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Flow of pH-responsive microcapsules in porous media

Wei Jin Gun, Alexander F. Routh *

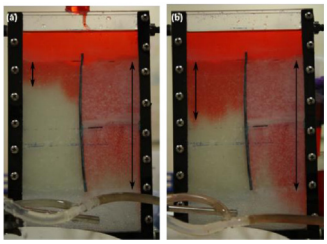
BP Institute for Multiphase Flow, Department of Chemical Engineering and Biotechnology, University of Cambridge, CB3 0EZ, United Kingdom

HIGHLIGHTS

- We demonstrate the triggering of pH sensitive micro-capsules in a porous media.
- The flow-paths in the porous media can be affected by introducing micro-capsules.
- Un-triggered capsules can affect the flow and the degree of blockage depends on the pore throat and micro-capsule sizes.
- Increased flow through low permeability regions is demonstrated.

GRAPHICAL ABSTRACT

Polymeric Microcapsules change flowpaths in porous media



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ABSTRACT

This article investigates the use micro-capsules, containing a gelling agent hydroxypropyl cellulose (HPC), to alter flow paths in porous media. The aim is to preferentially block-off high permeability regions, thereby diverting the flow into adjacent un-swept low permeability regions. Micro-capsules with 2–7 μm in diameter were made by polymer precipitation through solvent evaporation using poly(4-vinyl pyridine) (PVP) as the shell material. A customised flow tank was constructed to facilitate porous media flow and both single and dual permeability experiments were conducted. Even without gelling agent, the micro-capsules gradually blocked the pore throats of the glass beads network. Following acidification a drop in permeability was observed. This was because swelling of the PVP shell constricted the pore throats. The permeability drop was observed to be more significant for low permeability regions. Flowing micro-capsules through the tank with two permeability regions in parallel allowed the high permeability region to be selectively blocked.

1. Introduction

Micro-capsules are micron-sized particles. They comprise a shell, encapsulating an active ingredient, in the core. The shell acts as a barrier between the active ingredient and the potentially harsh external environments, which can be imposed on the micro-capsules. Such harsh environments can be mechanical, thermal or chemical depending on the situation. There are numerous examples in the pharmaceutical industry where encapsulation would be beneficial. For example, if biological materials such as enzymes, which are susceptible to denaturation, are encapsulated their biological activity can be retained (Keen et al., 2012; Nasseau et al., 2001). Other examples include the encapsulation of astaxanthin, a food supplement, which showed minimal heat degradation compared to free astaxanthin(Tachaprutinun et al., 2009). Encapsulation is also important in the digital display industry, for example by increasing the lifetime of organic light-emitting diodes, by preventing moisture and oxygen diffusion into the display area (Chwang et al., 2003; Seo et al., 2013).

Within the oil industry, no journal articles concerning the use of micro-capsules for enhanced oil recovery could be found. This is likely due to the lack of an appropriate time response, cost, the required sub-micronparticle size for low porosity reservoirs, and

* Corresponding author: Tel.: 01223 765718; fax: 01223 765701.

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harsh reservoir conditions with high salinities and temperatures. So far, only patents have been found studying this area (Bertkau et al., 2012; Montanato, 2012).

During secondary oil recovery, water is pumped into an oil field, through an injector, to maintain reservoir pressure and to sweep more oil towards the producer. Typically, the injected water will propagate through the path of highest permeability and can leave large regions of the oil field un-swept. The idea behind this work is to flow micro-capsules, containing a gelling polymer into a porous medium before a stimulus/trigger is applied to release the payload. The released polymer then forms a gelled network, causing a marked drop in permeability, or better still, completely blocking off that particular swept region. The following water is then diverted into the adjacent un-swept regions thereby mobilising the oil trapped in these regions.

Flow of micro-capsules in porous media, for temperature triggered micro-capsules, was investigated in a previous article (Gun and Routh, 2013b). In this article, pH is pursued as a release mechanism, by using micro-capsules with a poly(4-vinyl pyridine) (PVP) shell. The synthesis and characterisation of these micro-capsules were reported previously (Gun and Routh, 2013a) and release of the core material was demonstrated when exposed to acidic environments, because of dissolution of the polymeric shell.

The use of pH as the release trigger is fundamentally different to temperature. The temperature profile within a porous medium can be externally set, but for pH release, one needs to flow an acidic solution into the bed. Acid injection into reservoirs is an area that is extensively researched. One purpose of acid injection is to dissolve carbonate minerals, opening up the rock for fluid flow. These highly conductive channels can then form a comprehensive network allowing trapped oil to be swept out. If the acid was pumped at a high pressure, rock formations within the reservoirs can also be fractured, allowing the acid to etch into the fractures, forming more channels (Samuel and Sengul, 2003). This study uses acid to trigger microcapsule release and consequently is likely to be relevant to sandstone reservoirs.

Another possible application for these micro-capsules would be in the field of chromatography. It would be of interest to conduct experiments with a distributed system of permeabilities, rather than two distinctive permeability layers, as reported in this article. This would be relevant to preparative chromatography, where heterogeneity in the porosity of the chromatographic medium gives rise to greater dispersion of eluents. Permeability patterns in porous media strongly influence the flow as shown through flow visualisation work (Tchelepi et al., 1993). Using micro-capsules, one would decrease the permeability spread in the chromatographic column, allowing sharper peaks in the chromatogram, resulting in a higher separation purity.

In this article, we report the use of pH sensitive micro-capsules to release hydroxypropyl cellulose (HPC) into a bead pack, upon addition of acid. The aim of the article is to demonstrate that flow paths within a porous medium can be altered using micro-capsules.

2. Materials and method

2.1. Microcapsule formation and release profile

Micro-capsules that are pH-responsive were made with a PVP ($M_w \sim 160{,}000$, Sigma-Aldrich) shell and an aqueous core containing HPC (M_w 370,000, Sigma-Aldrich). They were made using a polymer precipitation method, which has been discussed previously (Gun and Routh, 2013a). These micro-capsules displayed an enhanced release when exposed to aqueous solutions below pH 3.5. The concentration of HPC in the core was 10 wt% in water and the capsules were determined from SEM images to be 2–7 μm in diameter. SEM images of the particles are shown in Fig. 1.

2.2. Tank set-up

To assemble, the tank was initially flooded with deionised water 18.2 MΩ cm (Purelab Ultra from ELGA process water) before pouring 3 mm diameter glass beads up to a height of 40 mm. A photo of the tank is shown in Fig. 2 with a schematic shown in Fig. 3. The main reason for flooding the tank with deionised water was to prevent trapped air pockets within the pack. This was frequently observed for glass beads less than 1 mm diameter and required the glass beads to be stirred vigorously to remove. The tank was then filled with 0.5 mm and 1.0 mm diameter glass beads on the two sides, separated with an impermeable Styrofoam partition, until they reached a height of 160 mm. A 40 mm layer of water was placed above the 0.5 mm and 1.0 mm beads to provide a constant pressure head. The pressure gradient, ΔP across the porous pack could be adjusted by changing the height of the outlet pipe. At the end of the outlet pipe was a mass balance, which recorded the outflow every second. By varying ΔP, we measured the change in actual flow rate. From the data-log, a graph of fluid mass against time was plotted and the gradient corresponded to the flow rate, Q. Fig. 4a shows the data one obtains. To ensure continual flow, the tank was never allowed to drain of water.

To predict the flow rate, the porous medium was made of various glass beads combinations in parallel and series as shown in Fig. 4b. Hence, the total tank permeability, K_T can be calculated as a function of lengths L_1, L_2, L_T and individual permeability layers K_1, K_2 and K_3. For two regions in parallel with a third in series, it is

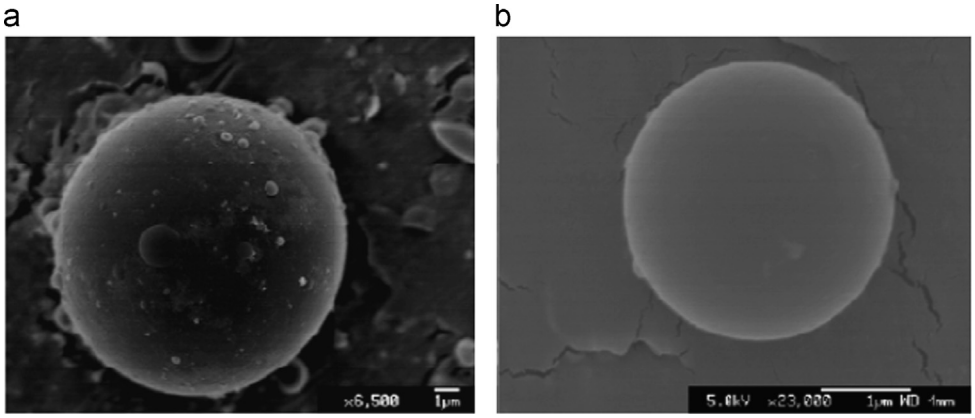

Fig. 1. Scanning Electron Microscope (SEM) images of Poly(lactic-co-glycolic) shell micro-capsules with hydroxypropyl cellulose in the core (Gun and Routh, 2013a).