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Development of a perfluoromethylcyclohexane (PMCH) permeation plug release vessel (PPRV) for tracer gas studies in underground mines

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ABSTRACT

Perfluoromethylcyclohexane (PMCH) is a member of the perfluorocarbon tracer (PFT) group of compounds. PMCH has been widely used in various tracer gas studies to characterize ventilation systems, atmospheric transport patterns, and pollution distribution schemes. PMCH exists as a volatile liquid at room temperature and pressure, a characteristic that prevents PMCH from being deployed using traditional means. This paper presents a design for a permeation plug release vessel (PPRV) for PMCH. The PPRV is designed to passively deploy PMCH vapor at constant rate as a function of temperature and plug thickness for quantitative tracer gas studies. Details regarding the development process and the release rate analysis are included.

1. Introduction

PMCH is classified as a perfluorinated cyclic hydrocarbon. Other compounds in this group classification include perfluoromethylcyclobutane (PMCB) and perfluoromethylcyclopentane (PMCP) (Galdiga and Greibrokk, 1997). These compounds are also known as perfluorocarbon tracers (PFT) due to their chemical inertness, low toxicity, and trace level environmental background presence thus uniquely suiting them for use as tracer gases (Dietz, 1991; Watson et al., 2007). Compounds of this type have been widely implemented in heating, ventilation, and air conditioning (HVAC) as well as in atmospheric monitoring studies (Dietz, 1991). PFTs exist as volatile liquids at room temperature and pressure due to their high molecular weights. A controlled tracer release is essential if quantitative data is desired. This paper presents a design for a permeation plug release vessel (PPRV) for PMCH. The PPRV passively deploys PMCH vapor at a constant rate as

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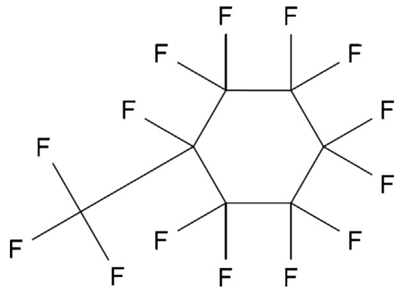

Fig. 1 – Molecular structure of PMCH.

a function of temperature and plug thickness. An equation to predict the release rate based on these two variables is provided. Details about the PPRV and the experimental design are also discussed.

2. Background

PMCH is a perfluorinated cyclic hydrocarbon whose chemical structure is composed of perfluoroalkanes (Watson et al., 2007). Compounds of this type are biologically inert, chemically inert, and thermally stable. The inert, non-reactive, and non-toxic nature of PMCH makes it an ideal choice as a tracer gas. PMCH is comprised of seven carbon atoms and fourteen fluorine atoms, which give it a chemical formula of C_7F_{14}. The molecular structure of PMCH is displayed in Fig. 1.

The PMCH molecule is composed of two main parts: the cyclohexane ring and the methyl group bonded off to the side. This fully fluorinated molecule has a molecular weight of 350 g/mol and a boiling point of 76 °C (169 °F). PMCH exists as a liquid at room temperature and pressure due to its molecular weight. The high volatility of PMCH simultaneously allows it to vaporize even at low temperatures. Once in a vapor state, PMCH remains a vapor even through cooler temperatures. Another advantage of PMCH is its detectability by GC even at low concentrations. This ability stems from PMCH's low ambient background in the atmosphere with concentrations in the low parts per quadrillion (PPQ) (Cooke et al., 2001; Simmonds et al., 2002; Watson et al., 2007) and high electron capture (EC) detection sensitivity (Simmonds et al., 2002). PMCH has already seen widespread use in other fields of study in conjunction with other PFT group compounds.

Building ventilation is one area that has implemented PFTs. PFTs have been used to investigate air infiltration into single family homes using passive PFT permeation sources coupled with passive capillary adsorption tube samplers (CATS) (Dietz and Cote, 1982; Leaderer et al., 1985) as well as to evaluate the performance of multi-zone deployments using passive PFT sources for categorizing air infiltration, air exfiltration, and air exchanges (Dietz et al., 1986). PFTs have also been used to evaluate ventilation rates in Swedish housing stock for the purpose of determining pollutant transport patterns (Stymne et al., 1994).

In the field of atmospheric tracing, PFTs have been used to characterize down-valley flow, canyon outflow, and interacting circulations on the lower slopes of the Wasatch Front (Fast et al., 2006). They have also been deployed to evaluate air flow patterns in New York City as part of the Urban Dispersion Program to improve wind station placements, to supplement knowledge of contaminant flow patterns, and to update atmospheric flow models (Watson et al., 2006). PFTs have additionally been used in long-term, large-scale investigations of the transport and diffusion of gases over the Alpine topography in Switzerland (Ambrosetti et al., 1998) as well as to evaluate the accuracy of meteorological air quality models in Washington, DC (Draxler, 1967).

The aforementioned examples of PMCH applications demonstrate the versatility of this compound and show that PMCH may be applied to analyze underground mine ventilation systems and to assist in the remote analysis of airflow patterns during emergencies. Although many applications of PMCH as a tracer have been introduced in various fields, little attention is paid to the actual release mechanism, which is a crucial element of any tracer study. In order to successfully deploy PMCH, the release source must not only be able to perform a controlled release, but it also must withstand ambient environmental conditions, such as dust and water. This paper presents a design for a permeation plug release vessel (PPRV) for PMCH. The PPRV is designed to passively deploy PMCH vapor at constant rate as a function of temperature and plug thickness. Details regarding the design of the PPRV, the development process, and the release rate evaluation are also provided. Underground mining conditions were not replicated in this study to isolate the release rate from being affected by uncontrolled, random variables. This isolation will establish a baseline for the PPRV's performance for further experimentation under different external variables. Future testing at an underground mine will be used to evaluate the ability of the release source to perform under field conditions.

3. Permeation plug release vessel (PPRV)

The basic concept of the PPRV detailed in this study was initially introduced by Brookhaven National Laboratory (BNL). The BNL source has been the predominant means of deployment for PFTs in tracer gas studies. However, limited information is provided regarding the source's operation or replication. Additionally, no advancement of the basic design has been introduced since its inception. In order to provide a cursory understanding of how the PPRV operates, the gas diffusion mechanism must first be discussed.

The controlled release of PMCH is facilitated by the permeability characteristics of silicone rubber. The passage of a gas through rubber-type mediums such as silicone is a well-documented phenomenon that has undergone extensive study for over 50 years (van Amerongen, 1946; Barbier, 1955; Hammon et al., 1977; Stern et al., 1977; Jordan and Koros, 1990; Zhang and Cloud, 2006). In silicone rubber, similarly to other rubber-type polymers, gas diffusion occurs in three distinct steps: solution of the gas molecules on one side of the silicone membrane, diffusion of the gas molecule through the silicone, and evaporation of the gas from the other side (Barbier, 1955; Zhang and Cloud, 2006). This diffusion through a seemingly impermeable medium can be achieved due to the chemical composition of silicone rubber.

Silicone, or polysiloxane, is a name used to define any compound derived from polymerized siloxanes. Polymerized siloxanes are substances whose molecular structure is created by combining monomers into large chains of alternating silicon (Si) and oxygen (O) atoms. The alternating atoms (e.g. Si—O) have either organic groups or hydrogen atoms bonded to the Si atom (Van Reeth and Wilson, 1994; Bondurant et al., 1999; Velderrain and Lipps, 2011). Silicone generally has two methyl groups attached to each siloxane thus producing a polydimethylsiloxane (PDMS) (Van Reeth and Wilson, 1994;