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Fiber refractometer to detect and distinguish carbon dioxide and methane leakage in the deep ocean

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ABSTRACT

Deep ocean injection of carbon dioxide into subsea geologic formations carries a risk of carbon dioxide leakage as well as leakage of methane from petroleum bearing formations that injection wells may penetrate. Therefore, leakage monitoring technology for this application must detect carbon dioxide and distinguish it from methane. Here we demonstrate an all-optical approach to detect and differentiate between liquid carbon dioxide and supercritical methane bubbles in synthetic seawater at 9.65 MPa. This method employs fiber tip refractometry, a fiber optic measurement technique that is sensitive to the refractive index of the surrounding medium. Carbon dioxide and methane bubbles are clearly detected as they pass the sensor tip and these species are clearly distinguished from each other. Interferometric signals are also observed in association with the transition of bubbles onto and off of the sensor tip.

1. Introduction

Deep ocean injection of carbon dioxide into subsea geologic formations, such as is planned for the Santos Basin offshore of Brazil (Melo et al., 2011), carries a risk of carbon dioxide leakage during and after injection. At these sites, there is also a risk of methane leakage from the petroleum bearing formations that injection wells may penetrate. Therefore, leakage monitoring technology for this application must both detect carbon dioxide and distinguish it from methane.

Monitoring carbon dioxide storage has been demonstrated at the Sleipner injection site located in the North Sea (Furre and Eiken, 2014; Chadwick et al., 2006). In this pilot test, seismic and gravimetric sensors were used to monitor a subsurface plume of carbon dioxide with a limit of detection of 500 t of carbon dioxide (Chadwick et al., 2006).

Methods have also been demonstrated to detect carbon dioxide rising as a stream of bubbles or droplets in the water column. Acoustic tomography has been used to detect such a rising stream based on the difference in the speed of sound propagating in different media (*i.e.* water and carbon dioxide) (Brewer et al., 2006). Brewer et al. (2002) demonstrated detection of a rising carbon dioxide stream using a camera mounted to a remotely operated vehicle. Brewer also used pH and conductivity sensors to detect carbon dioxide enriched seawater adjacent to the rising carbon dioxide stream (Brewer et al., 2005). Similarly, Shitashima et al. (2013) developed pH/pCO_2 (partial pressure of carbon dioxide) sensors which were installed in an autonomous underwater vehicle for detection of carbon dioxide leakage.

An alternative method to monitor carbon dioxide leakage from subsea injection sites is based on refractive index measurements. The refractive index (RI) of a liquid or gas varies with species, temperature, pressure and, in the case of solutions and mixtures, concentration. As a result, RI measurement is a broadly applicable method to determine the values of these properties. In recent years, a range of fiber optic methods to determine RI has emerged, including grating based methods (Fang et al., 2010; James and Tatam, 2003), interferometric methods (Wang and Tang, Jan 2012) and intensity based methods (Vurek et al., 1983; Munkholm et al., 1988; Cartellier, 1992; Goyet et al., 1992; Degrandpre, 1993; Hamad et al., 1997; Cartellier and Barrau, 1998; Neurauter et al., 2000; Chang et al., 2002; Chang et al., 2003; Ertekin et al., 2003; Fortunati et al., 2003; Avdeev et al., 2004; Kim and Su, 2004; Enrique Juliá et al., 2005; Lee et al., 2007; Zhao et al., 2009; Prada et al., 2011; Wang and Tang, Jan 2012; Xu et al., 2013). Fiber optic methods allow the sensing element to be located at a distance from

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the interrogation system and, as a result, sensing of RI in environments where conventional methods are difficult to apply (*e.g.* high pressure, high temperature). For measurements that require high accuracy, gratings used in conjunction with fine resolution wavelength interrogation is preferred. However, for applications in which the objective is to discriminate between different substances or between different states or phases of the same substance which have distinctly different values of RI, an intensity-based method, fiber tip refractometry (FTR) offers a relatively simple and low cost alternative.

The basis for FTR is Fresnel reflection. When light exits a medium with RI, n_1, and enters another with RI, n_2, the intensity of light reflected back into the first medium is dependent on the refractive indices of both media, as shown in Eq. (1). Hence, if n_1 is known, then the intensity of the reflected light, *I*, is a direct measure of n_2.

$$I = \frac{(n_1 - n_2)^2}{(n_1 + n_2)^2} \tag{1}$$

An FTR comprises the distal end of an optical fiber that is immersed in a target medium. Light propagating in the fiber undergoes Fresnel reflection at the interface between the fiber tip and the target medium. The intensity of this reflected signal is as defined above for the general case of Fresnel reflection with n_1 and n_2 being the RIs of the fiber and the target medium.

FTR has been applied by a number of researchers to measure RI of various fluids under static (*i.e.* no flow) conditions. For example, Xu et al., 2013) measured the RI of (*i.e.* benzene, ethanol, methanol, acetone glycerol) with a broadband light source centered at 1550 nm. Kim and Su (2004) performed similar experiments but measured RI at different wavelengths. Other studies present the use of FTR to measure salinity of aqueous solutions (Chang et al., 2002; Zhao et al., 2009).

Two studies have been identified in which FTR has been used for static RI measurements of carbon dioxide at high pressures. Avdeev et al. (2004) measured the RI of carbon dioxide in the gas, liquid and super critical states as well as mixtures of carbon dioxide and organic solvents. Prada et al. (2011) measured the RI of liquid carbon dioxide at pressures up to 5.5 MPa under static conditions. No FTR-based RI measurement of methane at elevated pressures, its solutions or mixtures have been identified.

There are several examples of FTR-based sensors that make use of either fluorescent or colorimetric coatings that react with carbon dioxide (Degrandpre, 1993; Ertekin et al., 2003; Goyet et al., 1992; Munkholm et al., 1988; Neurauter et al., 2000; Vurek et al., 1983). These methods have been demonstrated in aqueous solutions at atmospheric pressures to detect dissolved carbon dioxide rather than distinct phases. These methods have not been applied at high pressure

Interrogation of FTR systems is typically intensity-based. As a result, these systems offer fast response times, relative to grating-based systems, which typically depend upon wavelength-based interrogation. As a result, FTR has been used by a number of researchers to make dynamic measurements in two-phase flows (Hamad et al., 1997; Fortunati et al., 2003; Enrique Juliá et al., 2005; Chang et al., 2003; Lee et al., 2007; Cartellier, 1992; Cartellier and Barrau, 1998). Hamad et al. (1997) used FTR to distinguish kerosene droplets from water in two-phase pipe flow. Kerosene droplets were entrained in the flow and the optical probe was used to detect the passage of droplets. In another study, the size and velocity of air bubbles in pipe flow of water were measured with a four-point FTR device by Guet et al. (Fortunati et al., 2003). This system provided higher accuracy velocity measurements than a single point system. Chang et al. (2003), Enrique Juliá et al. (2005) and Lee et al. (2007) all used FTR to measure *void fraction* (*i.e.* bubble fraction) in entrained bubble flow. Cartellier et al. (Chang et al., 2003; Lee et al., 2007) did extensive work on velocity measurement in entrained bubble flow in an air-water system.

In most previous FTR studies in flowing liquids or gases, the fiber orientation is parallel to the flow (Hamad et al., 1997; Fortunati et al., 2003; Enrique Juliá et al., 2005; Chang et al., 2003; Lee et al., 2007; Cartellier, 1992; Cartellier and Barrau, 1998). Only one study was identified in which an effective FTR probe was mounted normal to the direction of flow (Rojas and Loewen, 2007). It is important to note, however, that this study focused on high speed, turbulent, aerated flows so the bubble direction was not necessarily normal to the fiber tip.

In the current study, an FTR probe is mounted normal to the flow and flush with a pipe wall, to monitor the passage of liquid carbon dioxide and supercritical methane bubbles in synthetic seawater at 9.65 MPa (1400 psi) and 20 °C. Throughout this paper, the term *bubble* is used to refer to a small and distinct volume of liquid or supercritical fluid and all pressures are gauge pressures. These experiments simulate the use of FTR to monitor leakage during and after deep (*i.e.* 950 m) ocean injection of carbon dioxide into subsea geologic formations.

2. Materials and methods

2.1. Sensor

The optical fiber used in this work is SMF 28e (Corning, USA). A length of this fiber is mounted in a standard FC/PC zirconia ferrule (F12070, Fiber Instrument Sales) and secured with epoxy (Thorlabs, F120) (see Fig. 1). The ferrule and fiber are epoxied to one end of a stainless steel tube with outer diameter 1/8″ (3.13 mm) and wall thickness 0.028″ (0.71 mm). The distal end of the fiber is cleaved normal to the fiber axis and is mounted in the ferrule so that the

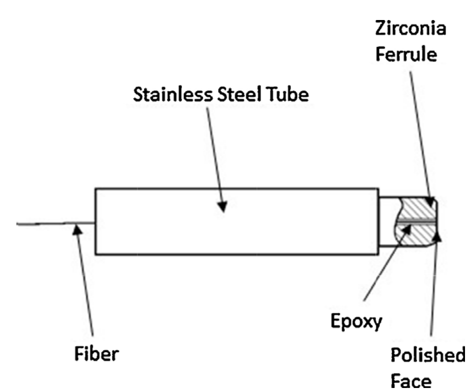

Fig. 1. Schematic of sensor tip with cutaway at the distal end.

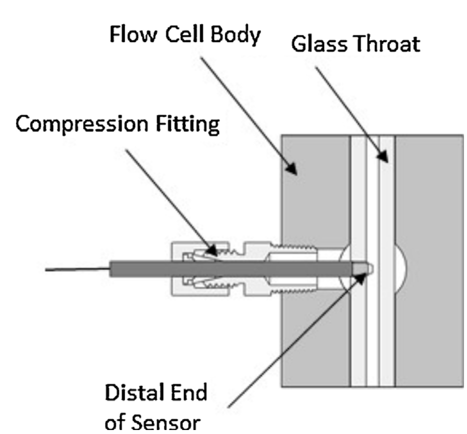

Fig. 2. Schematic of flow cell and sensor tip.