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Reaction Kinetics Control of Alkaline Activated Materials by Activator Encapsulated Microcapsules for EGS Well Construction

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ABSTRACT

During EGS well construction, cement slurry is pumped into a well between a tubular metal body (casing) and geologic formations to provide zonal isolation, to protect metal casing from corrosion and to support the well structure. One of the most important material design considerations for geothermal wells is material pumpability to enable its placement into an underground well. The LBNL team at the Center for Coupled Chemo- Mechanics of Cementitious Composites for EGS (C^4M) is addressing this gap with research on delayed solidification of alkaline activated materials (AAMs) in the high-temperature downhole environment of EGS reservoirs. Micro-encapsulation technology involves entrapment of a substance within microscopic (1 to 1000 μm size) particles of continuous shell with specific properties. For controlling the rection kinetics of AAMs, encapsulation of the reactants (alkaline activator) can be a potentially powerful strategy. The shell can be engineered/functionalized to protect the core materials and prevent reaction for a controlled duration of time, and denatured/breached by specific triggering events. By using a large number of sufficiently small capsules with a diameter <500 μm, the reaction sites can be well dispersed within the mixture. In this study, we present our microfluidic-based microencapsulation technology and demonstrate its performance for producing alkaline encapsulated microparticles. Once triggered by elevated temperature, the diffusion characteristics of alkaline solution and reaction with surrounding precursors are investigated via an in-situ HPHT visualization cell. A control test without the microcapsules will be compared, along with characterizations by transmission electron microscopy on the nano-scale structures to gain gaining fundamental understanding the reactions' pathways.

1. INTRODUCTION

Geothermal energy development requires access to the subsurface through deep wells that circulate fluids to extract thermal energy. During underground well construction, cement slurry is pumped into a well between a tubular metal body (casing) and geologic formation to provide zonal isolation, to protect metal casing from corrosion and to support the well structure. Most underground wells are currently cemented with Ordinary Portland Cement (OPC)- based composites. PC production emits ~900 kg of CO_2 per tonne. Also, it was estimated that the cement manufacturing process is responsible for ~ 7% of industrial energy consumption, which, in turn, accounts for 30–40% of global energy consumption (Kermeli et al., 2019). In addition to being energy intensive, OPC has poor durability in geothermal well environments, with severe challenges and often fail to provide casing corrosion protection and support, as well as zonal isolation in fragile, fractured geothermal formations. Although it is generally difficult to attribute an underground well failure to a single factor, cement failure by severe well environments and high bottom hole temperatures has led to the failure of wells in several geothermal fields (Radenti and Ghiringhelli, 1972; Berra et al., 1988). Supported by the US Department of Energy's Earthshot program, the Center for Coupled Chemo-Mechanics of Cementitious Composites for EGS (C^4M) is investigating a rational way of designing cost-effective and sustainable materials different from OPC, with appropriate mechanical properties and durability under the conditions of EGS. One of materials being studied by the center is the gibbsite-based alkali activated material (AAM) that involves sodium metasilicate (SMS) as the activator and gibbsite as the precursor.

To enable eventual placement of the AAM in deep wells, they must stay fluid (pumpable) for long-enough time before solidification under the EGS conditions. Typically, the slurry must stay fluid at least for 6-10 hours (and with low viscosity for entering narrow spaces) under the low shear and high temperature (150-300°C) conditions of cement pumping. Although the setting times of AAMs have been found strongly related to the factors including precursor composition (Kamath et al., 2021), alkaline activators (Liu et al., 2017), retarders (Tong et al., 2021), and water content (Dai et al., 2020), they are not expected to be able to delay the setting time considerably under the geothermal HTHP conditions. For example, chemical retarder additives, that modify and extend the setting time by altering dissolution of the main ions and the followed nucleation and growth of reaction products, quickly degrade under HPHT hydrothermal conditions.

Encapsulation of reactants (alkaline activator) can provide a potentially powerful alternative to pure chemical, reaction-time-based control of AAM solidification. By using sufficiently small capsules, the reaction sites can be well dispersed within the mixture. Microencapsulation is a process that involves entrapment of a substance within a microscopic, continuous film of a polymeric material with specific properties, to give the microcapsules a variety of useful properties. These microcapsules can hold liquid, solid, or gas, and typically have sizes ranging from 1 to 1000 μm, depending on the employed encapsulation technique. The unique advantage of applications employing microencapsulated reactants is that the core material is coated and isolated from the external environment. The shell can be engineered/functionalized to protect the core materials and prevent reaction for a controlled duration of time, and denatured/breached by specific triggering events, including thermal, electrical, magnetic, biological, chemical and photo stimuli (Esser-Kahn et al., 2011). Because this property can be used to reduce or delay the release of the core material to the surrounding environment, microencapsulated particles have been used to reduce dosing frequency and delay degradation of pharmaceutical drugs. In high-temperature thermal energy storage applications, encapsulated phase change materials (PCMs) have been widely used. In this case, the particle shells function as a thermal buffer, which protects the encapsulated content from sudden thermal shocks by absorbing and releasing heat during temperature-variation-induced phase changes (Liu et al., 2016). For EGS well cementing applications of microencapsulation technology, temperature plays a dominant role in triggering the decomposition of the shell, leading to the release of the activator and geopolymerization reaction after the placement is completed. The encapsulated alkaline activators can be Na(K)-metasilicate, Na(K)-hydroxide. Ultimately, the goal would be a well-controlled, predictable response to the time of the slurry set (hardening, becoming unpumpable) depending on the encapsulation of the activators and possibly its combination with the set retarder (an additive that slows setting reactions). The harsh and corrosive, HTHP hydrothermal environments in EGS wells, however, requires new encapsulation technology with inorganic shell that are functional up to a desired duration of time (i.e., 6-10 hours). The integrity of conventional polymer-based shell materials is not likely sustainable under such a period of time.

Inorganic shell materials (e.g., titanium dioxide, sodium silicate, calcium carbonate and silica) that are thermally stable at 300°C and above have been successfully applied for encapsulating phase change materials for high temperature thermal energy storage (Jacob et al., 2015). Among these materials, silica has shown potentials for encapsulating alkaline activators and delay solidification reaction for the desired period of time. Gunnarsson and Arnorsson (2020) reported the amorphous silica solubility data in a well-mixed system. Their results showed that the solubility of amorphous silica in deionized water increased from 600 ppm tested for 7 days at 150°C to 1430 ppm for 11 hours at 300°C. More specifically, He et al. (2014) reported an approach sol-gel synthesis of microencapsulated organic phase change material with silica wall. The sol-gel based hull material was synthesis using sodium silicate as the precursor and by controlling the pH of the solution which determines the silica condensation rate and the polycondensation of silica on the surface of an oil (n-octadecane) droplet. It is noticed that, however, the alkaline activators (Na(K)-metasilicate, Na(K)-hydroxide) cannot be directly encapsulated by silica through this approach as the miscibility of alkaline activator core and sodium silicate precursor-based shell. A new technology capable of encapsulating alkaline activators is required for EGS geothermal well cementing applications.

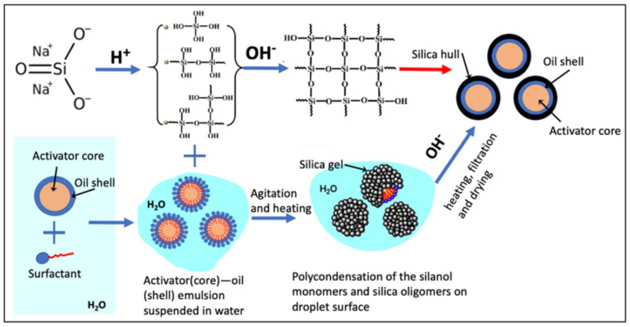

Figure 1. Schematic illustration of preparing the silica hull deposition on activator (core)-oil (shell) microcapsules (revised from Zhang et al. (2021))

At LBNL, we have developed the encapsulated microparticles for geothermal applications. We showed controlled/delayed reaction by 0.5-1 hours at 150-200°C (Chang et al., 2024). We applied this technology for controlling the solidification reaction of AAM based cement. With an aim to delay the reaction for more than 6 hours at temperatures up to 230°C, the activator encapsulated microcapsules in this project are produced in two steps: (1) generation of activator (core)-wax (shell) microcapsules by microfluidics and (2) Silica hull deposition (Figure 1). In this study, we focus on reporting the progress of the first step.

2. MATERIALS AND METHOD

2.1 Single-step generation of activator (core)-Wax (shell) microcapsule in water by microfluidics

The activator encapsulated microcapsules are produced by a single-step microfluidic technology, involving a combined co-current and counter-current flows in a capillary system (Figure 2a). The shell of the droplet is formed by 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 double-emulsion droplet suspended in the outer carrier fluid. The carrier fluid will be water based and will be used to stabilize the droplets with surfactants. Key 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 thin shelled core/shell particles; and (3) simpler system design and a smaller number of capillaries and connectors than the device composed of a more complex system with two sequential droplet generation units. At LBNL, we developed a dedicated microfluidic system and successfully produced microencapsulated particles of ~300 µm diameter with a polymer epoxy shell (Chang et al., 2024).

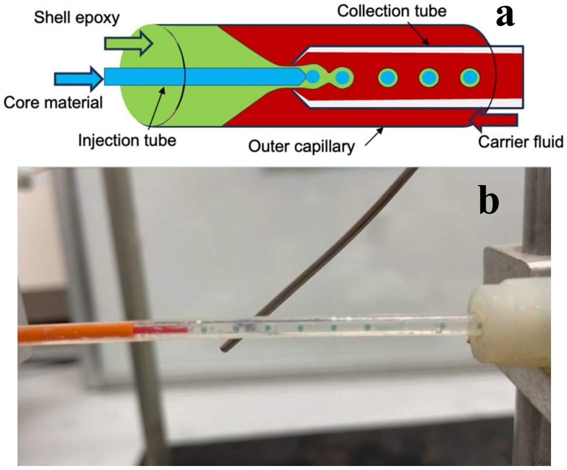

Figure 2. (a) Schematic of the microfluidic device for producing microcapsules. (b) Snapshot of produced microcapsules flowing in the collection tube.

The shell materials we used in this study are octadecane and paraffine wax, with different melting points at 30 and 60°C, respectively. During the experiments, temperature of the shell materials was well controlled either by a heating lamp or an oven so that they can be injected into the microfluidics with well-controlled rates. The core activator is 10 wt.% SMS in water stained with dye for better identification. Water was used as the carrier fluid. Figure 2b shows a snapshot of the microparticles flowing in the microfluidic system. At the effluent of the collection tube, the microcapsules were collected in cold water where the shell material solidified to form a sphere hard shell.

2.2 Direct visualization of microparticle degradation and controlled activator release at elevated temperatures

We developed an HTHP in-situ visualization system, which is used for understanding the processes involving (1) activator chemical release from microparticles with a thermally degradable shell, (2) dispersion of the chemical in the surrounding reactant matrix, and (3) the eventual solidification of the cement (Figure 3). The test can be conducted at temperatures up to 200-225°C, with a fluid pressure of ~10 MPa (1500 psi). To help visualize the degradation of small (300-500 µm) particles and time-dependent dispersion of the activator, fluorescent dye that performs well at elevated temperatures (disodium fluorescein) was used as a tracer, illuminated by a UV lamp. Preliminary tests were conducted to confirm the functionality of the test system. A small number of particles containing SMS solution within a low-temperature-melting (~55°C) wax shell were embedded within a gibbsite ($Al(OH)_3$) matrix, and then heated up to 150°C.

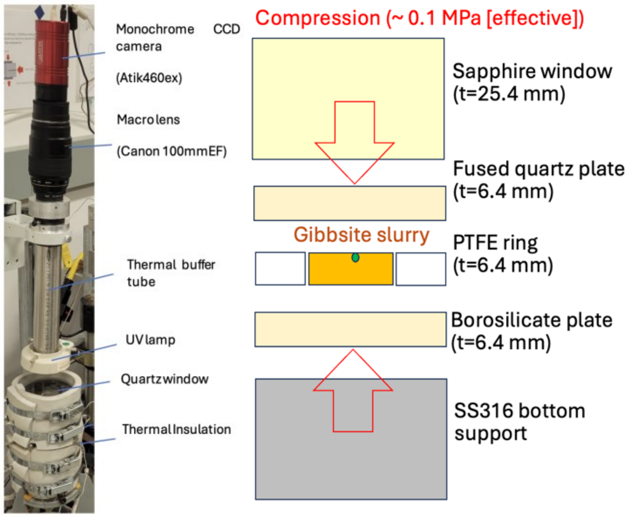

Figure 3. Photograph of the in-situ HTHP visualization system developed at LBNL (left) and schematic setting of the visualization cell with an emplaced microcapsule (green dot) and gibbsite slurry (right).

3. RESULTS AND DISCUSSION

3.1 Microscope imaging and geometry quantification of produced microcapsules

Figure 4a shows images of the collected microparticles with octadecane shell. These particles were produced by using a 1 mm ID collection tube and fluid injection rates of 5 µL/min (core), 50 µL/min (shell) and 300 µL/min (carrier fluid). The microscope image in Figure 4b indicates low successful rate of the product, particles exhibit shell defects, leakage and loss of the core fluid, and aggregation of multiple particles. For a small number of successfully made particles, the diameter was ~650 µm. Most importantly, all of the produced particles gradually degraded during imaging and handling, due to the low melting point of the shell material (30°C). From these observations, we concluded octadecane was not suited for this preliminary study as the shell material.

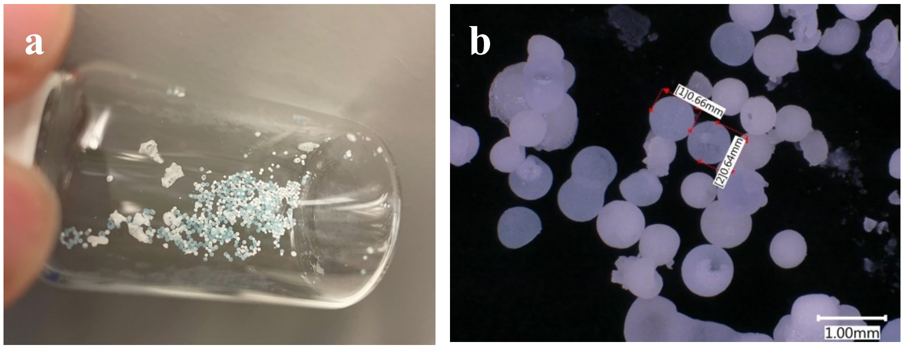

Figure 4. Photograph (a) and microscope image (b) of the produced microcapsules with octadecane shell.

Figure 5a depicts the microparticles with a paraffin wax shell produced from a 1 mm ID collection tube and by injection fluids at 20 µL/min (core), 50 µL/min (shell) and 300 µL/min (carrier fluid). The microparticles with a paraffine wax shell show much better quality with less defects on the shell and less particle aggregations. The images under UV light (Figure 5b,c) also indicate successful encapsulation of most of the SMS core with florescent dye. More microscope images of the particles indicate a size at ~600 µm by 700 µm (Figure 5d,e,f).

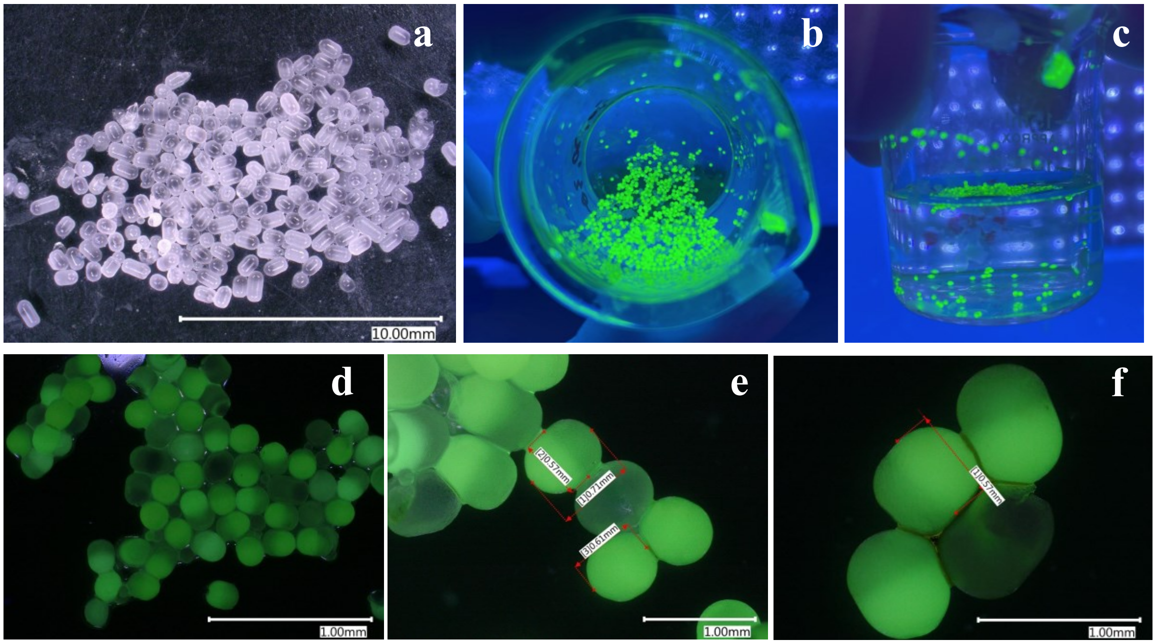

Figure 5. Photograph and microscope images of the produced microcapsules with a paraffin wax shell using 1 mm ID collection tube. Particles in images b-f are illuminate by UV light so that the disodium fluorescein dye contained in the core fluid indicates the presence of the fluid and the integrity of the shell.

In figure 5a, note that geometry of the microcapsules is not spherical. The sphericity and the size of the particles can be controlled by changing the flow rates of fluids and the tube diameters in the microfluidic system. Figure 6 shows much better shaped, spherical capsules with reduced diameters in the range of ~370 um to 440 um, via a reduced shell fluid injection rate and a collection tube with a smaller diameter of 0.55 mm (I.D.). This example demonstrates that the geometry and size of the microparticles are controlled by the configuration of the microfluidic system and the fluid injection rates.

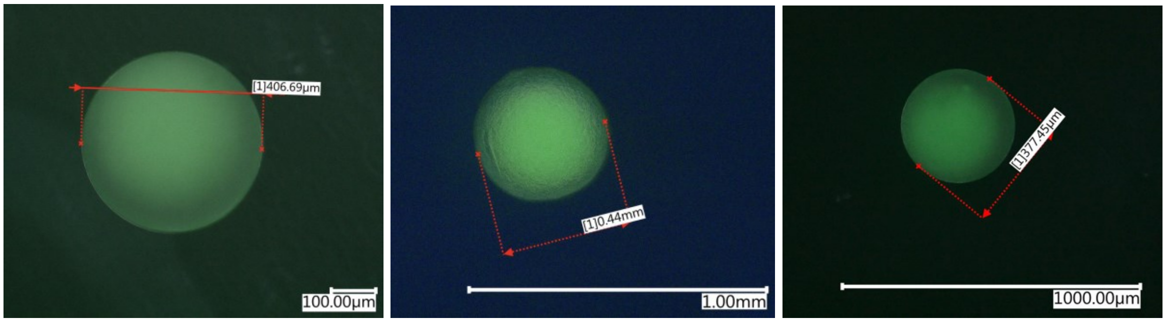

Figure 6. Microscope images of the produced microcapsules with a paraffin wax shell using a 0.55 mm ID collection tube.

3.2 Release and dispersion of activator chemical via thermal decomposition of encapsulated microparticles

Figure 7a presents examples of time-lapse UV fluorescence images of some of the produced microparticles collected from Figure 5b. The breach of the shell and the release of core fluid (10 wt.% SMS) can be seen when the temperature was in the rage of 55 to 70 °C. At 60 °C the larger particle started to leak the core fluid, as indicated by both brightening of the image and the fractured shell. Once the content leaks off and diffuses into the background matrix, the fluorescence decreases due to dilution. Figure 7b shows the temperature history during one experiment done on a single particle. For this test, the temperature was raised up to 150 °C in the testing cell. Again, shell degradation was observed at 55-60 °C, consistent with the melting point of the paraffin used for the shell. Figure 7c shows the normalized fluorescence intensity profile of the microparticle subject to heating, which demonstrates that the released SMS from a breached microparticle is well dispersed and evenly mixed with surrounding gibbsite suspension. For this test, however, we did not observe significant gelation reaction between SMS and gibbsite, which may be attributed to the relatively low SMS concentration in the mixture or low curing temperature in the test.

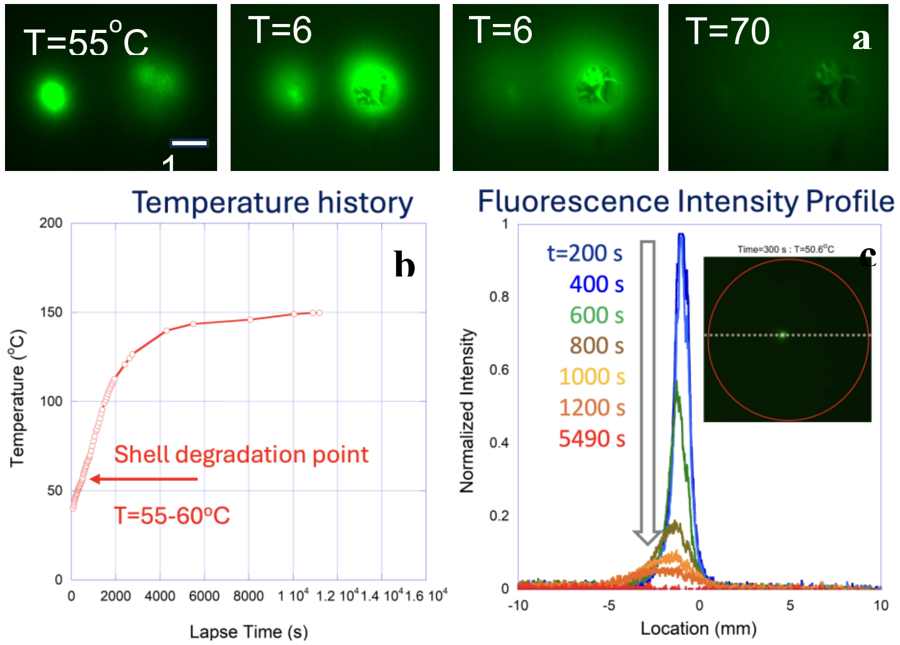

Figure 7. (a) Microscope images showing the breach of shell and release of CMS core at elevated temperatures. (b) Temperature profile with identified shell degradation point. (c) Fluorescence intensity profile of single microcapsule as a function of time.

4. CONCLUSIONS AND FUTURE WORK

In this paper, we report our first step toward producing activator-encapsulated microcapsules with the ultimate goal of keeping cement slurry pumpable for at least 6 hours at 230 °C within a geothermal reservoir. We demonstrated the capability of a microfluidic system for producing microcapsules with different shell materials and a range of particle sizes between 370-700 µm. We also developed a custom HTHP in-situ visualization system to observe and quantify the degradation characteristics of the produced particles and controlled release of the SMS core. When subject to temperatures below the melting point of the shell material, the microcapsules degraded and resulted in quick dispersion and even mixing of the SMS core fluid within the surrounding environment. The diffusivity and dispersity of core reactant is critical for uniform solidification reaction of cement slurries in geothermal wells.

In addition to the microcapsule development, experiments on the cementing materials without microcapsules are being conducted with in-situ TEM to characterize the nano-scale structure of hydrothermally treated gibbsite-based AAM, to gain the fundamental understanding of the reactions' pathways. Our next major step is to develop a technology to create microcapsules with a higher degradation temperature. For this, we are currently exploring the possibility of utilizing the silica hull deposition. Once this step is completed, the new microcapsules will be tested again in the visualization system at the ultimate HPHT conditions.

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