Establishing Vadose Zone Slow-Release Carbon Sources for Enhanced Bioremediation Using Silica Suspension

Lirong Zhong,* Brady Lee, and Shuo Yang

Delivery of C sources (nutrients) to the vadose zone and establishing a slow-release C source in this unsaturated zone are essential for promoting long-term, enhanced contaminant bioremediation at sites with deep vadose zones, such as the Hanford Site in the southeast of the state of Washington. Conventional solution-based injection and infiltration approaches face challenges in achieving delivery goals. Aqueous colloidal silica suspension has characteristics that can potentially be used for nutrient delivery and slow-release source setup. This research was conducted to (i) demonstrate delayed gelation of colloidal silica suspensions with the presence of nutrients; (ii) prove that gelation takes place in sediment and the gel slowly releases nutrients; and (iii) show that silica suspensions are injectable for vadose zone emplacement. Results demonstrated that nutrient-laden colloidal silica suspensions have low initial viscosity and then increase in viscosity with time until reaching gelation, allowing for a slow release of nutrients into the environment. Higher salt and silica concentrations increased the rate of viscosity climbing and the rate of gelation, whereas higher silica concentrations resulted in stronger gels. Nutrients were slowly released from gels in both batch and column experimental settings. The rheological and injection behavior of the silica suspensions revealed the injectability of these fluids. This study demonstrated that colloidal silica suspension could be used as a carrier to distribute nutrients to the vadose zone and to establish slow-release nutrient sources.

Abbreviations: DIW, deionized water; EC, electrical conductivity; FS, fumed silica; PV, pore volume.

Delivering nutrients to the vadose zone and establishing a slow-release C source in the unsaturated zone is essential for promoting long-term, enhanced contaminant bioremediation at sites with deep vadose zones, such as the Hanford Site in the southeast of the state of Washington. Conventional solution-based injection and infiltration approaches are not capable of providing slow-release nutrient sources, which are needed to promote enhanced, long-term bioremediation.

Colloidal silica suspensions have been studied for decades for their physicochemical properties and versatile applications (Iler, 1979; Bergna and Roberts, 2005). Fresh aqueous colloidal silica suspensions have similar viscosity to water, and the viscosity increases with time. The suspensions may eventually turn into rigid gels when the formulations of the suspensions are desirable (Persoff et al., 1999; Hunt et al., 2013). The suspensions also exhibit shear thinning behavior (Amiri et al., 2011; Yang et al., 2016, 2017). Because of the relatively low viscosity and shear thinning characteristic, fresh silica suspensions can be readily injected into porous media. The increase in viscosity over time and the eventual gelation enable the gelled suspension to remain at a target location in the subsurface. Because of their injectability and subsequent gelation feature, colloidal silica suspensions have been tested as media for remedial amendment delivery (Lee and Gupta, 2014) and have been applied as slow-release sources of remedial constituents (Yang et al., 2016, 2017) or as barriers after gelation for contamination containment in the subsurface (Persoff et al., 1995, 1999; Yossapol, 2002).

Colloidal silica-based delivery is a potential approach to achieve the goals of distributing nutrients to the vadose zone and establishing slow-release sources in the
unsaturated zone. Studies have demonstrated that (i) the aqueous colloidal silica suspension with addition of oxidant remedial amendments exhibits delayed gelation characteristics (Lee and Gupta, 2014; Yang et al., 2016, 2017), and (ii) the amendment in the so-formed silica gel is then slowly released into the environment (Lee et al., 2014; Yang et al., 2016). The time of delay in gelation is a function of the concentrations of silica particles, amendment, and salinity in the suspension (Hunt et al., 2013; Yang et al., 2016, 2017). The delayed gelation provides a time window for the injection of the suspension into the subsurface, and the gelation of the amendment–silica suspension enables the amendment-laden gel to stay in the target zone and slowly release the constituents for contaminant remediation. This approach can potentially be applied to deliver bionutrients to the vadose zone for enhanced bioremediation, which is important for contaminated sites with deep vadose zones and limited accessibility, such as the Hanford Site (Gee et al., 2007).

This study was conducted to demonstrate the delayed gelation of colloidal silica suspensions containing C sources and to prove that the gelation occurs in sediments under vadose zone conditions. The nutrient release rate from the gelled silica suspension was measured to show that a slow-release source can be established. Molasses and sodium lactate were tested as examples of C source amendments. The rheological properties of the silica suspensions during gelation were characterized. The influence of silica concentration, salinity, nutrient concentration, and the types of nutrients was studied. Nutrient release rates from silica–nutrient gel were quantified using molasses as the example, and the influence of suspension gelation time on the release rate was investigated. Injection behavior of the suspensions was revealed by monitoring their rheological properties during preparation and measuring the injection pressure.

 Morales and Methods

Materials

Fumed silica (SiO₂, FS), sodium lactate (C₃H₆NaO₃), and sodium chloride (NaCl) were all obtained from Sigma-Aldrich. Molasses was purchased from a local grocery store. Hanford Formation sediments obtained from a gravel pit in Pasco, WA, and Accusand (20/30 mesh grade, Unimin Corporation) were used in tests of silica suspension gelation and column experiments. The Hanford sediments were sieved to remove grains >8 mm. Accusand (20/30 mesh grade) is a laboratory sand that has a relative uniform particle size distribution, with a uniformity coefficient (d₆₀/d₁₀) of 1.19 (Schroth et al., 1996) and a packed porosity of 0.37 (Zhong et al., 2008). The Hanford sediment has a packed porosity of 0.35 (Thornton et al., 2006).

Rheological Measurements

The rheological properties (i.e., the viscosity and viscosity response to shear rate characteristics) of the silica–nutrient suspensions were studied with a Physica MCR 101 rotational rheometer (Anton Paar) using a CC-27 cup-and-spindle measuring system. To measure the viscosity of the suspensions, a shear rate of 4 s⁻¹ was used. The suspension was placed in the measuring cup, and the spindle was then inserted into the suspension and submerged in the fluid. The viscosity of the suspension was determined at predetermined time intervals. The duration of each measurement was 10 min at a constant shear rate. For viscosity response to shearing measurement, the shear rate range of 0.1 to 150 s⁻¹ was used. A built-in temperature control chamber allowed selection of the desired temperature (25 ± 0.1°C) for measurements.

Gelation Characterization

Batch tests, beaker tests, and column experiments were applied to test the gelation of silica suspensions without sediments and the gelation of suspensions in sediments. In batch tests, silica suspensions were placed in bottles or in the measuring cup of the MCR 101 rheometer, and the gelation status was monitored over time. In beaker tests, 80 cm³ of Hanford formation sediments with 4% (w/w) water content was placed into each of four 100-mL beakers. One pore volume (PV) of 5% (w/w) FS, 5% (w/w) molasses, and 0.3% (w/w, 3000 mg L⁻¹) Na⁺ suspension was injected into the bottom of the beaker to saturate the sediment. The gelation state was checked over time. The sediment–suspension mixture in one beaker was carefully poured out at a 24-h time interval to check the gelation progress.

In the column test, a glass column (i.d. = 2.54 cm, length = 30 cm) was packed with Accusand and saturated with deionized water (DIW). A 60-mL suspension of 5% (w/w) FS, 7% (w/w) molasses, and 0.3% (w/w) Na⁺ was then injected at a high rate (50 mL min⁻¹) into the column, manually using a syringe to saturate the sediment. After saturation, the suspension was then injected into the sediment through the column’s bottom inlet with a peristaltic pump (MasterFlex) at an injection rate of 0.32 mL min⁻¹. The gelation state of the suspension in the column was monitored by measuring the injection pressure using a pressure transducer and digital indicator (Cole Parmer Instrument Company).

Nutrient Release Rate Measurement

Batch tests were conducted to study the C release rate from gel into bulk water, and column experiments were performed to study the release rate into flowing pore water. Accusand and Hanford Site sediments were used as the porous media in column tests. To simulate the vadose zone sediment condition, 4% (w/w) of water was added to the porous media. Molasses was used as the C source.

In batch tests, 10 g of 7% FS and 7% molasses gel (w/w) was placed on the bottom of a 250-mL glass bottle. Deionized water (230 mL) was then added into the bottle carefully to minimize mixing at the gel–water interface. An electrical conductivity (EC) probe was placed into the water and fixed at the position 2 cm above the gel. The bottle was kept undisturbed and set at room temperature, and the EC reading was recorded at time intervals. The correlation between molasses concentration in bulk water and EC reading was developed before the test; therefore, the concentration was calculated from the EC reading.
Column experiments were used to study the release of C from silica–molasses gel into flowing pore water and to test the influence of sediment type and silica gelation time on the release rate. In each column test, a silica–molasses suspension or molasses solution of known amount was injected into a packed column. When the solution was injected, DIW was pumped into the column right after the injection to leach molasses out. When the suspension was injected, it was left to gel for a desired time before DIW was injected to leach molasses out from the column. An EC probe was installed in-line in the column effluent tubing. The flow rate, injection pressure, and effluent EC reading were recorded through the column test. The correlation between molasses concentration in flowing water and EC reading at the probe installed in the effluent line was developed before the test. To test the influence of gelation time and sediments, eight column tests were conducted. The parameters of the column tests are summarized in Table 1.

Results and Discussion

Rheological Behavior of Silica–Nutrient Suspensions

Shear Thinning of Silica Suspensions

When colloidal silica was mixed with water and nutrients, the initial viscosity was between 3 and 10 cP at a shear rate of 20 s$^{-1}$, depending on silica concentration. When no mixing was applied to the silica suspensions, their viscosity increased considerably with time. All silica suspensions exhibited shear thinning behavior. Figure 1 shows three flow curves of silica suspensions with molasses. With aging, the shear thinning was more profound.

The colloidal silica suspension in DIW and suspension with oxidant amendment also showed shear thinning property (Amiri et al., 2009; Yang et al., 2016, 2017). For suspensions containing colloidal particles that cross-link to form clusters, shear thinning is attributed to the breakdown of particle clusters caused by shear stress (Sonntag and Russel, 1986; Potanin, 1991; Ament et al., 2014; Yang et al., 2017). Shear thinning promotes easier injection of the suspensions into the subsurface.

Silica Concentration Influence

When the silica concentrations in FS–nutrient suspensions were low, the viscosity increase was limited. For suspensions at 1.0 and 3.0% (w/w) FS, both with 7% (w/w) sodium lactate, the viscosity increased from 1.5 to 1.6 and from 20 to 159 cP in 95 h, respectively (Fig. 2). No gelation occurred in these suspensions. With 5.0% (w/w) FS, the viscosity increased to 3700 cP in the same time period. Gelation occurred with this suspension after 100 h. The gelation process was faster when the FS concentration was higher.

Cross-linking (e.g., formation of siloxane bond) between the silica particles gives rise to the viscosity of the suspensions (Iler, 1979; Brinker, 1994; Yossapol, 2002). The connection among the particles occurs faster when higher concentrations of particles are present in the suspension, resulting in faster and more significant viscosity increase. A similar relationship between viscosity increase of colloidal silica suspensions and colloidal silica concentration was reported by others (Chen et al., 2005; Mondragon et al., 2012; Yang et al., 2016, 2017).

Salinity Influence

Although sodium lactate contains 20.55% of Na$^+$ mass (i.e., 5.0% [w/w] lactate solution already contained 1.03% [w/w,

Table 1. Parameters for C release in column experiments.

<table>
<thead>
<tr>
<th>Column test no.</th>
<th>Formulation</th>
<th>Porous medium</th>
<th>Gelation time</th>
<th>Flow rate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7% (w/w) molasses solution</td>
<td>Accusand</td>
<td>NA†</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>7% (w/w) fumed silica (FS), 7% (w/w) molasses gel</td>
<td>Accusand</td>
<td>96</td>
<td>0.54</td>
</tr>
<tr>
<td>3</td>
<td>7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ sol.</td>
<td>Accusand</td>
<td>NA</td>
<td>0.50</td>
</tr>
<tr>
<td>4</td>
<td>7% (w/w) FS, 7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ gel</td>
<td>Accusand</td>
<td>50</td>
<td>0.51</td>
</tr>
<tr>
<td>5</td>
<td>7% (w/w) FS, 7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ gel</td>
<td>Accusand</td>
<td>84</td>
<td>0.51</td>
</tr>
<tr>
<td>6</td>
<td>7% (w/w) FS, 7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ gel</td>
<td>Accusand</td>
<td>96</td>
<td>0.46</td>
</tr>
<tr>
<td>7</td>
<td>7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ sol.</td>
<td>Hanford sediment</td>
<td>NA</td>
<td>0.52</td>
</tr>
<tr>
<td>8</td>
<td>7% (w/w) FS, 7% (w/w) molasses, 3000 mg L$^{-1}$ Na$^+$ gel</td>
<td>Hanford sediment</td>
<td>72</td>
<td>0.50</td>
</tr>
</tbody>
</table>

† NA, not applicable.
10,300 mg L$^{-1}$ Na$^+$), addition of Na$^+$ to the silica suspensions still enhanced viscosity increase and the gelation process for the suspensions, as shown in Fig. 3. When more Na$^+$ was added, the rate of viscosity increase was promoted. Thus, the amount of salt addition can be applied as a controlling factor to achieve the desired time of gelation according to the needs of suspension preparation and injection.

The electrical double layer theory sheds light on the mechanism of the salinity influence on suspensions' viscosity. In the FS suspension, a double electrical layer surrounds the negatively charged silica particles. The addition of salt causes a depression of the electrical double layers, allowing the particles to move closer to one another and make connections (Roberts, 2006), thereby increasing the viscosity. The ions can also act as a bridge between silica particles to form groups of particles, thus increasing the viscosity (Bergna and Roberts, 2005). Previous work has also reported enhanced SiO$_2$ coagulation and increased viscosity of suspensions with the addition of cations (Milonjic, 1992; Depasse, 1997; Amiri et al., 2009; Yang et al., 2017).

### Lactate Concentration Influence

For the tested suspensions containing 5% (w/w) FS and 3000 mg L$^{-1}$ added Na$^+$ with lactate concentration ranging from 3 to 9% (w/w), viscosity increased with time to a peak value. The viscosity then decreased significantly in later measurements (Fig. 4). The decrease in viscosity of the suspension indicates the breaking down of the gelling structure (i.e., the three-dimensional network of silica particles). Gel breaking was caused by the rotational mixing applied to the suspension during viscosity measurement. The increase in sodium lactate concentration slowed the rate of viscosity increase for the suspensions. However, the maximum viscosity of the suspension–gel measured before gel breaking was higher in suspensions with higher lactate concentrations (Fig. 4).

As demonstrated in Fig. 3, the increase in Na$^+$ concentration in the silica suspensions caused by adding NaCl increased not only the viscosity, but also the rate of increase in the viscosity of the suspensions. The results in Fig. 4 revealed that the increasing of lactate anion (C$_3$H$_5$O$_3^-$) had a counterinfluence, compared with that of Na$^+$, on the rate of viscosity increase. Further studies are needed to reveal the microscopic mechanism.

After gel breaking, the viscosity for all tested suspensions decreased to about the same level, ~350 cP (Fig. 4). The mixing broke the three-dimensional network of silica particles into clusters (Sonntag and Russel, 1986; Potanin, 1991) and reduced the viscosity. Since the mechanical stirring intensity of the mixing applied to the suspension in each run of viscosity measurements was the same, the size of the clusters after three-dimensional structure breaking would be similar in all samples. Thus,
the viscosities of the suspensions after gel breaking were about the same. A more intensified mixing applied to the gelling suspension would result in a lower viscosity after gel breaking.

**Gelation**

**Gelation of Molasses–Silica Suspensions and Gelation with Sediments**

Molasses–FS suspensions with FS at concentrations from 1 to 9% (w/w) and 3000 mg L\(^{-1}\) added Na\(^+\) gelled in <70 h (Fig. 5a). By visually checking the flowing behavior of the suspensions in the vials, it was qualitatively observed that the suspensions with higher FS concentrations gelled faster. The later formed gel had a higher rigidity when the silica concentration was higher, as was revealed by the shape of gels observed at the end of rheology measurements. The suspensions were gelled in the measuring cup of the MCR 101 rheometer at the completion of rheology measurements. When the spindle was lifted from the cup, the soft gel (i.e., formed from the suspension with lower FS concentration) stayed on the top of the spindle and deformed from its original cylindrical shape quickly over time (Fig. 5b). More rigid gels, formed from suspensions with higher FS concentrations, deformed significantly less from their original cylindrical shape (Fig. 5c and 5d). When the 5% (w/w) FS, 7% (w/w) molasses, and 3000 mg L\(^{-1}\) Na\(^+\) suspension was mixed with sediment, the mixture gelled in <24 h. Details are presented in Supplemental Fig. S1.

**Gelation in Column**

The injection pressure increased with time for the column filled with 5% (w/w) FS, 7% (w/w) molasses, and 3000 mg L\(^{-1}\) Na\(^+\) suspension, indicating that the suspension in the column became increasingly viscous over time (Fig. 6). The pressure was still increasing at the end of the experiment (58 h), and the suspension eventually gelled. The test was stopped at 58 h, when the injection pressure approached 413.7 kPa due to the concern of failing glass columns under higher pressure. The pressure of water injection at the same flow rate for the column saturated with water is included in Fig. 6 for comparison.

**Carbon Slow Release**

**Release in Batch System**

Slow release was observed in batch tests where molasses was tested as the C source (Fig. 7). The release rate was a function of the molasses concentration in the gel. Higher molasses concentration in the gel resulted in a higher rate (Fig. 8). Through the C release process, the gel did not disperse or change its shape. It only showed a color change, from dark brown to light brown (Supplemental Fig. S2).

Diffusion of MnO\(_4\^-\) from the silica gel was reported as the mechanism for permanganate slow release from the silica–KMnO\(_4\) gel (Yang et al., 2016). This mechanism also applies to the release of molasses. Gelation of the silica particle suspensions is a process in which the silica particles link together through siloxane bonds to form a continuous three-dimensional solid network (Iler, 1979). Enclosed in this solid network composed of silica particles is a continuous liquid phase (Bergna and Roberts, 2005). The molasses in the liquid phase diffuses through the network into the water surrounding the gel. A higher molasses concentration provided a
higher concentration gradient for diffusion, resulting in a high release rate.

Release in Column Systems
The column experiments results also revealed slow nutrient release from silica–molasses gel compared with that from molasses solution. The effluent molasses concentration and the cumulative molasses mass recovery for Column Tests 7 and 8 (Table 1) are shown in Fig. 9 and the calculated release rates are presented in Fig. 10. The mass release rates calculated from the effluent concentrations and the total molasses injected for Tests 3, 4, 5, and 6 (Table 1) are plotted in Fig. 11.

Release Behavior. A release peak was observed at the beginning of the test for all columns. When DIW was injected into the column filled with molasses solution, it washed out the solution and produced a high concentration peak; the effluent concentration decreased rapidly after the peak. When gel was present in the column, injected water washed out the molasses spread through the porous medium during silica–molasses suspension injection and the molasses at the surface of the gel; a concentration peak in the effluent was therefore produced. After the peak, concentrations decreased, but not as quickly as observed in the columns with solution injection (Fig. 9). The gel provided a much longer lasting nutrient source. In Column 8, ~8% of the emplaced nutrient was kept in the column after 86 PVs of water flushing, whereas in Column 7, <2.5% of nutrient was left in the column after 32 PVs of flushing (Fig. 9). The longer duration of nutrients from gel was also indicated by the release rate, as shown in Fig. 10. In Column 7, the molasses release rate dropped to <0.06 mg h\(^{-1}\) g\(^{-1}\) at 32 PV water flushing; in comparison, the release rate was still 0.17 mg h\(^{-1}\) g\(^{-1}\) at 86 PV flushing for Column 8.

When gel is present in the sediment, the injected water flows around the gel, washing away the molasses slowly diffusing out from the gel. The size and surface area of the gel control the release rate of the inclusions in the gel (Yang et al., 2016).

Influence of Gelation Time. A longer gelation time produced a gel with a lower initial molasses release concentration peak but a higher molasses release rate at the later stage and a longer release duration in column tests (Fig. 11). For Columns 3 (solution), 4 (gelation time = 50 h), 5 (84 h), and 6 (96 h), the molasses mass release rate dropped to 0.09 mg h\(^{-1}\) g\(^{-1}\) at 7.3, 14.1, 22.9, and 42.6 PVs, respectively.

The cross-linking among silica particles increases with time. The rigidity of a gel increases gelation time (Scherer, 1999). Thus, a longer gelation time produces a gel from which the diffusion of enclosed contents is more difficult due to higher rigidity.
Influence of Sediments. Sediments showed remarkable influence on the nutrient release behavior of the silica–molasses gel. The release from the Hanford vadose zone sediment (Column 8) was much slower than that from the Accusand (Columns 2, 4, 5, and 6). The release peak concentrations were significantly higher from the Accusand columns than from the Hanford sediment column (Fig. 10 and 11). The release period was much longer for the Hanford sediment column (Table 2). The release rates decreased to <0.1 mg h\(^{-1}\) g\(^{-1}\) in <35 PVs for the columns with Accusand (Fig. 11), whereas the rate remained >0.1 mg h\(^{-1}\) g\(^{-1}\) for >85 PVs in the column packed with Hanford sediment (Fig. 10).

Injectability of Silica Suspensions

Viscosity Change When No Mixing Is Applied to Suspension

The viscosity of silica–molasses suspensions increased with time when no mixing was applied to them. For the 7% FS, 7% molasses, and 3000 mg L\(^{-1}\) Na\(^+\) suspension, its viscosity increased from 4.4 to 109 cP in 18 h. When salt concentration was increased to 6000 mg L\(^{-1}\), the viscosity increased faster, from 4.7 to 147 cP in 18 h (Fig. 12). After 18 h, the suspensions started to become gels. Although the measured viscosity still increased slightly, the results might not represent the true viscosity of the gel due to the measurement approach applied.

The silica–molasses suspensions showed shear thinning at all the times when measurements were made (Fig. 13). When the viscosity of a silica suspension at a low shear rate was higher, the suspension exhibited more profound shear thinning. The shear thinning property of the suspensions facilitates the injection of the fluids into the subsurface.

Viscosity Change When Mixing Is Applied to Suspension

When constant mixing provided with a stirring bar was applied to the 7% FS, 7% molasses, and 3000 or 6000 mg L\(^{-1}\) Na\(^+\) suspensions, the increase in viscosity with time was limited (Fig. 14). For both of those tested suspensions, the viscosity increased to a maximum value at 7 h. It dropped to <45 cP after 24 h. This result indicates that the silica–molasses suspensions should be ready for injection due to the relative low viscosity if the suspensions are kept under mixing.

The viscosity increase and gelation of silica suspensions is attributed to the formation of three-dimensional silica particle networks. Mixing the suspension prevents the formation of the networks or destroys the networks and therefore reduces the viscosity and prevents gelation of the suspension (Yang et al., 2016, 2017). Constant mixing results in a limited increase in the viscosity of the silica suspension.

Table 2. Mass recovery of molasses from column effluent at two, four, and six pore volumes (PVs) of water injection. All solutions of gel had 7% (w/w) molasses, and all gels had 7% (w/w) fumed silica.

<table>
<thead>
<tr>
<th>Column</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trait</td>
<td>Solution</td>
<td>Gel (96 h)</td>
<td>Solution</td>
<td>Gel (50 h)</td>
<td>Gel (84 h)</td>
<td>Gel (96 h)</td>
<td>Solution</td>
<td>Gel (72 h)</td>
</tr>
<tr>
<td>Na(^+) (mg L(^{-1}))</td>
<td>0</td>
<td>0</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>Mass recovery (%) at 2 PVs</td>
<td>69.07</td>
<td>50.10</td>
<td>70.15</td>
<td>44.43</td>
<td>44.61</td>
<td>45.91</td>
<td>22.35</td>
<td>5.50</td>
</tr>
<tr>
<td>Mass recovery (%) at 4 PVs</td>
<td>88.11</td>
<td>73.51</td>
<td>90.10</td>
<td>70.01</td>
<td>69.71</td>
<td>60.97</td>
<td>53.50</td>
<td>11.98</td>
</tr>
<tr>
<td>Mass recovery (%) at 6 PVs</td>
<td>92.75</td>
<td>80.57</td>
<td>93.07</td>
<td>81.63</td>
<td>78.79</td>
<td>68.01</td>
<td>71.15</td>
<td>17.64</td>
</tr>
</tbody>
</table>
Injection Pressure

When the 7% FS, 7% molasses, and 3000 mg L\(^{-1}\) Na\(^+\) suspension was injected into a column packed with Hanford vadose zone sediment, the injection pressure increased with the aging time of the suspension (Fig. 15a). At an aging time of 0.1 h, the injection pressure was low (1.72 kPa). A slight pressure increase with injected suspension volume was observed, up to 2.55 kPa at 0.63 PV of injection (Fig. 15b). The injection pressure was low, indicating that the field injection of this suspension into the Hanford Site vadose zone can be implemented with no challenge.

In field applications using silica suspensions to deliver microbial nutrient to the vadose zone, the most critical step will be the injection of the suspension into the subsurface. Results of this study showed that several parameters, including silica concentration, salinity, and nutrient concentration, influence the increase in viscosity and the injection behavior of the silica suspensions. The formula of the nutrient–silica suspension should be optimized according to the delivery objectives and the timing of injection.

**Summary and Conclusions**

Gelation and rheology tests have been conducted on colloidal silica suspensions containing sodium lactate and molasses. Carbon release from molasses-laden gels has been tested in batch and column experiments. The injectability of these suspensions was evaluated by monitoring the viscosity change and conducting column injection tests.

In the gelation tests, the suspensions containing 5% (w/w) FS with lactate and molasses gelled with a delay in gelation after the mixing of silica suspension with a C source. When the 5% FS–7% molasses (w/w) suspension was delivered into Hanford sediment under vadose zone conditions, it gelled and grouted the sediment in <24 h. The injection pressure increased considerably over time in the column gelation experiment, indicating the gelling of the molasses suspension being injected in pore space of sediment inside the column.

Rheology tests showed that, in batch systems, the rates of gelation changed as a function of silica, salt, and C source concentrations. Higher salinity and silica concentration increased the rate of viscosity increase and the rate of gelation. Higher silica concentration also resulted in stronger gels. When the silica concentrations in suspensions were low (1 or 3% [w/w]), these suspensions did not gel but only showed a limited viscosity increase up to 350 cP.

A significantly slower release of molasses from gel vs. solution was observed in batch tests. Column study results also showed slower molasses release from the silica–molasses gel in sediments than from molasses solution. Longer gelation time in sediments of the injected suspension resulted in overall slower release rate and a longer release period. Sediments showed a considerable impact on nutrient release rate. Between the tested Accusand and Hanford vadose zone sediments, the same silica–molasses gel in the latter showed a much slower overall molasses release rate and thus exhibited a much longer release period.

The freshly prepared silica suspensions had viscosities in the range of 2 to 6 cP. With favorite geochemical formulations,
the suspensions underwent viscosity increase and eventually converted into gels. When constant mixing was applied to the suspensions, their viscosity increase was limited to <45 cP, and gelation was prevented. Shear thinning was observed for all the suspensions and at all aging times. The injection pressures were low due to the low viscosity and shear thinning behavior of the suspensions. It is expected that field injection of these silica suspensions can be implemented readily.

In conclusion, colloidal silica suspensions containing nutrients have low initial viscosity. These suspensions can readily be injected into the subsurface. The suspensions undergo viscosity increases with time and eventually become gels. The nutrients in the gels are slowly released into the environment, which is important for the delivery of nutrients in promoting enhanced and long-lasting bioremediation in the environment. Colloidal silica suspensions can be used to deliver microbial nutrients to the subsurface vadose zone and establish slow-release nutrient sources.

Acknowledgments

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Supplemental Material

Supplemental Fig. S1 shows the gelation of silica suspensions in the presence of sediments. The 5% (w/w) FS, 7% (w/w) molasses, and 3000 mg L\(^{-1}\) Na\(^+\) suspension mixed with sediment gelled in <24 h. When the sediment was poured out from the first beaker after 24 h of contact with the silica suspension, the sediment had already been grouted together by the silica gel (Supplemental Fig. S1). The sediments in the other beakers were also grouted by gel when poured out at later times, as expected.

Supplemental Fig. S2 compares the C-laden silica gel before and after C release. Comparing the shape and size of the gel before and after C release, it was noticed that through the C release process, the gel did not disperse or change its shape. Only a color change from dark brown to light brown (Supplemental Fig. S2) was apparent. This observation indicated that the C source diffused out from the gel.

References


