Hydrogel-Assisted Enzyme-Induced Carbonate Mineral Precipitation

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Abstract: Benchtop experiments demonstrate the promise of hydrogel-assisted enzyme-induced carbonate precipitation (EICP) as a means of enhancing EICP for soil stabilization. Enzyme-induced carbonate precipitation uses hydrolysis of urea (ureolysis) catalyzed by the urease enzyme to precipitate $CaCO_3$ in the presence of urea and calcium in a water-based solution. Xanthan and guar gum biopolymers and an inert polyol-cellulose hydrogel were used to assess the ability of a hydrogel to enhance EICP by retaining reaction product around the soil particles. The experiments were conducted in sand-filled paper cups and soilless glass beakers at 1.66 and 0.33 M of initial calcium chloride ($CaCl_2$) concentrations using high-activity and low-activity plant urease. Ureolysis and $CaCO_3$ precipitation occurred in all hydrogel-assisted EICP tests, suggesting that the hydrogels used in this study do not interfere with EICP. Furthermore, hydrogel-assisted EICP appeared to retain moisture for extended periods of time and reduce penetration of the EICP solution into the soil, extending reaction time, increasing precipitation efficiency, and enhancing the formation of a crust. Gas bubble formation in the hydrogel solutions suggests that ammonia (NH_3) and/or carbon dioxide (CO_2) off-gassing may be reduced, which may also increase precipitation efficiency. Guar and xanthan gums were found to have the greatest water retention ability and to significantly reduce water evaporation. **DOI: 10.1061/(ASCE)MT.1943-5533.0001604.**

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Introduction

Benchtop experiments were performed to assess the feasibility of creating a viscous, water-laden solution using a hydrogel to enhance enzyme-induced carbonate precipitation (EICP). In EICP, the hydrolysis of urea, or ureolysis, promotes the geochemical conditions conducive to carbonate mineral precipitation. Ureolysis is catalyzed by the urease enzyme (urea amidohydrolase), which hydrolyzes urea $[CO(NH_2)_2]$ into carbon dioxide (CO_2) and ammonia (NH_3), leading to increased pH and alkalinity and precipitation of calcium carbonate in the presence of calcium ions. Potential engineering applications of EICP include stabilization of surficial soils susceptible to wind-induced erosion (e.g., the suppression of fugitive dust) and improvement of low-volume road surfaces by formation of a durable and long-lasting calcium carbonate ($CaCO_3$) mineral crust (Bang et al. 2009; Meyer et al. 2011; Hamdan and Kavazanjian 2015). Enzyme-induced carbonate precipitation has also been suggested as a means of improving the bearing capacity of soils, facilitating excavation and tunneling, and mitigating the potential for earthquake-induced soil liquefaction (Kavazanjian and Hamdan 2014).

The overall ureolytic reaction is

$$CO(NH_2)_{2(aq)} + 3H_2O = CO_{2(aq)} + 2NH^+_{4(aq)} + 2OH^-_{(aq)}$$

Under the appropriate geochemical conditions and in the presence a suitable divalent cation such as calcium, carbonate mineral precipitation can occur

$$H^+_{(aq)} + HCO^-_{3(aq)} + 2OH^-_{(aq)} + Ca^{2+}_{(aq)} = CaCO_{3(S)} + 2H_2O$$

The net urease catalyzed precipitation reaction for $CaCO_3$ can be written as

$$CO(NH_2)_{2(aq)} + 2H_2O + CaCl_{2(aq)} = CaCO_{3(s)} + 2NH_4Cl_{(aq)}$$

Enzyme-induced carbonate precipitation is similar to microbially mediated ureolysis, a process that falls within the category of biomediated processes known as microbially induced carbonate precipitation (MICP). Because it mimics MICP but does not involve any living organism, EICP may be considered a bioinspired process. The advantages of EICP over MICP for surficial stabilization by formation of a calcium carbonate crust include eliminating the need to nurture urease-producing microbes; greater efficiency with respect to carbon utilization in the substrate for $CaCO_3$ formation; and rapid carbonate precipitation (Hamdan and Kavazanjian 2015). These advantages make EICP well-suited (in contrast to microbial methods) for surface treatments and other carbonate precipitation applications that have a relatively short timeframe within which they need to become effective.

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Using a hydrogel to create a viscous, water-laden solution may potentially enhance EICP by reducing migration of the EICP solution, retaining reaction products in the soil pores, and thereby extending reaction time and increasing precipitation efficiency. In surficial stabilization applications, the hydrogel-based EICP solution may also enhance the formation of a crust by retaining moisture for extended periods of time and reducing penetration of the EICP solution into the soil. This paper presents the results of experiments to assess the potential for a hydrogel-based solution to enhance EICP, with a focus on surficial stabilization of soils.

The work by Hamdan and Kavazanjian (2015) on EICP through ureolysis as a bioinspired method for fugitive dust control serves as the basis for the work presented in this paper. Hamdan and Kavazanjian (2015) noted that, in tests on EICP stabilization for fugitive dust control, native Arizona silty sand and silt-sized mine tailings tended to exhibit hygroscopic behavior that accelerated the desiccation of the EICP solution at the soil surface. Water is a necessary component of ureolysis, and it is postulated that using a hydrogel solution to enhance moisture retention may improve the EICP process by extending the reaction time. Furthermore, in experiments conducted by Hamdan and Kavazanjian (2015) on clean, uniform, fine-grained silica sand, rapid penetration of the applied EICP solutions into the soil reduced the amount of cementation solution available at the soil surface. Therefore, it is further postulated that surficial stabilization through EICP will be enhanced if rapid penetration of the EICP mixture into the soil is reduced by the increased viscosity of a hydrogel-based EICP solution. The tests described in this paper were conducted to test these two hypotheses.

Hydrogels are three-dimensional networks of hydrophilic polymers that are primarily composed of water [typically >90% weight-to-weight ratio (w/w)] and are capable of large volume changes. Hydrogels include both synthetic polymers and biopolymers. Synthetic and nonsynthetic hydrogels have many historic and modern uses in food products, industry, and medicine (Chudzikowski 1971; Hoffmann 1991; Talukdar and Kinget 1995; Anseth et al. 2002). Extrapolymeric substances (EPS), biopolymers found in biofilms, have been studied for geotechnical applications focused on mineral precipitation and bioplugging (Chou et al. 2011; Dejong et al. 2013).

The impacts of EPS through organic additives (e.g., amino acids) on biotic and abiotic carbonate precipitation processes and on the resulting crystal morphologies have been widely studied. Abiotic experiments conducted by Braissant et al. (2003) using amino acids (AA) of varying acidity and xanthan gum (proxies for EPS) showed that vaterite-phase $CaCO_3$ was favored over calcite at higher xanthan concentrations and that increased AA acidity resulted in needle/rod-shaped $CaCO_3$ over the rhombohedral calcite. Braissant et al. (2003) also showed that at greater concentrations these organics resulted in the formation of spherulitic calcite (globular, sphere-like crystals) and that spherulitic vaterite always precipitated in the presence of these organics.

Ercole et al. (2007) studied the impacts of organics on carbonate precipitation by using EPS and capsular polysaccharides (CPS) from *Bacillus firmus* and *Bacillus sphaericus*. They showed that CPS and EPS extracted from both organisms mediated the formation of calcite precipitates and that crystal morphology depended on the fractions of CPS and EPS used. Estroff et al. (2004) studied the impacts that organic hydrogels have on the precipitating $CaCO_3$ microenvironment. In addition to similar conclusions reached by others that certain organics mediate $CaCO_3$ precipitation and influence crystal morphology, they also note that some hydrogel aggregates may be incorporated into calcite crystals at lattice imperfections, which may adversely affect the physical properties of the crystals (e.g., increased dissolution).

The ability of hydrogels to produce microenvironments favorable to mineral precipitation has been noted by many investigators, including the aforementioned studies by Braissant et al. (2003), Estroff et al. (2004), Ercole et al. (2007), and Decho (2010). An overview by Decho (2010) on biopolymer-induced mineralization focused on microbial biofilms as microenvironments that can promote either precipitation or dissolution depending on the specific nature of the biofilm. Decho (2010) underscored the similarities between biofilms and hydrogels, particularly their ability to produce microenvironments that can lead to mineral precipitation or dissolution.

There is little information in the literature on the application of biopolymers for soil stabilization. Chen et al. (2013) investigated xanthan and guar gums for the stabilization of mine tailings and found that these hydrogels increased the liquid limit and the undrained shear strength (S_u) of mine tailings. They noted that S_u is an important parameter for surficial stabilization and that S_u increased with higher hydrogel concentrations mainly because of increases in viscosity. However, to the best of the authors' knowledge, no work has been undertaken on the use of hydrogels to assist in $CaCO_3$ precipitation for soil stabilization.

On the basis of these previous studies, application of a hydrogel-EICP solution was postulated to provide a viscous, water-laden reaction matrix with increased water retention capacity that would extend the reaction time for EICP. Increased water retention and reaction times should lead to greater substrate utilization and $CaCO_3$ precipitation and thereby improve EICP efficiency. Through increased viscosity, hydrogel-assisted EICP may also focus $CaCO_3$ precipitation in the soil through a temporary reduction in local soil permeability. Furthermore, a viscous hydrogel-assisted EICP solution may temporarily slow the off-gassing of CO_2 and NH_3, which may lead to greater $CaCO_3$ precipitation, further enhancing the EICP process.

Scope of the Study

This paper presents the results of bench-scale experiments conducted to assess the applicability of a hydrogel-based solution to enhance EICP, with an emphasis on EICP for surficial stabilization of soils. These experiments focused on evaluating hydrogel-assisted $CaCO_3$ precipitation in soilless glass beakers and on the soil crusts that formed on clean, fine-grained silica sand (crystal silica F-60 sand, or simply F-60 sand) that was topically treated with a hydrogel-assisted EICP solution. A theoretical evaluation of the water retention characteristics of the three hydrogels used in these experiments was also performed and validated with laboratory experiments. The primary objectives of these experiments were to determine the following: (1) can EICP occur in a biodegradable hydrogel, i.e., will the hydrogel interfere with enzyme-mediated $CaCO_3$ precipitation; (2) does the EICP-hydrogel matrix retain moisture for an extended period of time and thereby enhance EICP; and (3) can a hydrogel temporarily retain the EICP solution at the surface of a permeable granular soil?

Materials and Methods

Hydrogel-$CaCO_3$ in Glass Beakers and Paper Cups

One experiment was set up using seven 50-mL glass beakers to evaluate hydrogel-assisted EICP without the complication of soil (Table 1). A second experiment was set up using 15 unwaxed

Table 1. Summary of the Chemical Formulations, Enzyme Activities, and Types of Hydrogel Used in the Soilless Glass Beakers

Test	Beaker number	[$CaCl_2$] (M)	Enzyme activity
Polyol-cellulose	20	2.0	Low
	21	2.0	High
Guar gum	17	2.0	Low
	19	2.0	High
	22	2.0	—
Xanthan gum	16	2.0	Low
	18	2.0	High

Note: “High” and “low” enzyme activities correspond to approximately 26, 100, and 200 units/g, respectively. A unit of urease enzyme is defined as the amount of enzyme that will liberate 1.0 mmol of NH_3 from urea per minute at pH 7.0 at 25°C. The dashed line indicates the control specimen.

89-mL tapered paper cups filled with clean F-60 sand (mean grain size = 0.275 mm; coefficient of uniformity = 1.74) to assess the applicability of hydrogel-assisted EICP for surficial stabilization of soils (Table 2). The paper cups were approximately 55 mm high with an opening at the top of approximately 50 mm in diameter. Approximately 100 g of F-60 sand was added to the empty cups by using a funnel (drop height ≈ 25 mm) and filled to a height of approximately 15 mm below the rim. The cups were then gently shaken to level the sand in the cups, and then sand was added or removed as necessary to achieve a uniform depth of 15 mm below the rim of the cup.

The following three hydrogels were used in this study to evaluate hydrogel-assisted EICP: the biodegradable biopolymer hydrogels xanthan and guar gums and an inert polyol-cellulose hydrogel. Xanthan and guar gums are polysaccharide biopolymers. The inert polyol-cellulose hydrogel is a polysaccharide polymer composed mostly of methyl cellulose and glycerol. Xanthan and guar gums were obtained in powder form, and the polyol-cellulose hydrogel was procured in liquid form. High- and low-concentration solutions of urea and calcium chloride dihydrate ($CaCl_2 \cdot 2H_2O$, laboratory grade, Sigma-Aldrich, St. Louis, Missouri) were prepared in reverse osmosis–purified (RO) water at pH 9.40 as follows to achieve an initial urea to $CaCl_2$ ratio of 1.5:1: (1) a 200-mL “high-concentration” solution consisting of 3.0-M urea and 2.0-M $CaCl_2 \cdot 2H_2O$; and (2) a 200-mL “low-concentration” solution consisting of 0.6-M urea and 0.4-M $CaCl_2 \cdot 2H_2O$. The following two grades of urease enzyme were used in these experiments, each prepared in RO water containing 4.0-g/L stabilizer: (1) Sigma-Aldrich high-activity Type III Jack Bean, 26,100 units/g average activity, defined in this paper and in Tables 1 and 2 as “high-activity” enzyme; and (2) Fisher Chemical (Waltham, Massachusetts) low-activity Jack Bean ≈ 200 units/g, defined in this paper and in Tables 1 and 2 as “low-activity” enzyme. A unit of urease enzyme is defined as the amount of enzyme that will liberate 1.0 mmol of NH_3 from urea per minute at pH 7.0 at 25°C. The enzyme solutions were prepared to reach target concentrations of 0.44 g/L for the high-activity urease enzyme and 0.85 g/L for the low-activity urease enzyme when added to the urea-$CaCl_2$ solutions.

Table 2. Summary of the Chemical Formulations, Enzyme Activities, and Types of Hydrogel Used in the Soil Filled Paper Cups with F-60 Sand

Test	Cup number	[$CaCl_2$] (M)	Enzyme activity
Polyol-cellulose	7	2.0	Low
	8	2.0	High
	9	2.0	—
	10	0.4	Low
	11	0.4	High
Guar gum	1	2.0	Low
	2	2.0	High
	3	2.0	—
	12	0.4	Low
	13	0.4	High
Xanthan gum	4	2.0	Low
	5	2.0	High
	6	2.0	—
	14	0.4	Low
	15	0.4	High

Note: “High” and “low” enzyme activities have the same meaning as in Table 1. Dashed lines indicate control specimen.

A test that used either xanthan gum or guar gum was started by adding approximately 15 mL of urea-$CaCl_2$ solution into a 50-mL glass beaker and then slowly adding the hydrogel powder under high-speed stir at approximately 60°C. Tests that used xanthan and guar gums received approximately 0.2 and 0.3 g of hydrogel powder, respectively, per 15 mL of high-concentration urea-$CaCl_2$ solution and 0.05 and 0.1 g of powder, respectively, per 15 mL of low-concentration urea-$CaCl_2$ solution. After the hydrogel powder appeared to be fully dissolved (i.e., little to no solids visible), 3 mL of urease enzyme solution was added to the beaker while stirring. The percent weight of hydrogel solids after adding 3 mL of urease solution to the high-concentration urea-$CaCl_2$ solutions were approximately 1.1% w/w (0.2 g) for xanthan and 1.6% (0.3 g) for guar (assuming a $CaCl_2$-urea solution density of ≈ 1 g/mL). The percent of hydrogel solids by weight for the low-concentration urea-$CaCl_2$ solutions were approximately 0.2% w/w (0.05 g) for xanthan and 0.5% (0.1 g) for guar. The polyol-cellulose hydrogel experiments were started by adding approximately 15 mL of urea-$CaCl_2$ solution into a 50-mL glass beaker and then adding 3 mL of diluted liquid polyol-cellulose hydrogel (50:50 RO water–to–hydrogel ratio). Next, 3 mL of urease enzyme solution was added to the beaker while stirring. The hydrogel-urea-$CaCl_2$-enzyme solutions (i.e., the 18-mL complete hydrogel-EICP solutions) were stirred for approximately 30 s after adding the enzyme solution.

The seven glass beaker experiments that used a hydrogel-EICP solution without any soil used only the high-activity enzyme (Table 1). The hydrogel-EICP mixtures were left in the beakers in which they were made. Beakers 1–6 contained the following hydrogel-EICP mixtures: Beakers 1–2 used xanthan gum with high- and low-concentration EICP solutions, respectively; Beakers 3–4 used guar gum with high- and low-concentration EICP solutions, respectively; and Beakers 5–6 used polyol-cellulose hydrogel with high- and low-concentration EICP solutions, respectively. A control beaker, Beaker 7, contained high-concentration EICP solution without hydrogel.

In the paper cup experiments (Table 2), the hydrogel-urea-$CaCl_2$-enzyme solutions (i.e., the 18-mL complete hydrogel-EICP solutions) were poured onto the soil after stirring the solution for approximately 30 s. Because the hydrogel-EICP solution was viscous and tended to stick to the beaker, less than the entire 18 mL of solution was added to the paper cups. It was estimated that approximately 10–12 mL of solution was poured from the glass beakers into the soil-filled paper cups. In three of the 15 cups, high-concentration hydrogel-urea-$CaCl_2$ controls were set up, each using xanthan, guar, or polyol-cellulose hydrogel in paper cups with soil but without enzyme solution (3 mL of RO water was used instead). The initial urea-$CaCl_2$ concentrations of 2.0 and 0.40-M $CaCl_2$ were reduced to 1.66 and 0.33 M, respectively, by adding 3 mL of urease solution (or RO water for the control cups).

The seven soilless glass beakers (Table 1) and 15 paper cups containing soil (Table 2) were loosely covered and allowed to stand for 7 days. Because they remained hydrated at the end of the 25-day air-drying period, the guar and xanthan EICP specimens in the beakers were dried in an oven for 24 h at ≈90°C before further testing. Summaries of the chemical formulations, enzyme activities (high/low), and types of hydrogel used in the soilless glass beakers and soil-filled paper cups are shown in Tables 1 and 2, respectively.

Observations and Sampling

The soilless glass beakers appeared to still be wet after the 7-day experiment period. Therefore, the beakers were allowed to dry uncovered for an additional 18 days. However, the residue in the guar and xanthan EICP beakers still appeared to be wet even after 18 days of additional drying, so these specimens were dried in an oven for 24 h at ≈90°C before further testing. The nonhydrogel EICP solution in Beaker 7 was dry within 7 days. The polyol-cellulose mixtures were dry in by the seventh day in the glass beakers and in all of the soil cups by the second day. Color changes were not seen in the cups containing soil, possibly because the soil had a natural white to grayish appearance. All of the glass beakers that contained hydrogel-EICP solutions contained a white precipitate. Some of the white precipitate was partially suspended within the hydrogel for the guar and xanthan specimens, whereas the rest of the precipitate fell to (or formed at) the bottom of the hydrogel. The white precipitate appeared to be entirely at the bottom of the beakers in both polyol-cellulose-EICP specimens.

After 7 days, a vertical "window" approximately 20-mm wide and 55-mm high was cut out of the paper cups and peeled open as shown in Fig. 1. The cups were then tilted and tapped to allow loose soil to pour out, leaving behind a hard surficial soil crust in some cups. The thickness of the soil crust (if present) was measured, and then observations were made regarding its durability by using metal tweezers to score the remaining soil exposed by the vertical window. The soil that remained in the cups was either (1) bound to well-defined surficial crusts; (2) weakly cemented in thicker layers penetrated by the EICP solution (rather than a surficial crust); or (3) held together by some other mechanism, believed likely to be residual unreacted $CaCl_2$ salt (controls). A soil crust was considered well-defined if the soil unit could remain intact after being lightly scored three to four times by using a metal tweezer. The terms *well-defined* and *intact* are used in this paper to describe the hydrogel's ability to retain the EICP solution to form a surficial crust (of any perceived strength) and not necessarily an indication of mechanical strength. After the physical observations were completed, the soils were rinsed three times in 18.2-MΩ deionized (DI) water and allowed to dry for approximately 18 days before further testing.

Chemical Analysis and Physical Characterization

Limited chemical and physical analyses were performed on the residue in the soilless glass beakers and on the crusts from the soil-filled cups. The analyses were chosen to chemically and visually confirm the presence of $CaCO_3$ and to observe evidence of the mode of soil improvement (e.g., interparticle cementation). Acidification using 1.0-M HCl acid for carbonate mineral detection was

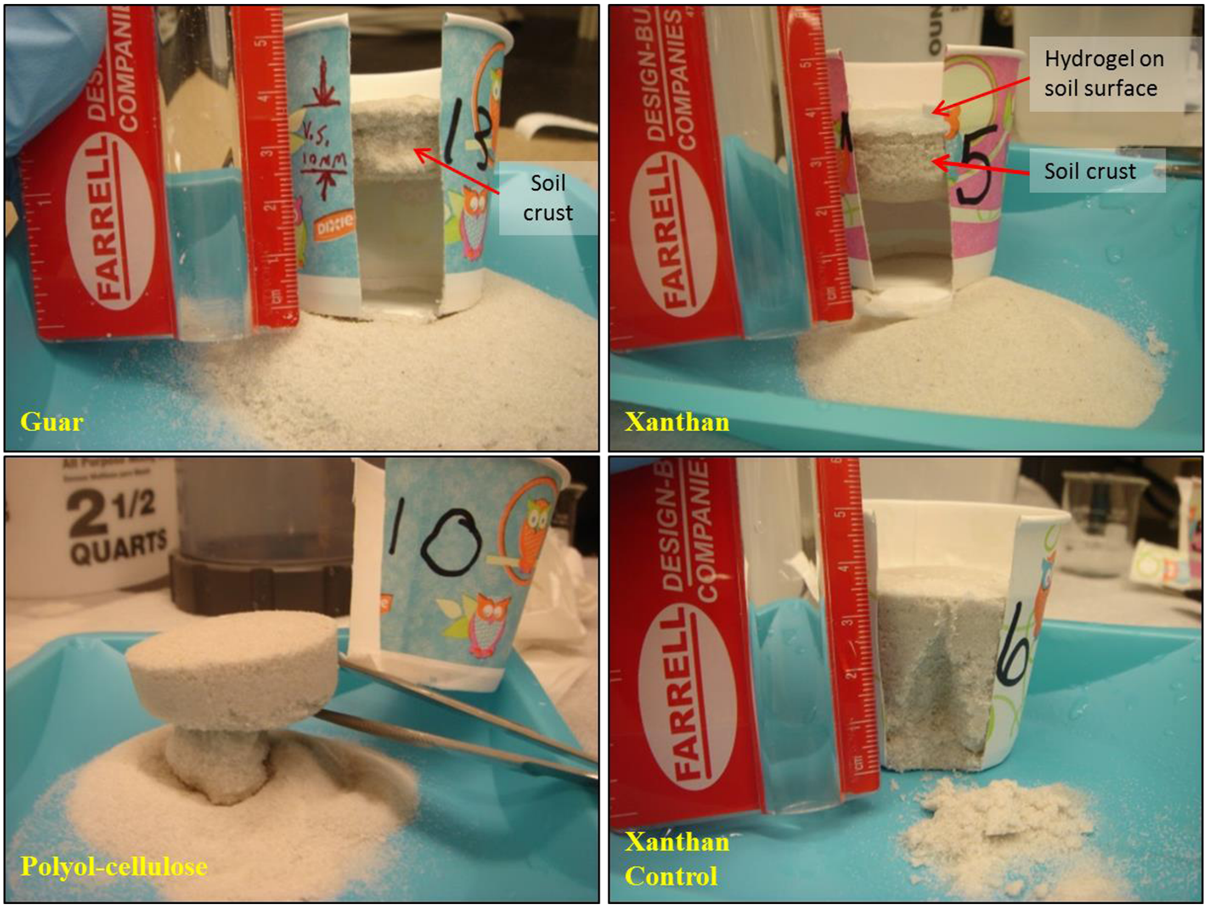


Fig. 1. Window was cut into paper cups longitudinally to provide a view of the soil profile; the cups were tilted and tapped to allow loose soil to pour out

performed on all hydrogel-assisted EICP soilless beaker residues and soil crusts. The presence of NH_3 was qualitatively monitored on the basis of the odor of NH_3 over individual paper cups and glass beakers. Color changes and the appearance of moisture on the soil surface caused by the hydrogel-EICP solution (and color changes in the beakers) were also monitored. Observations were made every 30 min during the first 3 h of the experiment and then daily thereafter. Scanning electron microscope (SEM) imaging was used to visually confirm the presence of $CaCO_3$ on a few selected specimens of the soil crusts and to provide evidence of the mode of soil improvement.

Water Vapor Pressure Tests

Vapor pressure is the pressure exerted by a vapor that is in equilibrium with its liquid phase at a given temperature in a closed system. In general, a liquid with a lower vapor pressure has a lower tendency to evaporate. The addition of a solute may influence the vapor pressure of a liquid through enthalpic (intermolecular interactions) and/or entropic (mixing) effects. Whereas the entropic effect is identical for all solutes, the enthalpic effect depends on specific molecular interactions and may vary greatly between solutes. Solutes that form strong associations with a solvent significantly decrease a solvent's (water in this case) vapor pressure, indicating greater water retention ability. The enthalpic effect of a solute on a solvent can be determined through vapor pressure measurements. The water vapor pressures of xanthan gum, guar gum, and polyol-cellulose hydrogel solutions were measured by a monometer (Fisher Scientific Traceable manometer, Waltham, Massachusetts). Each sample solution was prepared by directly dissolving the desired polymer in 18.2-MΩ DI water. The polymer concentrations tested in this work were 0.1, 0.2, 0.5, 1, and 2% by weight for guar; 0.1, 0.2, 0.5, 1, 2, and 5% by weight for xanthan; and 5, 10, 20, and 30% by weight for polyol-cellulose hydrogel. The saturated vapor pressure of DI water was also measured. For each measurement, 100-mL liquid was poured into a clean air-dried 250-mL Erlenmeyer flask, which was immediately plugged with a rubber stopper fixed to a glass tube and then quickly connected to a manometer through rubber tubing. Each measurement lasted for at least 10 min to allow the system to reach equilibrium.

Results and Discussion

Hydrogel-$CaCO_3$ Precipitates in Glass Beakers and Crusts in Paper Cups

The results of the hydrogel-$CaCO_3$ experiments in the soil-filled paper cups are summarized in Table 3. The presence of carbonate was detected by acidification in the glass beaker precipitates and soil crusts of all specimens that received enzyme solution, indicating that hydrogel-assisted EICP does not prevent carbonate precipitation. However, Cups 1 and 2 that used guar gum and Cups 7, 8, and 10 that used polyol-cellulose hydrogel had to be tested in several locations before carbonate was detected (indicated by an asterisk in Table 3). Carbonate was not detected in any of the control specimens.

Tiny bubbles (presumably NH_3 and CO_2) developed in the glass beakers and cups that received guar- and xanthan-assisted EICP solutions; the amount of bubbles that developed appeared to be independent of enzyme activity. No gas bubbles were seen in any of the soil-filled cups that received polyol-cellulose-EICP solution, nor were any bubbles seen in any of the control specimens. The odor of NH_3 was detected in all cups and beakers that received enzyme and was not detected in any of the no-enzyme controls.

By the second day of the experiments, the gas bubbles that developed during the first 3 h became smaller and appeared to increase slightly in number in the xanthan-EICP solutions for the soil cups and soilless beakers. The amount of gas bubbles in the guar-EICP solutions decreased by the second day and was completely gone by the third day as the guar-EICP solutions advanced into the soil. In the soilless beakers that received guar-EICP solutions, the amount of gas bubbles appeared to decrease over several days but was still visible by the third day. The odor of NH_3 was strong on Day 2 of the experiment in all of the guar- and xanthan-EICP specimens but was only faintly detectable by Days 3–4 of the experiment and without any specific pattern between the specimens. The odor of NH_3 was faintly detectable on Day 2 of the experiment with the polyol-cellulose-EICP specimens and was undetectable by Day 3.

During the first 3 h of the experiment, a visible but unmeasured amount of guar-EICP and xanthan-EICP solutions remained on the

Table 3. Summary of the EICP Solution Penetration Depth, Crust Thickness, and the Perceived Hardness of the Crusts in Paper Cups with F-60 Sand

Test	Cup number	Carbonate present	Solution penetration depth (mm)	Approximate crust thickness (mm) and relative hardness	$[CaCl_2]$ (M)	Enzyme activity
Polyol-cellulose	7	Yes[a]	40	2, soft	2.0	Low
	8	Yes[a]	40	2, soft	2.0	High
	9	No	40	None	2.0	—
	10	Yes[a]	25	2, medium	0.4	Low
	11	Yes	25	2, medium	0.4	High
Guar gum	1	Yes[a]	25	2, soft	2.0	Low
	2	Yes[a]	13	10, hard	2.0	High
	3	No	17	2, soft	2.0	—
	12	Yes	10	10, hard	0.4	Low
	13	Yes	10	10, hard	0.4	High
Xanthan gum	4	Yes	15	10, hard	2.0	Low
	5	Yes	15	10, hard	2.0	High
	6	No	40	2, soft	2.0	—
	14	Yes	25	5, hard	0.4	Low
	15	Yes	15	12, hard	0.4	High

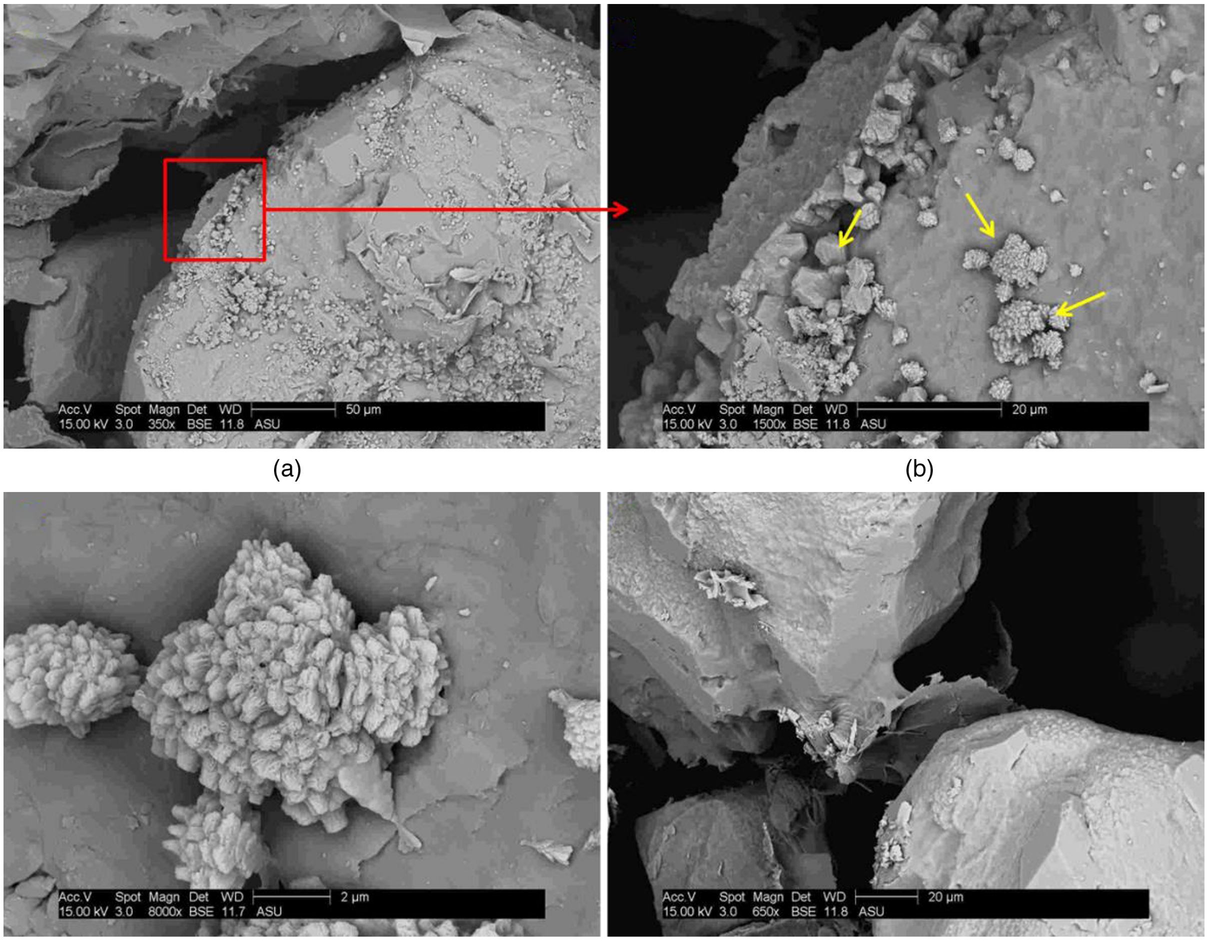
Note: Observations pertaining to relative hardness are intended to provide a general sense of the test outcome that may not necessarily be an indication of mechanical strength.
[a] Several spots were tested before carbonate was detected.

soil surface of all of the paper cups treated with these hydrogel-assisted solutions. Guar and xanthan solutions that did not receive enzyme were also visible on the soil surface of the control cups. The polyol-cellulose hydrogel solutions (both enzyme and control) infiltrated the soil within approximately 1 min after application. All of the xanthan mixtures applied to sand appeared glossy until the third day of the experiment, and the guar mixtures were glossy until the second day of the experiment. The lack of a glossy or wet appearance in the cups that received hydrogel was assumed to mean the soil surface was essentially dry (desiccated or dehydrated).

The following principal observations were made regarding the soil crusts: (1) soil crusts of varying thicknesses (2–12 mm) were formed in all cups where enzyme solution was added (these crusts were later confirmed to contain $CaCO_3$); (2) the soil crusts formed with xanthan and guar were generally thinner and well-defined, whereas the soil crusts formed by using polyol-cellulose were highly variable; and (3) the soil crusts were thicker and harder than crusts that formed in previous surficial soil stabilization tests conducted without hydrogel by Hamdan and Kavazanjian (2015). These principal observations indicate that at least some the physical properties observed in the soil crusts appear to be independent of enzyme activity (high versus low activity). These observations are intended to provide a general sense of the test outcome that may not necessarily be an indication of mechanical strength.

The depth of EICP solution penetration in the soil cups was determined by the fraction of loose sand that fell out of the viewing window after shaking and tapping. Sand that was penetrated with EICP solution or the urea-and-salt-only solution did not fall out of the cup. For example, the sand in the "Xanthan Control" cup shown in Fig. 1 did not fall out of the cup even after being scored with a metal tweezer, whereas the soil below the soil crust in the "Xanthan" cup (hydrogel-EICP) fell out as loose sand. The following principal observations were made regarding the effectiveness of the hydrogels at limiting penetration of the EICP solution into the cups filled with 40 mm of soil (Table 3): (1) xanthan gum limited solution penetration to approximately 18 mm on average; (2) guar gum limited penetration to approximately 15 mm on average; and (3) polyol-cellulose hydrogel limited penetration to approximately 33 mm on average. A summary of solution penetration depth, crust thickness, and perceived hardness of the crusts formed are shown in Table 3, along with a summary of the initial conditions. Crusts with a perceived hardness of "soft" were flexible, indicating that the hydrogel may be the primary agent holding sand particles together. The "hard" crusts were brittle, and the "medium" crusts had some initial flexibility before a brittle break. In general, less penetration of the hydrogel-EICP solution resulted in harder, thinner crusts. These principal observations indicate that the effectiveness of the hydrogels at limiting penetration of the EICP solution into the cups filled with 40 mm of soil appears to be independent of enzyme activity.

The SEM images of the soil crust obtained from Cup 4 (xanthan-assisted EICP at high $CaCl_2$ concentration) are shown



(a) (b)

(c) (d)

Fig. 2. SEM imaging of the soil crust obtained from Cup 4 using xanthan-assisted EICP at high $CaCl_2$ concentration; arrows indicate $CaCO_3$: (a and b) interparticle $CaCO_3$ detachment; (c) $CaCO_3$ mass growing on a sand particle; (d) hydrogel detachment from a sand particle

in Fig. 2. Unfortunately, the images in Fig. 2 were unintentionally saved in a low-resolution format, which makes them appear pixilated. In addition to the initial rinsing previously described, the soil crust shown in Fig. 2 was aggressively rinsed to help reduce charging during SEM analysis. However, rinsing did not remove the residual materials entirely, as shown in Fig. 2(d), in which a thin connective film (presumed to be a hydrogel polymer) detached from one sand particle while still attached to another. Figs. 2(a–c) clearly show the presence of $CaCO_3$ bound to the surface of the soil particles. A broken interparticle soil contact is evident in Figs. 2(a and d) as a concave $CaCO_3$ detachment point, highlighting the mode of attachment between the silica sand soil particles in the crust.

Water Vapor Pressure Tests

Fig. 3 presents the normalized vapor pressures (p/p^0) of solutions containing the previously mentioned hydrogels, where p = water vapor pressure of the solution and p^0 = saturated vapor pressure of pure water (i.e., the zero "Polymer wt%"). The vapor pressures of the guar and xanthan gum solutions are shown in Figs. 3(a and b), respectively. The decline in vapor pressures for the guar and xanthan gum solutions with increasing polymer content followed very similar trends with maximum declines of approximately 17 at 2% (w/w) guar and a 47% decline at 5% (w/w) xanthan (compared with pure water). The decline in water vapor pressure at relatively low hydrogel concentrations illustrates the strong water retention ability of both guar and xanthan gums, a phenomenon observed at very low hydrogel concentrations, i.e., 1.0% (w/w), as illustrated by Fig. 3. However, the xanthan gum solutions showed slightly lower vapor pressures than the guar gum solutions at similar polymer concentrations. The polyol-cellulose solutions showed very little change in vapor pressure with increasing concentration, with a maximum decrease of ≈4% at the highest polyol-cellulose concentration (30% w/w).

Water Vapor Pressure Theoretical Evaluation

According to Flory-Huggins theory on polymer solutions, solvent activity of a macromolecule solution can be defined by the following equation (Eliassi et al. 1999; Bercea et al. 2011; Emerson et al. 2013):

$$\ln a = \chi_{i-j}\Phi_p^2 + \ln(1-\Phi_p) + \left(1-\frac{V_i}{V_j}\right)\Phi_p \tag{1}$$

where a = solvent activity; Φ_p = volume fraction of polymer; χ_{i-j} = interaction parameter of the system; and V_i and V_j = molar volumes of the solvent and polymer, respectively. The value of χ_{i-j} can be used to quantify solvent-polymer interactions. By definition, χ_{i-j} is proportional to the molar enthalpy change (ΔH_m) induced by the solvent-polymer interaction (i.e., $\chi_{i-j} \propto \Delta H_m$). A negative χ_{i-j} value indicates that the polymer possesses positive water retention ability. The more negative the χ_{i-j} value is, the stronger the solvent-polymer interaction will be, which leads to greater water retention.

The solvent activity (a) for a polymer solution is the same as p/p^0, the normalized vapor pressure that was previously determined for the three aforementioned hydrogels. By rearranging Eq. (1) to solve for solvent activity in terms of the interaction parameter, the following is derived:

$$\ln a - \ln(1-\Phi_p) - \left(1-\frac{V_i}{V_j}\right)\Phi_p = \chi_{i-j}\Phi_p^2 \tag{2}$$

Therefore, the value of χ_{i-j} can be extracted by plotting the left side of Eq. (2) against Φ_p^2, as shown in Fig. 4. It is apparent from Figs. 4(a and b) that the χ_{i-j} values for both systems are negative, indicating a negative enthalpy change during mixing. In other

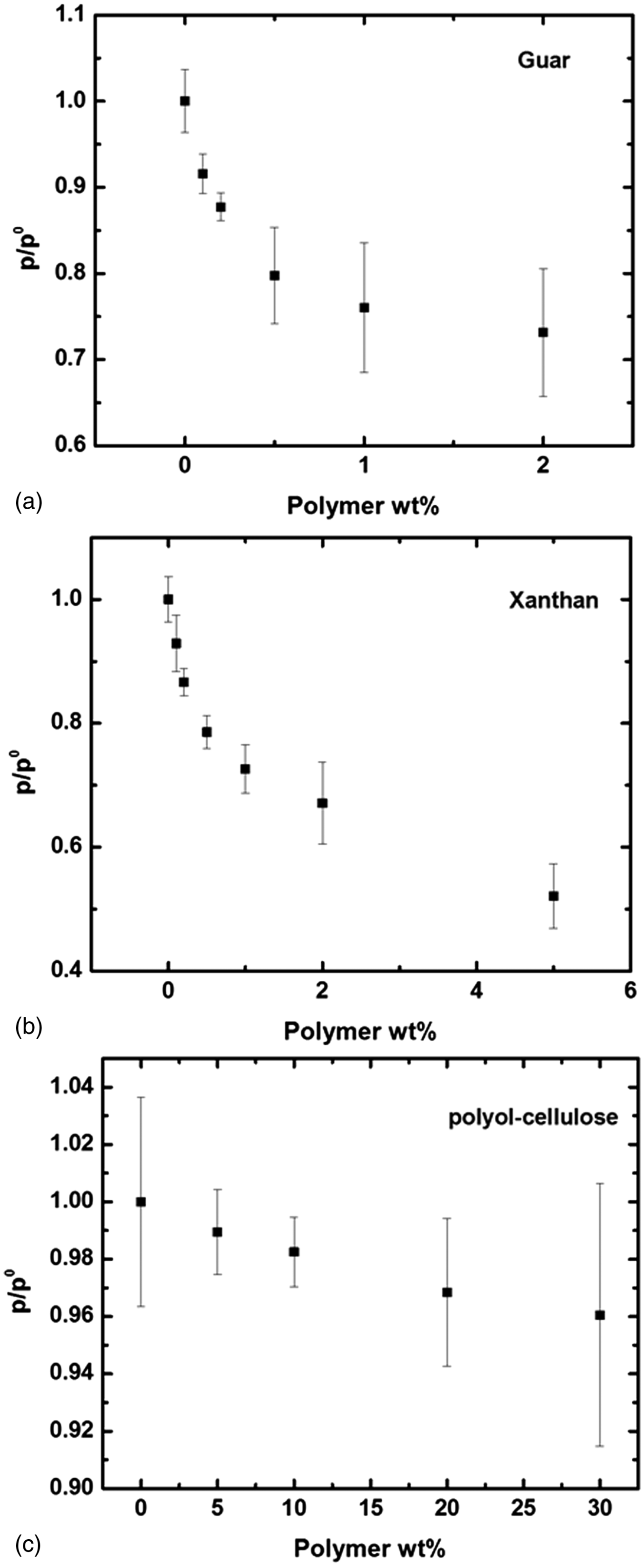


Fig. 3. Normalized vapor pressure changes of different polymer solutions at various concentrations: (a) guar gum; (b) xanthan gum; (c) polyol-cellulose

words, the interaction between water molecules and guar/xanthan polymer is stronger than the intermolecular forces of each pure component, which is likely because of the hydroxyl rich structure of both hydrogels. The bonds formed between the hydrogel hydroxyl groups and water molecules can hold water tightly to the hydrogel polymer chain and prevent significant evaporation. As a comparison, the χ_{i-j} value of polyol-cellulose hydrogel was close to zero, indicating no or weak binary interactions [Fig. 4(c)]. These weak interactions lead to poor water retention and help explain why polyol-cellulose-EICP solution dried sooner than the xanthan or guar solutions.

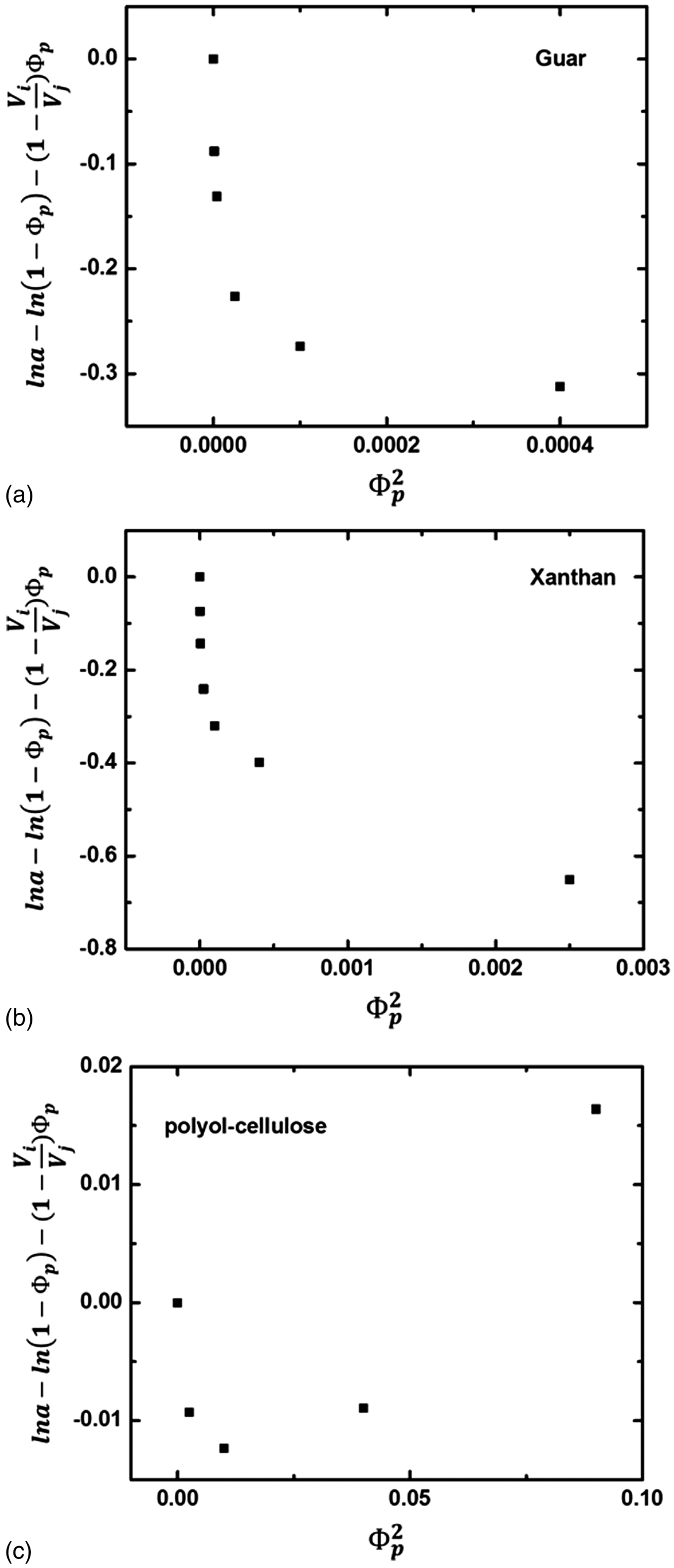


Fig. 4. Plots of the differences between the natural log of solvent partial pressure and the entropic contribution versus Φ_p^2: (a) guar gum; (b) xanthan gum; (c) polyol-cellulose; the slope of each curve represents the χ_{i-j} value

Conclusion

Experiments described in this paper using xanthan gum, guar gum, and polyol-cellulose hydrogels indicate that adding hydrogel to an EICP solution of urea and calcium chloride does not hinder carbonate precipitation. Furthermore, these experiments show that a topically applied hydrogel-EICP solution can be used to mediate the formation of a $CaCO_3$ soil crust. Hydrogel-assisted EICP occurred in soilless glass beakers and sand-filled paper cups at both 1.66 and 0.33-M initial $CaCl_2$ concentrations and with high- and low-activity urease enzymes. Evidence for ureolysis was observed in all hydrogel-assisted EICP tests through the detection of an odor of NH_3 after the application of the precipitation solutions. Acid testing provided additional evidence for the precipitation of a carbonate mineral in all specimens that received hydrogel-EICP solution. Direct evidence of the presence of $CaCO_3$ was also found through SEM analyses of the soil crust obtained from soil-filled Cup 4 using xanthan gum. On the basis of the SEM images, it appears that the mode of soil improvement in these specimens was through interparticle cementation by precipitated carbonate.

Hydrogel-assisted EICP appears to retain the reaction matrix for extended periods of time, extending the EICP reaction time and potentially increasing precipitation efficiency. Furthermore, observations of gas bubble formation in xanthan and guar hydrogels imply that off-gassing of NH_3 and/or CO_2 may be temporarily reduced, which may also increase precipitation efficiency. Hydrogel-assisted EICP also appears to have "localized" the EICP reaction matrix by reducing solution penetration into the soil.

Among the three hydrogels used in this study, guar and xanthan gums have the greatest water retention ability with increased concentration of the hydrogel, resulting in maximum declines in vapor pressure of approximately 17% at 2% (w/w) guar and a 47% decline at 5% (w/w) xanthan (compared with pure water). Furthermore, guar and xanthan gums were found to significantly reduce water evaporation at concentrations as low 1% (w/w) polymer (25 and 30% reductions for guar and xanthan gums, respectively). Polyol-cellulose hydrogel was found to be the least effective hydrogel for the reduction of water evaporation with a maximum decrease of ≈4% at 30% (w/w) polyol-cellulose hydrogel. The weak water retention behavior of polyol-cellulose hydrogel may be caused by the high water saturation as formulated from the manufacturer coupled with the additional dilution performed in this study. Nonetheless, these results suggest that xanthan and guar gums are superior to polyol-cellulose hydrogel with respect to mediating EICP.

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