of the selected area for the direct observation of gelation. The red arrow in Figure 5 represents the direction of the lapse of time. Gelation was seen as the disappearance of the slant, which indicated the time-dependent translation in the stirred gelling mother solution, as marked by the yellow circle shown therein.

For a more quantitative evaluation, the temporal profile of the zoomed motion picture along the red horizontal line shown in Figure 4 was represented in Figure 6. The long slip-like profile shows the time dependence of the flow curve for 1 s and includes the instant of the arrest of the flow as marked in the figure. The inflection of the flow curve was magnified to evaluate the timescale in which the flow underwent the instantaneous termination. The slanted pattern in the left-hand side of Figure 6 represents the continuation of the unidirectional flow until it was instantaneously arrested due to gelation. The present interest was focused on the transition, which appeared as the disappearance of the slant in Figure 6. In order to evaluate the timescale in which the slant abruptly vanished, the appropriate part for the purpose of finding the arrest of the flow was selected, as depicted with a drawn rectangle in Figure 6.

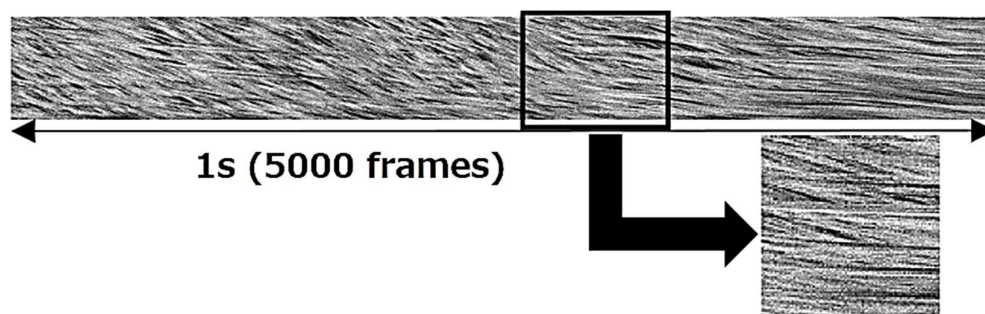


Figure 6. 1-s long temporal profile of the projection of the translation in the gelling mother solution. The part corresponding to the gelation period was magnified and shown aside.

Figure 7 presents the magnified temporal profile wherein each tiny cube that constitutes the profile corresponds to $(1/5000)$ s in the vertical direction in the figure. A guide for eyes was drawn in Figure 7 in order to show an example of the inflection of the flow curve, which took approximately five cubes to complete the transition from the slanted direction to the vertical one. Therefore, the flow termination at the observed spot was considered to have occurred in or within 1 ms in order of magnitude. As seen in Figures 6 and 7, the slant did not reappear once it turned to a plateau. This irreversibility obviously corresponded to the irreversible transition from the macroscopically mobile state to the immobile state. This result showed that gelation occurred as a straightforward and entirely irreversible transition toward a completely immobile state and intrinsically differed from a diminishing semi-periodic repetition between the mobile and immobile state in the midst of the course toward the ultimate gelation. The visual impression of oscillatory behavior that appeared when watching the megascopic gelation captured in motion pictures, such as in Video S1 or Video S3, was shown not to be the result of the solidification behavior in an oscillatory manner between liquid and solid but rather the macroscopic rotational agitation.

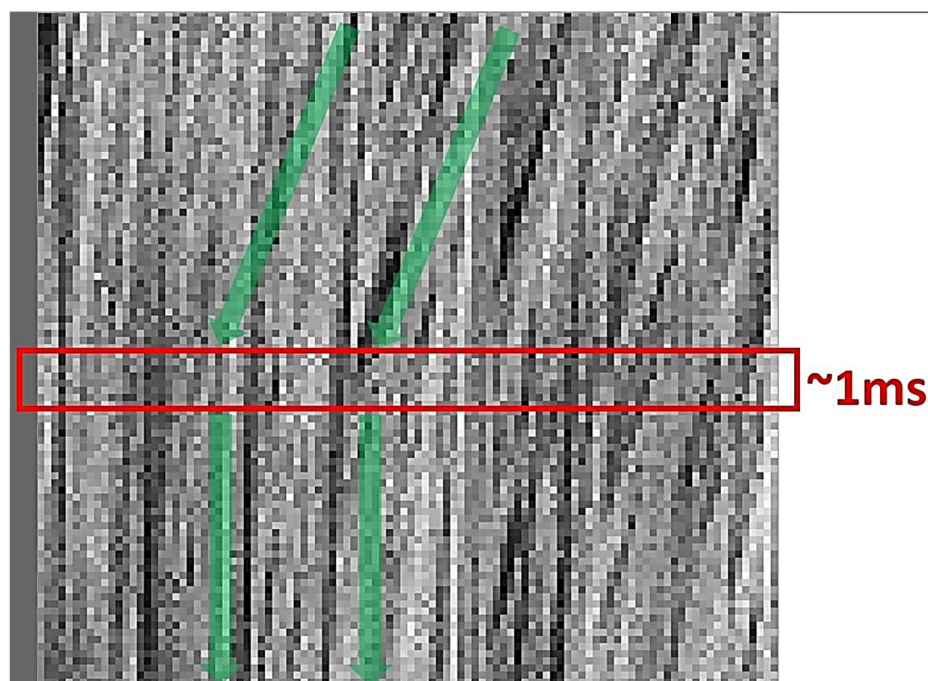


Figure 7. Magnified view of the temporal profile of the near-gelation zone. Each tiny cube corresponds to 0.2 ms in the vertical direction in this figure. Arrows are shown as guides for eyes to make it easier to find where the slant disappeared. Arrays of only a few tiny cubes corresponded to the estimate of the gel time (~ 1 ms).

Such a tiny timescale as 1 ms for gelation to occur could have not been derived if we had merely relied on our naked-eye observation of the whole gelling system as presented in Videos S1 and S3, which were displayed in real time. Those who watched these motion pictures, including the overall macroscopic gelling behavior, were supposed to conclude that the vigorously stirred mother solution exhibited a gel time of approximately 0.5 s from the kinematic naked-eye visual impression. The spotted termination of the flow that lead to the ultimate gelation was only 1 ms, which was much shorter than the abovementioned apparent gel time in the naked-eye impression. The naked-eye observation could not possibly reach such a sufficiently minute estimate of the gel time, which could be unveiled depending on the advanced high-speed-camera-based technique. Being quite distinct from the impression-based gel time, a certain local spot was revealed to undergo a much more instantaneous “freezing” than speculated from the overall naked-eye observation. The prominent undulation behavior caused by the vigorous agitation obviously hindered

us from accurately grasping the moment of gelation depending on only our naked eyes. Nevertheless, gelation occurred much more quickly than we could perceive through a naked-eye observation, as the present experimental study has shown.

4. Conclusions

The most straightforward method for evaluating the gel time of a quickly gelling system was proposed. A direct observation and the following image analyses of the high-speed motion picture taken at a frame rate of 5000 per second were used. In the present study, the gelation of silica-based alcogel derived from silicate oligomer through its quick polycondensation reaction was recorded in a high-speed motion picture. The choice of direct observation of quick gelation in the present study was unavoidable considering that implementing serial rheological measurements to obtain the storage and loss modulus, including careful sampling and setting the sampled solution on the apparatus, is impossible within only a few seconds. As seen in Video S1 or Video S2, gelation can be completed almost instantaneously, to which only direct observational methods supported by some “augmented eye”, such as a high-speed camera, can be applied.

The 5000-fps high-speed motion picture could capture the exact moment of the quick gelation. The image analyses of the serial translation of the flowing gelling liquid showed that the arrest of the flow occurred in the timescale of 1 ms in order of magnitude, which was much shorter than that elucidated from the naked-eye observation. In observing the flow behavior using the high-speed camera at thousands of frames per second, the vigorous blade agitation that incessantly entrained the outside air from the undulating upper surface of the gelling liquid was of use since the entrained air immediately fragmented to sub-millimeter-sized bubbles, which worked as appropriate visualization tracers for the turbulent flow of the agitated gelling liquid. The time-series snapshots of the gelling liquid in the vicinity of the instant of gelation showed the invisibly quick gelation that occurred in only 1 ms.

The quickly gelling materials, such as the silica-based alcogel investigated in this study, need to be swiftly handled considering that the irreversible elimination of the flowability can be brought about during gelation as promptly as only a few milliseconds once gelation is triggered. Such a quick loss of flowability can be an appeal for its use in stabilizing weak sandy ground surfaces and similarly fragile natural or artificial structures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su151914460/s1>, There are six supplementary videos. Video S1: Motion picture of gelation of silicate oligomer solution triggered by injecting imidazole solution.; Video S2: Motion picture of the transparent polypropylene cylinder containing silicate oligomer solution and being shaken at 5 Hz with 60 mm amplitude. The gelation was progressed inside the cylinder triggered by injecting catalytic imidazole solution into the cylinder.; Video S3: Motion picture of silicate oligomer solution under vigorous stirring with blades at 1500 rpm. The gelation was triggered by injecting catalytic imidazole solution into the container.; Video S4: Motion picture which corresponds to Figure 1. The three attached high-speed motion pictures present the kinematic morphology of the object before, during, and after the gelation from the left to the right, respectively.; Video S5: High-speed motion picture for capturing the gelation near the inner wall of the cubic container. The original 5000-fps motion picture was displayed at 500 fps. This motion picture corresponds to Figure 3.; Video S6: Magnified high-speed motion picture for capturing the gelation at the selected spot. The original 5000-fps motion picture was displayed at 10 fps. This motion picture corresponds to Figure 4.

Author Contributions: Conceptualization, K.K.; methodology, K.K.; formal analysis, K.K. and H.U.; investigation, K.K., J.S. and H.U.; writing—original draft preparation, K.K.; writing—review and editing, K.K.; visualization, K.K. and H.U.; funding acquisition, K.K. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by JSPS KAKENHI Grant Numbers 20K05202.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Acknowledgments: The corresponding author (K.K.) gratefully acknowledges the support by JSPS KAKENHI Grant Numbers 20K05202.

Conflicts of Interest: The authors declare no conflict of interest.

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