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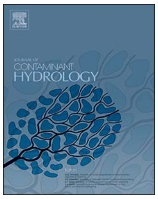

Real rock-microfluidic flow cell: A test bed for real-time in situ analysis of flow, transport, and reaction in a subsurface reactive transport environment

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ABSTRACT

Physical, chemical, and biological interactions between groundwater and sedimentary rock directly control the fundamental subsurface properties such as porosity, permeability, and flow. This is true for a variety of subsurface scenarios, ranging from shallow groundwater aquifers to deeply buried hydrocarbon reservoirs. Microfluidic flow cells are now commonly being used to study these processes at the pore scale in simplified pore structures meant to mimic subsurface reservoirs. However, these micromodels are typically fabricated from glass, silicon, or polydimethylsiloxane (PDMS), and are therefore incapable of replicating the geochemical reactivity and complex three-dimensional pore networks present in subsurface lithologies. To address these limitations, we developed a new microfluidic experimental test bed, herein called the Real Rock-Microfluidic Flow Cell (RR-MFC). A porous 500 μm-thick real rock sample of the Clair Group sandstone from a subsurface hydrocarbon reservoir of the North Sea was prepared and mounted inside a PDMS microfluidic channel, creating a dynamic flow-through experimental platform for real-time tracking of subsurface reactive transport. Transmitted and reflected microscopy, cathodoluminescence microscopy, Raman spectroscopy, and confocal laser microscopy techniques were used to (1) determine the mineralogy, geochemistry, and pore networks within the sandstone inserted in the RR-MFC, (2) analyze non-reactive tracer breakthrough in two- and (depth-limited) three-dimensions, and (3) characterize multiphase flow. The RR-MFC is the first microfluidic experimental platform that allows direct visualization of flow and transport in the pore space of a real subsurface reservoir rock sample, and holds potential to advance our understandings of reactive transport and other subsurface processes relevant to pollutant transport and cleanup in groundwater, as well as energy recovery.

1. Introduction

The characterization of subsurface reactive transport in the Earth's shallow-to-deep crust is of fundamental importance to understand a wide variety of pressing societal issues regarding environmental impact and energy recovery. These include the linked objectives of supercritical CO_2 injection and sequestration, storage of liquefied natural gas, enhanced conventional and unconventional hydrocarbon recovery, groundwater quality control, and hazardous waste remediation. The majority of studies have relied on controlled laboratory experiments to characterize subsurface reactive transport processes, where water, hydrocarbons, and microbes are fluxed through centimeter-to-meter long columns containing either synthetic or natural unconsolidated packed sands (Cortis and Berkowitz, 2004; Wu et al., 2014). However, an inherent limitation of these column and core-plug experiments is that, although samples can be collected and analyzed from influent, intermediate, and effluent ports, the incipient stages of transport and reaction cannot be continuously sampled and tracked in situ within the context of the sediment or rock mineralogy, porosity, permeability, and hydrology. It therefore remains a challenge to accurately predict pore-scale biogeochemical processes.

To overcome the limitations associated with in situ characterization

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of core and column experiments (Cortis and Berkowitz, 2004; Wu et al., 2014), non-invasive techniques such as neutron radiography (Fredd and Fogler, 1998a,b), high resolution optical profilometry (Elkhoury et al., 2013), magnetic resonance imaging (Olson et al., 2004; Zhang et al., 2007), X-ray computed tomography (Nguyen et al., 2013; Agbogun et al., 2013; Menke et al., 2016; Wildenschild and Sheppard, 2013), and synchrotron-based μ-CT have been used, as reviewed by Werth et al. (2010) and Cnudde and Boone (2013). Among these, μ-CT methods have perhaps experienced the most growth in recent years as advancements in data analysis have permitted 3D, high resolution (i.e., 1 μm or less), direct, non-invasive imaging of fluid and solid phases in opaque geological materials (Menke et al., 2016; Wildenschild and Sheppard, 2013). However, lack of imaging resolution, availability of equipment, and/or temporal scanning limitations often impede continuous real-time monitoring of reactive transport processes in porous media.

Microfluidic-based etched pore networks (i.e., micromodels) have been developed as another alternative to core and column experiments, and are being widely used to represent simplified subsurface environments in both shallow groundwater aquifers (Auset and Keller, 2004; Auset et al., 2005; Lanning and Ford, 2002; Lanning et al., 2008; Nambi et al., 2003; Singh and Olson, 2011, 2012; Werth et al., 2006; Willingham et al., 2008; Fanizza et al., 2013) and deep reservoir rock systems (Nguyen et al., 2013; Boyd et al., 2014; Singh et al., 2015; Wang et al., 2013; Zhang et al., 2010, 2011; Zuo et al., 2013). Micromodels allow direct in situ and real-time visualization and spectroscopic characterization of flow and reactive transport in two-dimensional (2D) pore networks. They have been used extensively to study single and multiphase flow, including the effects of pore geometry, capillary pressure, fluid phase saturation, and relative permeability on the latter (Avraam and Payatakes, 1995; Lenormand et al., 1983; Sahloul et al., 2002; Chomsurin and Werth, 2003; Jerauld and Rathmell, 1997; Keller et al., 1997; Soll et al., 1993; Wang et al., 2006), as well as bacteria and colloid transport (Auset and Keller, 2004; Auset et al., 2005; Singh and Olson, 2011, 2012; Baumann and Werth, 2004; Wan and Wilson, 1994), biofilm formation dynamics (Nambi et al., 2003; Singh et al., 2015), and mineral precipitation/dissolution (Boyd et al., 2014; Singh et al., 2015; Zhang et al., 2010). Numerical models are often used to simulate the resulting data in order to interpret and predict controlling mechanisms (Boyd et al., 2014; Singh et al., 2015; Ferrari et al., 2015; Joekar Niasar et al., 2009; Laleian et al., 2015; Yoon et al., 2012). Micromodels are generally a few centimeters in length and width; they contain ~2D pore spaces or channels that are 10's to 100's μm in depth and surround raised posts 100's of μm's in diameter that represent grains of porous media (Willingham et al., 2008). Fabrication of these micromodels involves either: (1) etching a porous medium framework into silicon or glass substrates using reactive ion etching or hydrofluoric acid (Fig. 1A) (Lanning and Ford, 2002; Nambi et al., 2003; Willingham et al., 2008; Singh et al., 2015; Chomsurin and Werth, 2003); or (2) allowing a liquid phase polymer (e.g., poly-dimethylsiloxane (PDMS)) to cure and harden after pouring it into a mold fabricated from either etched silicon or patterned photoresist (i.e., soft-lithography) (Auset and Keller, 2004; Singh and Olson, 2011). Most recently, researchers have also begun developing 3D-printed microfluidic devices and have used them for organic and inorganic reactions (Capel et al., 2013; Kitson et al., 2012), flow control (Au et al., 2015; Rogers et al., 2015), and different biological applications (Lee et al., 2015a; Nejdl et al., 2014).

Conventional micromodels are made using highly spatially accurate imprinting of digitized pore geometries. Regular arrays of cylinders and other uniform geometries are common (Auset and Keller, 2004; Singh and Olson, 2011; Willingham et al., 2008; Long and Ford, 2009), as well as digitized images of actual rock sample pore structures (Zuo et al., 2013; Chomsurin and Werth, 2003; Sirivithayapakorn and Keller, 2003). In the latter, 2D pore structures are created using: (1) High-resolution digital images of fine sand porous media (Sirivithayapakorn and Keller, 2003); (2) Scanning electron microscope (SEM) images of rock deposits such as sandstone (Aktas et al., 2008; Buchgraber et al., 2011); and (3) Focused ion beam scanning electron microscopy (FIB-SEM) images of real sandstone or limestone cores (Gunda et al., 2011). For example, in a recent study, Gunda et al. (2011) developed a 'reservoir-on-a-chip' micromodel where FIB-SEM images of an actual rock core were used to create a 3D micromodel porous framework. Microstructural information from this was then used to fabricate a 2D pore-network with a stochastic random network generator, which was then etched into a silicon wafer. Similarly, Kim et al. (2013) developed an 'aquifer-on-a-chip' micromodel using a PMMA (poly(methyl methacrylate)) fabrication process where CO_2 laser ablation was used for etching, and a solvent assisted process was used for bonding in a hydraulic press. These micromodel experiments often provide data for development and verification of pore scale models (Willingham et al., 2008; Avraam and Payatakes, 1995; Lenormand et al., 1983).

While the aforementioned approaches have provided significant insights, most existing micromodel systems have two inherent limitations. First, the use of engineered materials like silicon, glass, or PDMS to create the porous media does not replicate the natural chemical and mineralogical reactivity of real rock grain surfaces. Second, 2D pore geometries do not fully replicate the inherently complex heterogeneous flow that occurs in natural subsurface rock and sediment deposits (Fig. 1B). As a result, these micromodels have been limited in their ability to evaluate the fundamental mechanisms of flow, transport, and reactions within the context of an actual subsurface aquifer or reservoir. In the last six years, there have been several efforts to address these limitations by altering surface wetting properties (Grate et al., 2013; Lee et al., 2015b; Song and Kovscek, 2015), developing more representative pore structures (Gunda et al., 2011; Song and Kovscek, 2015; Buchgraber et al., 2012; Joseph et al., 2013) and using real rock samples to fabricate microfluidic pore-networks (Porter et al., 2015; Song et al., 2014). However, none of these approaches have captured the complex pore-scale geometries, 3D flow fields, and multiphase fluid interactions, which are present in subsurface sedimentary rock reservoirs.

The objective of this study was to develop a next-generation microfluidic device, called the Real Rock-Microfluidic Flow Cell (RR-

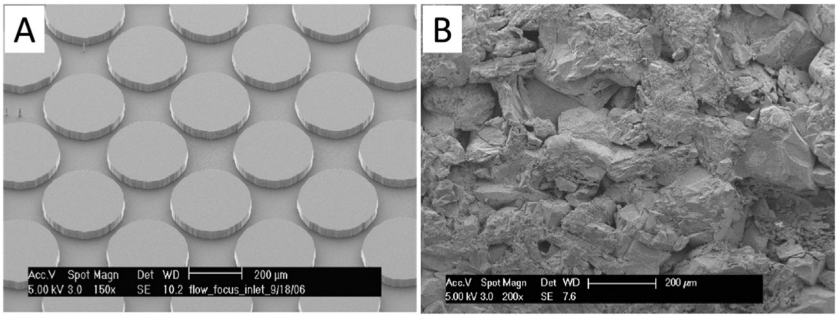

Fig. 1. Scanning electron microscope (SEM) images of pore networks in microfluidic flow cells created from A) a silicon wafer etched using reactive ion plasma and B) a real rock sample from the Clair Group sandstone.