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Development of Chemical-Encapsulating Microparticles for Delayed Flow Diverter Formation in EGS Reservoirs Away from Wells

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ABSTRACT

Although enhancing permeability is vital for successful development of an Enhanced Geothermal System (EGS) reservoir, high-permeability pathways between injection and production wells can lead to short-circuiting of the flow, resulting in inefficient heat exchange with the reservoir rock. For this reason, the permeability of such excessively permeable paths needs to be reduced. Controlling the reservoir permeability away from wells, however, is challenging, because the injected materials need to form solid plugs only after they reach the target locations. To control the timing of the flow-diverter formation, we are developing a technology to deliver one or more components of the diverter-forming chemicals in microparticles (capsules) with a thin polymer shell. The material properties of the shell are designed so that it can withstand moderately high temperatures (up to ~150 °C) of the injected fluid for a short period of time (up to ~30 minutes), but thermally degrades and releases the reactants at higher reservoir temperatures. A microfluidic system has been developed that can continuously produce reactant-encapsulating particles. The diameter of the produced particles is in the range of ~250-650 μm, which can be controlled by using capillary tubes with different diameters and by adjusting the flow rates of the encapsulated fluid and the UV-curable epoxy resin for the shell. Preliminary experiments have demonstrated that (1) microcapsules containing chemical activators for flow-diverter (silicate gel or metal silicate) formation can be produced, (2) the durability of the shell can be made to satisfy the required conditions, and (3) thermal degradation of the shell allows for release of the reaction activators and control of reaction kinetics in silica-based diverters.

1. Introduction

EGS involve subsurface reservoirs where there is hot rock (175 to 300+°C) but little to no natural permeability and/or a sufficient volume of producible fluid. As identified by the U.S. Department of Energy's (DOE's) Geothermal Technologies Office's (GTO) 2019 GeoVision report, the development of EGS-enabling technologies could increase geothermal power generation nearly 26-fold from today, representing 60 gigawatts-electric (GWe) of 'always-on', flexible electricity-

generation capacity by 2050. This would comprise 3.7% of the total U.S. installed capacity and 8.5% of all U.S. electricity generation in 2050 (US DOE, 2019).

During EGS development, subsurface permeability is enhanced via stimulation processes that re-open pre-existing fractures, create new ones, or achieve a combination of both. These newly created, highly conductive conduits allow fluid to circulate throughout the stimulated rock volume. However, even when a well-distributed flow network is created successfully, because of the heterogeneity of the fracture properties such as geometry, aperture, connectivity, and their time-dependent evolution, some fractures will take more flow than others. This potentially leads to heat extraction from only a small portion of the reservoir, resulting in rapid thermal decline of the heat extraction fluid (Doe and McLaren, 2016). Thus, the ability to control the fluid flow within a created reservoir and optimize the subsurface heat exchange performance in stimulated fractures, is critical for developing sustainable and economical EGS. Currently, standard approaches for altering reservoir fluid flow target the near-wellbore environment, including a variety of well completion and zonal isolation methods by which fluid flow into or out of a well is controlled.

Although management of near-wellbore fluid flow is critically important for maintaining fluid production from EGS reservoirs, it has limited impact in controlling the fluid flow away from the wells for optimization of heat recovery and reservoir performance. The focus of this study is to reduce and manage the permeability of fast flow paths within an EGS reservoir far away from both injection and production wells, to divert and distribute the flow to a larger reservoir volume. Three key components of the technology are (1) microparticles (capsules) containing the reactants ("encapsulated microparticles"), for delaying the diverter-forming reactions until the particles are transported to a desired reservoir location, by optimizing the capsule's shell properties, (2) silica-gel and metal-silicate-based flow diverters that are stable under EGS conditions and can be dissolved and disintegrated when needed, and (3) controlled reaction of the diverter-forming components to produce effective diverter plugs away from the well, which is made possible by the understanding of the degradation (or triggering) and transport characteristics of the reactant-delivering microcapsules.

2. Materials and Method

2.1 Microcapsules production by single-step microfluidic encapsulation

The single-step microfluidic encapsulation method, which involves a three-phase glass capillary device, is a promising technique for generating microcapsules with well-controlled geometry (Arriaga et al., 2015; Nabavi et al., 2015). The technique involves a combined co-flow and counter-current flow in a glass capillary device. The microcapsules are then produced through a flow focusing mechanism in which fluids containing core and shell materials are forced through a narrow junction. In addition to the core and shell fluid, the system consists of an outer carrier fluid. The capillary junction simultaneously pinches off the interior core and exterior shell fluids, forming a double-layer droplet suspended in the outer carrier fluid (as shown in Figure 1). The carrier fluid is used to stabilize the droplets. Once the double-layer droplets are formed, the outer shell, consisting of a photopolymer material, is photopolymerized by UV light to form the microcapsule. Compared to the classic two-step microfluidic encapsulation approach (e.g., Okushima et al., 2004; Kim et al., 2011), the advantages of the single-step microfluidic encapsulation are (1) the easy control of individual flow rates, because the flow rates of the inner and middle fluid do not need to be synchronized; (2) the capability to generate very thinly shelled

particles; (3) the simpler system design and smaller number of capillaries and connectors, which makes it easier to fabricate than the device composed of two sequential drop generation units.

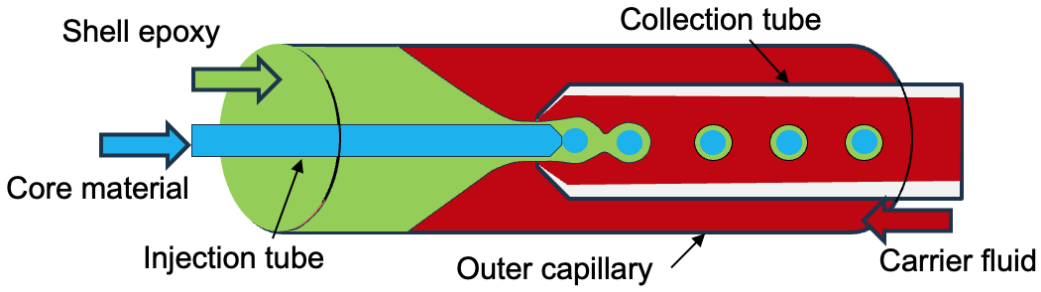

Figure 1: Schematic of the microfluidic device for producing microcapsules.

After a systematic evaluation of the polymer shell materials that could be potentially used for geothermal applications, NOA 61 UV-curable epoxy (Norland Products, NJ) was selected for its low viscosity, fast UV curing time, and most importantly, high temperature stability. The two core materials which we used in our investigation are water stained with a fluorescent tracer dye, and acetic acid (10-50 wt.%) stained with blue food dye. The carrier fluids were either silicone oil or mineral oil with a lower viscosity. During production, the particle size and shell thickness were changed by controlling the relative magnitudes of viscous, capillary and inertial forces of the three fluids used in the microfluidic device.

2.2 Silicate-gel-based flow diverter

The precursor used for diverter formation in this study is sodium silicate, which starts the gelation reaction in the presence of acid activators (e.g., An-Peng, 1963). The acid activators could be either strong acids (e.g., HCl, H_2SO_4, HNO_3) or weak acids such as acetic acid, citric acid and formic acid. When acid activators are delivered via microcapsules, the total amount of the acid that can be delivered to the target location would be limited by the volume and concentration of the particles in the injected fluid. This makes it necessary to use highly concentrated acid. Weak, organic acids are preferable to keep the pH at a safe, acceptable level, while providing the necessary amount of H^+. When organic weak acids are used, however, their temperature stability under the EGS conditions needs to be considered. In this research, we selected acetic acid, since it has been shown to be stable up to ~230°C for 72 hours (Li et al., 2017). The reaction between sodium silicate and acetic acid can be summarized as follows:

$$(Na_2O)_x(SiO_2)_{y(\text{liquid})} + 2x\text{CH3COOH}_{(\text{liquid})} \rightarrow (SiO_2)_{y(\text{solid})} + 2x\text{CH3COOH}_{(liquid)} + xH_2O \quad \text{Eq. (1)}$$

2.3 Hydrothermal experiments

Hydrothermal experiments were conducted on the produced microcapsules and sodium silicate solutions to investigate the thermal degradation behavior of microcapsules and control of silica gel plug formation. The primary equipment used in this research is a series of small, stainless-steel Parr reactor vessels. We also used small, sealable internal cells made of corrosion-resistant grade-2 titanium with high-temperature Viton O-rings (rated for 230°C) (e.g., Nakagawa et al., 2022). We demonstrated that the system could contain water vapor at 200°C without any pressure loss over 1 month, which is important for maintaining constant reaction environment and simulating EGS conditions.

Figure 2: Equipment used for hydrothermal experiments involving produced microcapsules and sodium silicate solutions. To minimize fluid loss and chemical contamination of the samples, sealable internal cells (a) were used in combination with small Parr reactor vessels (b). These vessels were heated in a convection oven at 150-200 °C (From Nakagawa et al., 2022).

3. Results and discussion

3.1 Microfluidic-based encapsulation system

At LBNL, we developed a dedicated system to produce reactant-encapsulating microcapsules (Figure 3a). The system is composed of three syringe pumps and capillary tubes to deliver core, shell materials and the carrier fluid. A 100-watt UV lamp was used for curing the epoxy shell in tube. Figure 3b depicts the microcapsules (marked by the red arrows) appearance in the collection tube that is exposed to UV light to cure the epoxy shell. Figure 3c is the photograph of the microcapsules exiting the capillary tube and being collected in a glass flask.

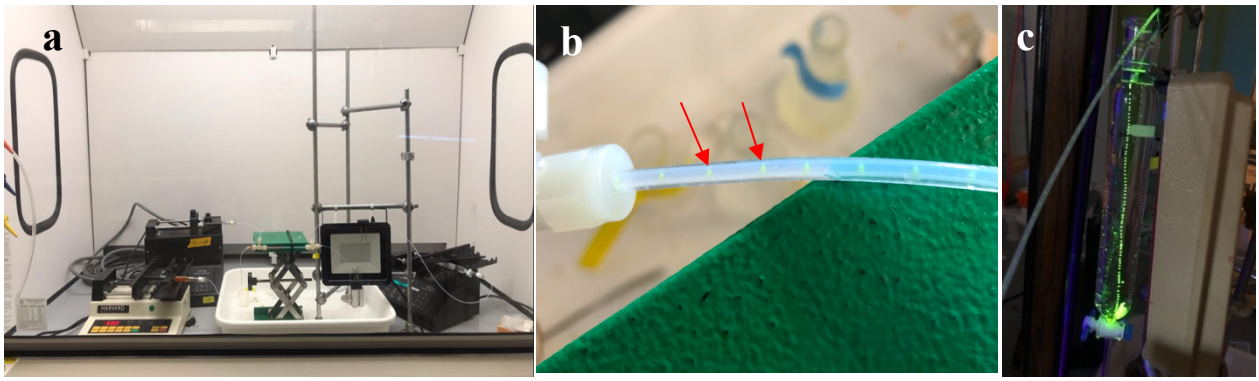

Figure 3: The microfluidic system developed at LBNL for producing microcapsules (a) and example images showing the produced microcapsules (marked by red arrows) in the capillary tube (b) and collection flask under UV light (c). Here the core fluid (water) was stained by a fluorescent tracer dye.

3.2 Microscope imaging and geometry quantification

Figure 4 shows microscope images of produced microcapsules including different core materials, i.e., (a) water stained with fluorescent tracer dye, (b) 10 wt.% acetic acid solution and (c-d) 50% acetic acid solution stained with blue food dye. Figure 4 also demonstrates the capability of the system in producing microcapsules with a particle diameter of ~250 to 650 µm and a core diameter of ~220 to 540 µm. After being UV cured and dried, the microcapsules were tested under elevated temperature and pressure relevant to EGS conditions.

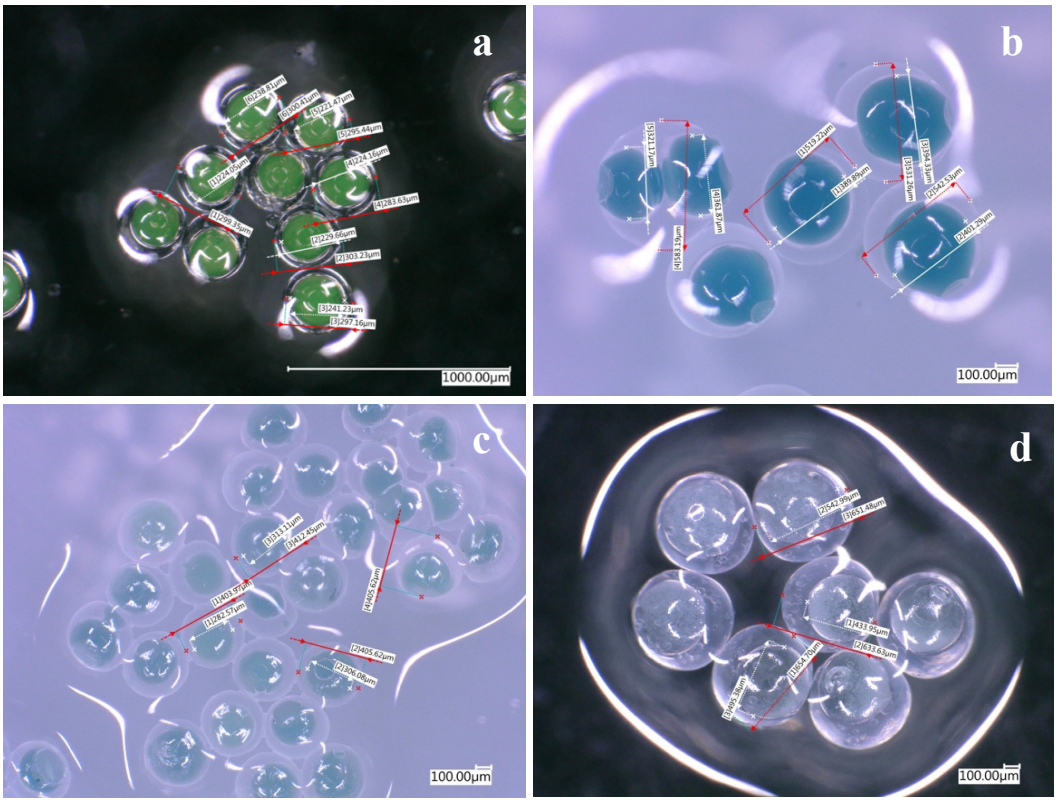

Figure 4: Example microscope images showing the produced microcapsules, including (a) water core stained with fluorescent dye, (b) 10 wt.% acetic acid core stained with blue food dye, and (c, d) 50 wt.% acetic acid core stained with blue food dye at different particle sizes.

3.3 Thermal degradation of microcapsules and control of silicate gel plug formation

The microcapsules in Figure 4d were collected and hydrothermal tests were conducted at temperatures between 150-200°C, with 10 g each of 10 wt.% and 40 wt.% sodium silicate solutions. Figure 5 shows images from the tests, with the microcapsules and 40 wt.% sodium silicate solution at 150 °C for up to 1.5 hours. As shown in the figure, the epoxy shell successfully isolated and protected the core reactant (50 wt.% acetic acid) from sodium silicate solution for at least 30 min at 150°C. After heating for 1.5 hours, the degradation and breach of the epoxy shell released acetic acid and initiated reaction with the surrounding sodium silicate solution, forming an intact gel plug with a length up to 2.0 cm. Microscope images of the gel plug clearly showed the degradation of microcapsules, leaving a semi-spherical shell structure within the plug (Figure 5e, f).

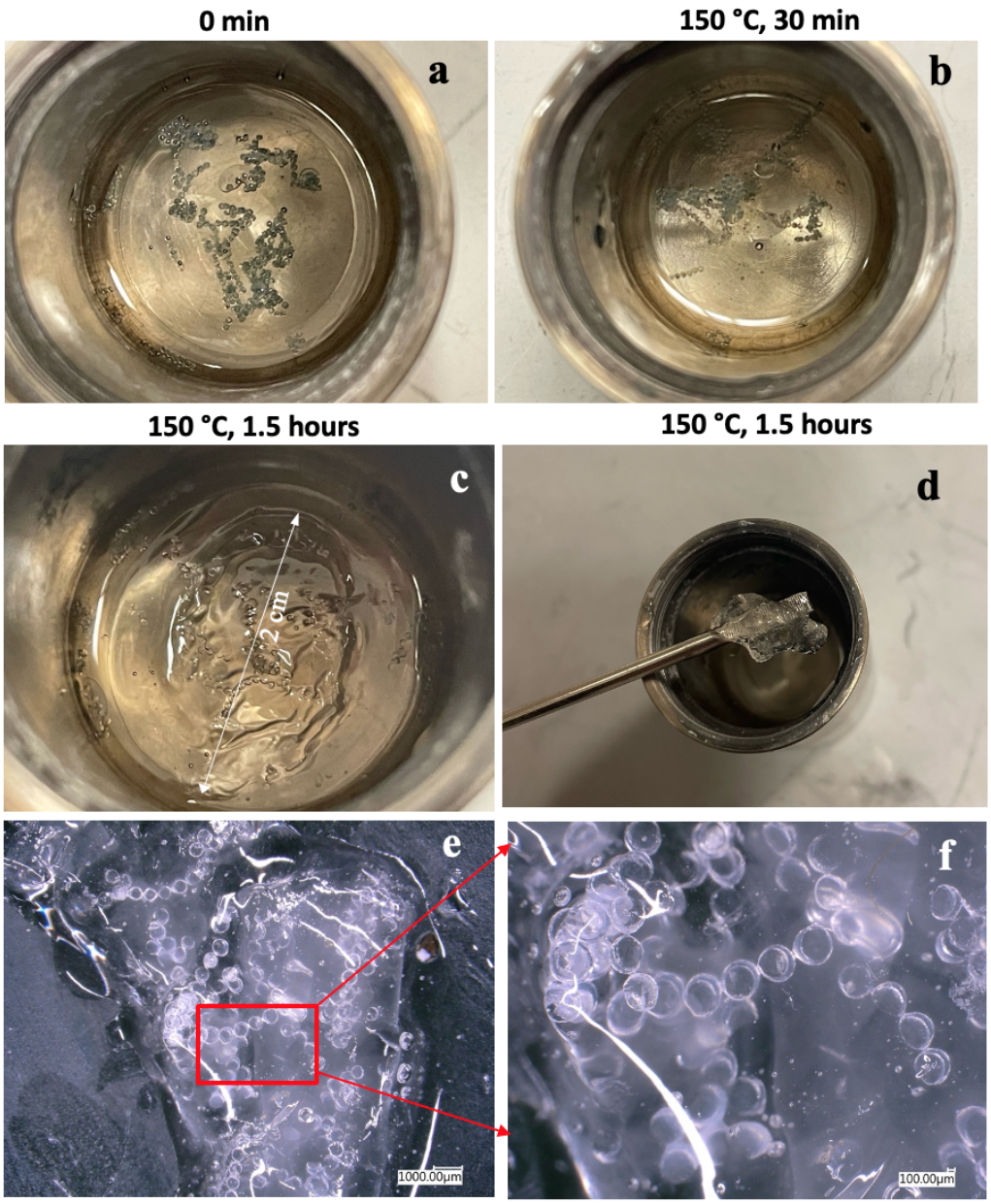

Figure 5: (a-d) Photograph of the hydrothermal tests using acetic acid (50 wt.%) encapsulated microcapsules with 40 wt.% sodium silicate at 150 °C.(e-f) Microscope images of the silica gel plug after shell breach.

We also conducted hydrothermal experiments on the produced microcapsules with 10 wt.% sodium silicate at temperatures of 150-200°C. Similar to Figure 5, Figure 6b demonstrates the stability of produced microcapsules after 30-min heating at 150 °C. We then continued heating of the system at 200°C for another 30 min. Figure 6c shows partial degradation of the microcapsules and scattered, local formation of silica gel. Extensive silica gel formation occurred in Figure 6d after 30 min heating at 150°C and 1 hour heating at 200°C. The microscope images in Figures 6e and f after plug formation indicate breach and degradation of the microcapsules.

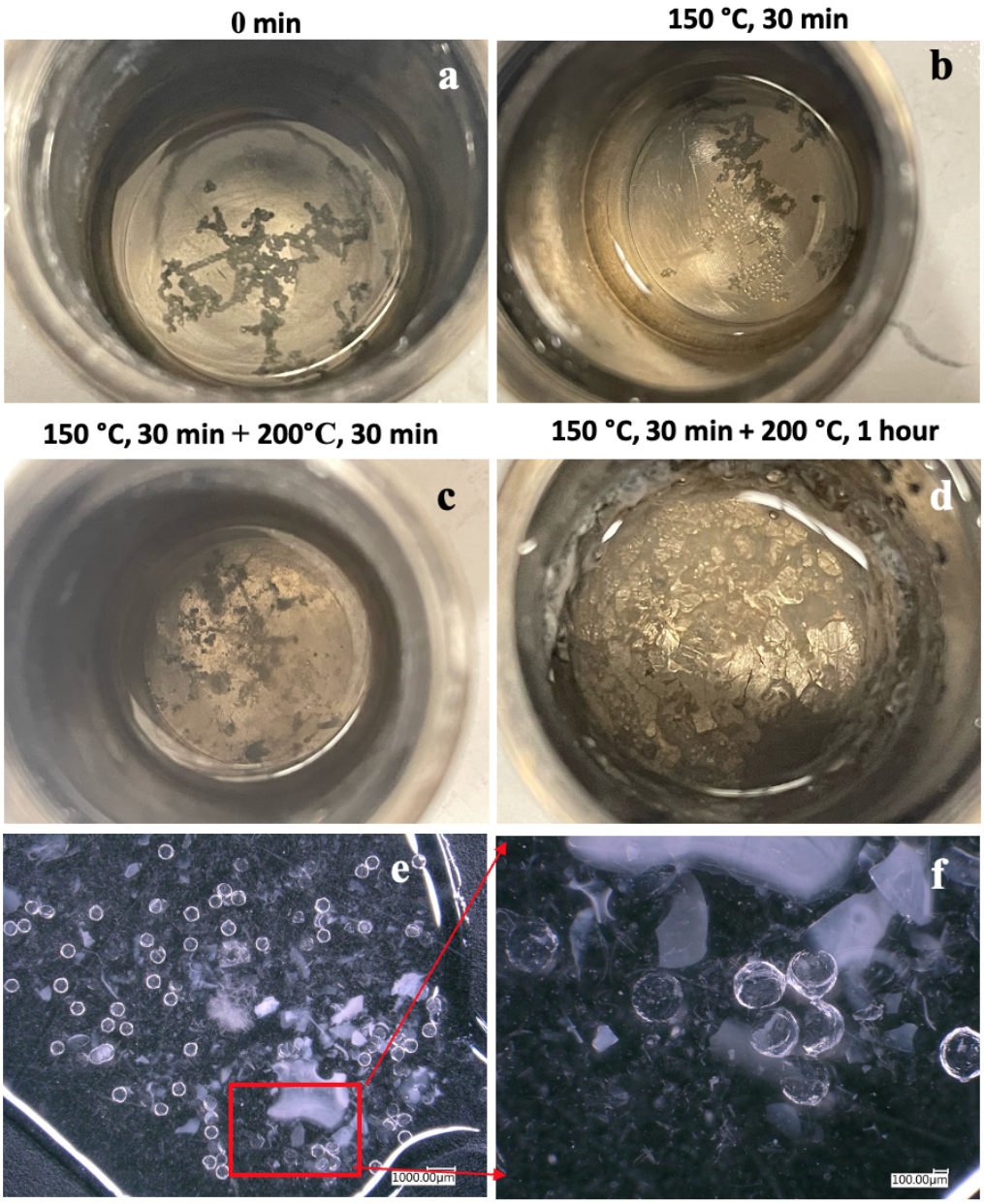

Figure 6: (a-d) Photograph of the hydrothermal tests on acetic acid (50 wt.%) encapsulated microcapsules with 10 wt.% sodium silicate at 150 °C.(e-f) Microscope images of the silica gel plug after shell breach.

Note that the habits of the silicate gel plugs are very different in the two hydrothermal tests using 40 wt.% vs 10 wt.% sodium silicate solutions. 40 wt.% sodium silicate produced a single, cm-scale solid plug. In contrast, 10 wt.% resulted in interconnected smaller plugs, exhibiting a porous and mesh-like overall structure.

Although using reactant-encapsulating microcapsules will allow delayed reaction and formation of diverter plugs, we anticipated that the presence of the shells might severely restrict mixing of the reactants, resulting in undesirable plug geometry and even incomplete reaction by barrier formation. Fortunately, the results shown in Figures 5 and 6 indicate this may not be the case. This may be primarily thanks to the small size of the microcapsules, which reduces the necessary diffusion length

for mixing, and to efficient degradation of the shell. We also observe that relatively high concentrations of the sodium silicate solution and the particle volume are necessary to achieve high-quality diverter plugs (Figure 7). For practical application, optimization of the particle size and concentration would be necessary for controlled, high-quality plug formation in desired reservoir locations after microcapsule delivery.

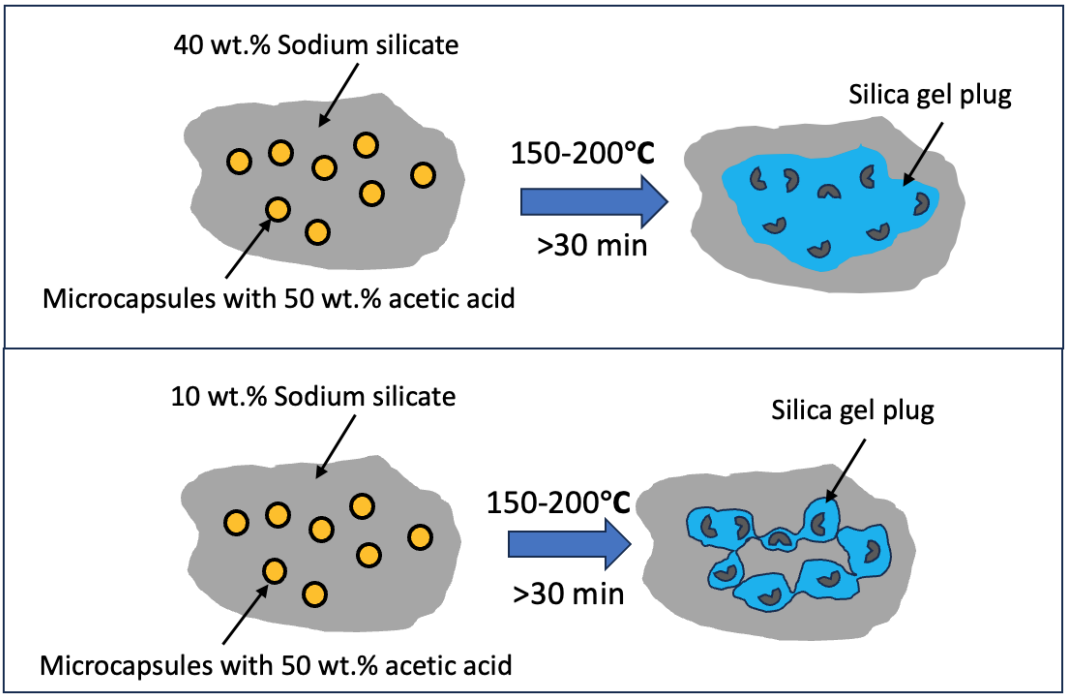

Figure 7: Schematics of the different silica gel structures induced by microcapsules and 40 wt.% vs. 10 wt.% sodium silicate. Once the epoxy shell is degraded and breached at elevated temperature, reaction can be significantly accelerated by the natural mixing of reactants, increased interfacial area and reduced diffusion length. Higher reactant concentration led to more extensive gelation and solid plug formation.

4. Conclusions

For EGS applications, we successfully developed a microfluidic system for producing shelled microcapsules containing fluid cores, based upon a microencapsulation technology. We demonstrated the capability of the system for producing microcapsules with different flow-diverter-forming reactants, sizes from ~250-650 μm and shell thickness from 30 to 80 μm. We also conducted hydrothermal experiments at temperatures between 150-200°C on the produced microcapsules, confirming that (1) the delayed reactions by 0.5-1 hours and that (2) once triggered, reaction can be enhanced by the increased reactive interfacial areas and reduced diffusion length. These properties of reactant-encapsulating microcapsules are critically important for delivering gel-forming chemicals away from the injection wells, delaying the reaction kinetics, and then achieving the objective of manipulating EGS reservoir fracture permeability. Further work will focus on scaling up the microcapsule production and testing the thermal degradation and reaction characterizations of different particle sizes, shell thickness and concentrations.

Acknowledgements

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