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Study of gas tracers for CO_2 monitoring

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Abstract

Gas tracers have been tested for monitoring and detecting CO_2 displacement in the underground and eventually leakages to the upper layers in geological storage sites. Commonly used tracers are perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6). In Brazil, we are carrying out gas tracers studies in laboratory for further application in field test facilities. These experiments consist of injecting CO_2 with perfluorocarbon (perfluoropropane – PP and perfluormethylcyclopentane – PMCP) at low pressure (ca. 290 psi) in pressurized vessels with different types of sediments and soil samples. After flowing through the sample pores, the tracer is adsorbed into a capillary adsorption tube (CAT) with a specific fiber for perfluorcabon. Then, the tracer is extracted from the CAT through a Thermal Desorption System and subsequently analyzed in a Gas Chromatograph with an Electron Capture Detector (GC - ECD). The objective of these experiments is to evaluate the PFCs as a monitoring tool, analyzing the tracer retention times in different sediments, as well as understanding the CATs adsorption capacity and performance. After laboratory tests, field experiments will be conducted in the course of this project. Several experiments of CO_2 injection and controlled leaks will be developed in shallow vertical wells at the project site as a continuity of the experiments started at Ressacada Farm Site (Florianópolis, Brazil). The project aim is to understand the flow and dispersion of CO_2 in soil and atmosphere simulating an eventual leakage from a geological reservoir using an automated system with a dedicated module for tracers injection into CO_2 stream.

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1. Introduction

Gas tracers are widely used for monitoring purposes in multiple research areas, but its implementation still needs to be proven specifically in the case of CO_2 monitoring in geological storage sites [10, 11]. The method consists basically in the mixture of exotic compounds (tracers composed of extremely fine particles of artificial substances) in the CO_2 injected in order to identify and distinguish it from natural sources of CO_2. In addition it is to evaluate the CO_2 migration in the reservoir and in the adjacent layers.

Common gas tracers used in recent CO_2 monitoring projects of geological storage sites are perfluorocarbons (PFCs) and sulfur hexafluoride (SF_6). According to Hanna [3] PFCs have advantages compared to SF_6, not only because they are detectable at lower concentrations, but also by the fact that several types of PFCs may be used in the same study and detected in a same sample. In other studies on air quality, in which SF_6 and PFC are compared to CO_2 adsorption, PFCs have more representative results than those found with SF_6 [1]. They have lower detection limits and also various types of PFCs may be

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used in the same study and detected in a single sample. Therefore they appear to be a viable alternative as a tool for CO_2 monitoring.

This work will present preliminary results of bench experiments conducted to test the adsorption capacity of CATs, retention time with different soil sediment and its lifetime. In addition, PFCs will also be tested in the field in order to evaluate the CO_2 migration considering the retention due to interactions with the environment.

2. Recent developments on gas tracer for CO_2 monitoring

Several projects are using gas tracers for CO_2 monitoring, among which the most well known benchmarkings are: the research pilot under the sponsorship of the National Energy Technology Laboratory (NETL) in West Pearl Queen (New Mexico, USA); ZERT's (Zero Emission Research and Technology Center) monitoring field lab., in collaboration with the University of Montana; and the Frio Brine Pilot Project, located in Dayton (Texas, USA).

In the West Pearl Queen project 2090 tons of CO_2 were injected in a depleted oil reservoir. A leakage was detected and then monitored using a radial array with 40 CATs, for a period ranging from days to months [11]. The grid initially proposed was composed of six concentric circles spaced by 50 m each, with a 600m diameter total area. The initial monitoring phase was focused on potential sources of leaks and the main objectives of the CATs were to assess the extent of soil that was contaminated, and determine how long this could recover from contamination with the tracer agent. Three types of PFCs were used as tracers. The injection rate was slow (approximately 12 hours for each tracer agent), and each type of PFC was injected separately at an interval of 1 week. For 20 tones of CO_2 injected 500 ml of tracer were introduced. Exposure times were determined according to type of PFC injected and ranged from 6 to 54 days. After this period, the CATs were carefully removed so that no contamination occurred before and after their use. Therefore before inserting them into steel pipes and after the exposure time, the CATs were sealed with rubber stoppers and sent for analysis. The maximum time for switching CATs was no longer than 1 minute and did not occur significant contamination with CO_2 in the atmosphere. Analyses were performed using a Gas Chromatograph (GC) with Electron Capture Detector (ECD) coupled to a Thermal Desorption (TD) [11].

The ZERT study was conducted in the University of Montana campus (Bozeman, USA), an area of approximately 12 hectares in which injections were being performed since 2007 reaching rates of 0.3 ton/day [9]. The tracer injection occurred in two phases: 1) in a first experiment with CO_2 injection in shallow vertical wells done to simulate a point source leakage, which could possibly occur due to failure of a deep well completion. According to Strazisar [10] a distance of 50 meters between the injection and the monitoring wells was established. A total of 3 ml of perfluoromethylcyclopentane (PECH) were injected into the CO_2 stream in a 12 hours period, with a total rate of 800 ml/min; 2) in a second phase, the experiment was conducted in a horizontal well at 2 m of depth. The conceptual model of this experiment considered leakage through fractures and/or faults. The horizontal well was a stainless steel tube with 98 m long and 10 cm of diameter. It was divided into six independent zones delimited by packers but just one of them was used for the tracer experiment. The monitoring grid was established perpendicular to the injection well with monitoring wells 1 meter deep. CATs were exposed at different times: for active monitoring during the injection of 50 mL of tracer and for passive monitoring 6 hours with 200 mL of tracer. NETL laboratories ran CATs analysis using a Thermal Desorption and Gas Chromatography.

In Frio Brine Pilot Project, gas tracers were also used to monitor CO_2 leakage in depleted oil fields. Since 2004 PFCs are being injected to detect CO_2 potential leaks [6]. CATs were installed in 1 meter deep aluminum tubes. Different types of PFCs were separately injected into CO_2 stream over a 20 hours period. CATs were suspended within the aluminum tubes, and when removed from them, immediately sealed to prevent losses between collection and analysis periods. The tubes were removed periodically and sent to the laboratory for Thermal Desorption and Gas Chromatograph.

In Brazil, for the first time, research on CO_2 leakage resorting to gas tracers so far have been run on lab scale, by carrying out lab tests with a especially designed apparatus, customized by CEPAC, for promoting the flow of CO_2 with PFC through porous samples (soil, sand, etc). The purpose of these experiments is to understand the behavior of PFC as a gas tracer and analyze some parameters such as adsorption capacity, CAT's fiber life cycle and retention time. Since 2011 several field experiments of

CO_2 controlled leaks are being developed in shallow vertical wells at Ressacada Site (Florianópolis, Brazil). As a continuity of the studies started at this site, another field experiment is being planned for 2015 in a different area. This project aims to understand the flow and dispersion of CO_2 in soil and atmosphere simulating an eventual leakage from a geological reservoir using an automated system with a dedicated module for tracer injection into the CO_2 stream. This module will prevent possible contamination of medium by tracers. For these field experiments PMCP will be used.

3. Methods and Materials

The experimental set up for laboratory tests will be performed according to the scheme in Figure 1. The equipment was developed by CEPAC and consists of a stainless steel vessel that allow the mixing of the liquid perfluorcarbon with CO_2 The vessel is connected to a 1 m long stainless steel tube with ¼"NPT diameter filled with porous sample (soil, sediment, etc). The CAT's support is connected to the other side of the tube, and consists of a stainless steel vessel in which input has an internal thread for placing and removal CATs and output has a septum for gas sampling during the experiments. The vessel has also an internal hook that remains CATs suspended.

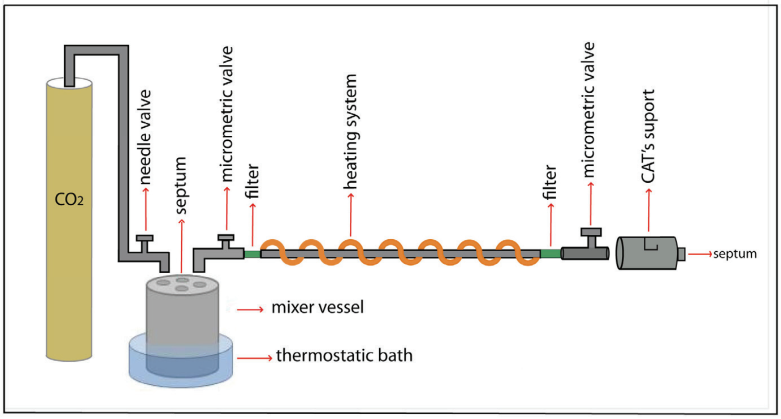

Figure 1: Diagram showing the experimental apparatus developed to test gas tracers for CO_2 monitoring.

The capillary tubes were developed by Perkin Elmer® with a specific fiber for PFC's adsorption (Carbosieve® S-III) and preconditioned by the supplier. The tubes are made of glass and stainless steel (Figure 2) especially to test the materials and enhance the understanding about the best performance for each one on field experiments.

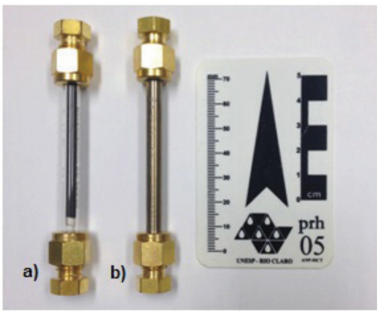

Figure 2: Capillary Adsorption Tube (CAT) made of a) glass and b) stainless steel from Perkin Elmer® with Carbosieve® S-III fiber.

The lab tests consist in introduce 2 different standard's concentration of the tracer (200ppt, 100ppt) and forcing the flow through soil sediment per 1 hour. After each run the CATs were removed analyzed in a Thermal Desorption (Shimadzu®, Model TD20) coupled in a Gas Chromatograph (Shimadzu®, Model GC 2010). The method performed in TD was set to sampling with a 60ml/min flow for 10 minutes and a trap heat temperature set in 280°C for 5 minutes. The total duration of each run was 20 minutes. For GC-ECD the method used TD as an injector and a Supel-Q Plot® Column with 30 m leght and 0.53 mm diameter. The following configurations were established: Column temperature = 150°C; ECD temperature = 200°C; N2 make up flow =25mL/min; Runtime =10 min.

For the field experiment, the system will be configured with a syringe pump whereby liquid perfluorcabon volumes are pre-set before introduction into a vaporizer. Tracers will be monitored in shallow wells built exclusively to host the CATs in a rectangular grid over the experimental area. PFCs must be injected into CO_2 stream from a single input flow distribution, totally independent of the main CO_2 current input system, in order to avoid contamination. This process should be slow and depending on the injection rates it can take 6 to 12 hours. The option to use only a PFC type for each injection campaign prevents system's contamination with other tracers. After finishing the injection, CATs exposure time will be approximately 24 hours.

4. Results

The results of the first lab experiments are shown in Figure 3. It is possible to see the PP peaks (green arrows) in different concentrations: a) 100ppt; b) 200ppt.

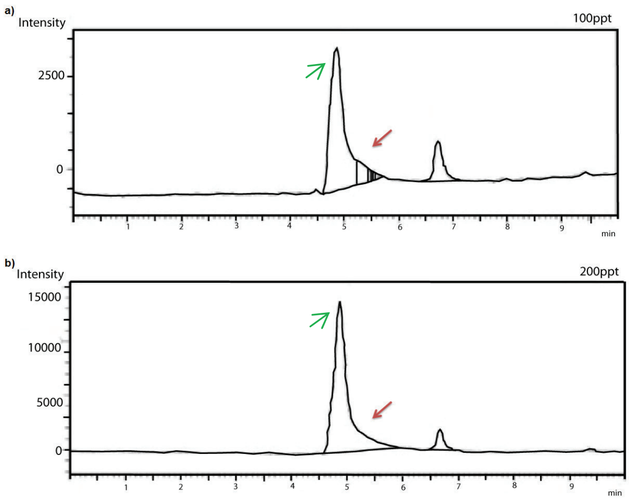

Figure 3: Chromatograms result from lab experiments in: a) peak with 100 ppt PP standard and b) peak with 200 ppt PP standard

The shape of perfluoropropane peaks show a tail due (red arrows) to the use of Supel-Q Plot® Column chosen for this study, as described above. The CATs analyzed showed very close retention times for both concentrations, with 4.864 minutes for 100 ppt standard and 4.873 minutes for 200 ppt standard. The peak intensity for 100 ppt standard showed a lower value when compared to the 200 ppt standard. These readings are consistent with the expected behavior, since the 200 ppt standard, with higher concentration should have a higher intensity than the 100 ppt's.

5. Conclusions

Bench experiments allowed to observe that PP can be used as a gas tracer for laboratories tests, but it is important to emphasize that it is extremely necessary to work in an inert atmosphere to avoid any contamination with the medium. We can also conclude that ECD is a very sensitive detector but for meaningful results we suggest working with ppt concentrations for better peaks resolution and interpretation.

The next field injection campaign will be held in 2015 and the acquired data is expected to provide: (1) understanding of the CO_2 subsurface movement and (2) validation of the selected perfluorcabons as tracers for CO_2 monitoring.

Finally both laboratory and field data of perfluorcabon tracers will be compared with other monitoring tools in order to improve the comprehension about these studies.

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