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# Strategies for detection and monitoring of CO<sub>2</sub> leakage in sub-seabed CCS

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#### Abstract

Carbon dioxide (CO<sub>2</sub>) capture and storage (CCS) in sub-seabed geological formations is currently being studied as a potential option to mitigate the accumulation of anthropogenic CO<sub>2</sub> in the atmosphere. For the verification of CO<sub>2</sub> storage integrity in the sub-seafloor, developments of the techniques to detect and monitor CO<sub>2</sub> leaked from the seafloor is vital. Seafloor-based acoustic tomography is a technique that can be used to detect emissions of liquid CO<sub>2</sub> droplets or gas CO<sub>2</sub> bubbles from the seafloor. An in-situ pH/pCO<sub>2</sub> sensor can provide rapid and high-precision measurements in seawater, and is therefore able to detect pH and pCO<sub>2</sub> changes caused by the leaked CO<sub>2</sub>. An autonomous underwater vehicle (AUV) installed with the pH/pCO<sub>2</sub> sensor provides an automated observation technology that can detect and monitor CO<sub>2</sub> leakage from the seafloor. By towing a multi-layer monitoring system consisting of a number of pH/pCO<sub>2</sub> sensors and transponders, the dispersed area of leaked CO<sub>2</sub> and depth sensors, collecting intermittently a CTD-like data as it ascends and descends. Hence, CO<sub>2</sub> leakage from the seafloor is detected and monitored as follows. Step 1: detect the CO<sub>2</sub> leakage by the seafloor-based acoustic tomography. Step 2: map the distribution of the leakage points using the pH/pCO<sub>2</sub> sensor installed on the AUV. Step 3: monitor the impacted area using a remotely operated underwater vehicle or the automatic elevator or by towing the multi-layer monitoring system.

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## 1. Introduction

The global warming issue is influencing international energy and environmental policies, and is so serious a problem that the whole human life may be altered. Therefore, it is necessary to collect carbon

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dioxide (CO<sub>2</sub>) generated by the combustion of fossil fuels before it is discharged into the atmosphere and then to isolate this CO<sub>2</sub> from the atmosphere a long time. CO<sub>2</sub> capture and storage (CCS) in sub-seabed geological formations is currently being studied as a feasible option to mitigate the accumulation of anthropogenic CO<sub>2</sub> in the atmosphere. As a result, on-site verification experiments for sub-seabed storage of CO<sub>2</sub> have recently been conducted. In implementing sub-seabed CCS, monitoring the impact of the sequestered CO<sub>2</sub> on the ocean environment is highly important. In particular, monitoring is needed to establish that there is no leakage of CO<sub>2</sub> sequestered in the sub-seabed; and if leakage does occur, detection of the leakage point and monitoring of CO<sub>2</sub> behavior is indispensable for assessing the impact on the ocean environment. However, observation technologies that can realize these objectives are not yet established. Therefore, in order to move forward with sub-seabed CCS, the development of new costeffective technology is necessary for monitoring the diffusion behavior of leaked CO<sub>2</sub> into the ocean, as well as for indentifying CO<sub>2</sub> leakage points and monitoring of CO<sub>2</sub> leakage. We have been developing efficient observation equipment and technologies that can observe the diffusion behavior of low pH/high CO<sub>2</sub> seawater in the ocean, and we have verified their effectiveness through sea-going observation [1], [2], [3].

#### 2. Detection and monitoring technologies

#### 2.1. Seafloor-based acoustic tomography

The ocean acoustic tomography [4] was then applied as the coastal acoustic tomography; the 3D distribution of the seawater temperature together with its current velocity in a wide area (such as the spatial scales from several kilometers to several tens of kilometers) can be obtained by conducting an inverse analysis of the travel times of sound propagating between multiple acoustic transponders that have been arranged to cover the target coastal area [5]. In the general-purpose ocean acoustic tomography, sound is transmitted from one acoustic transponder (A) to another acoustic transponder (B), and its travel time is measured with high precision. Suppose that the travel time from A to B and vice versa are obtained in a field observation. Since the speed of sound in seawater depends on its temperature, salinity, pressure and current, the sum of these travel times provides information about the speed of sound in the seawater's physical properties such as temperature, salinity and current, which are related to density turbulence and influence the speed of sound, can be obtained by measuring the travel times of sound in the ocean acoustic tomographic techniques.

The key in this research is that the measurement principle of ocean acoustic tomography can be used to measure the density turbulence that affects the travel time of sound waves propagating between two acoustic transponders. In this regard, seafloor-based acoustic tomography was developed for detecting  $CO_2$  leakage from the seafloor (Figure 1a). If  $CO_2$  leakage occurs somewhere between any two seafloor-mounted acoustic transponder pair, the induced currents that flow upward from the seafloor (Figure 1b), acoustic scattering (due to the  $CO_2$  issuing as gas bubbles and/or liquid droplets) or temperature fluctuations as well as density turbulence influence the travel time of sound propagating between the two acoustic transponders, and thus the leakage phenomena will be detectable. When multiple acoustic transponders are mounted on a seafloor, the measurements can be conducted for every pair of transponders, enabling to detect  $CO_2$  leakages over a wide area (Figure 1c). Since the travel time measurements of sound is critical in the observation, the clock on each acoustic transponders were equipped with synchronized rubidium atomic clocks in our observation. The effectiveness of such measurements can be improved further in the future if the stations are connected in a network and are controlled

intensively as shown in Figure 1c. Furthermore, a centralized control of this system and monitoring of the data on land enable the real-time monitoring of  $CO_2$  leakage.



Fig. 1. Application of seafloor-mounted acoustic tomography technology to detection of CO<sub>2</sub> leakage. (a: Photo of prototype of acoustic tomography measurement, c: Deployment of detection system at the CO<sub>2</sub> storage site)

## 2.2. In-situ pH/pCO2 sensors

A newly developed of in-situ pH/pCO<sub>2</sub> (partial pressure of CO<sub>2</sub>) sensor [6], [7], which uses an ionsensitive field effect transistor (ISFET) as a pH electrode and a chloride ion-selective electrode (Cl-ISE) as a reference electrode, was employed in this research. An ISFET is a semiconductor made of p-type Si coated with SiO<sub>2</sub> and Si<sub>3</sub>N<sub>4</sub> as the gate insulator surface that is the ion sensing layer [8]. A Cl-ISE is a pellet made of several chloride materials and, in an aqueous solution, responses to chloride ion, which is a major element in seawater. The electric potential of a Cl-ISE shows high stability in the seawater because it has no electrolyte solution part in the assemblage. The particular in-situ pH sensor has a quick response time (within a few seconds), high accuracy ( $\pm 0.005$  pH) and its depth rating is 6000 meters depth. The pH sensor was then applied as a basis to develop the pCO<sub>2</sub> sensor for in-situ pCO<sub>2</sub> measurement in seawater. Both the pH electrode and the Cl-ISE of the pH sensor are sealed within a gas permeable membrane filled with an inner solution in order to measure pCO<sub>2</sub> in seawater. The pH sensor can measure changes in pCO<sub>2</sub> from changes in the pH of the inner solution, which is caused by CO<sub>2</sub> gas permeation through the membrane. The photographs shown in Figure 2 are an overview of the in-situ pH/pCO<sub>2</sub> sensor and a close view of the pH and pCO<sub>2</sub> electrodes. An electric circuit board of pH and pCO<sub>2</sub> with data logger and lithium-ion battery are housed in a pressure vessel.

#### 2.3. AUV installed with chemical sensors

An autonomous underwater vehicle (AUV) is useful for narrowing the search area in locating  $CO_2$  leakages from a wide area on the seafloor. An AUV is a marine robot capable of operating autonomously if the direction and the depth of navigation are set in advance. The AUV used for narrowing the  $CO_2$  leakage point in this paper was REMUS 100, a small and lightweight AUV capable of navigating long distances, which is the result of research and development at Woods Hole Oceanographic Institution (WHOI). Various in-situ chemical sensors have been installed on REMUS 100 as the platform, including the above-mentioned pH and pCO<sub>2</sub> sensors, the oxygen sensor, chlorophyll-a sensor, turbidity mater, salinity sensor and temperature sensor in the main body. In this study, in addition to the above-mentioned pH/pCO<sub>2</sub> sensor, an oxidation-reduction potential (ORP; A platinum electrode as a working electrode and the CI-ISE as a reference electrode are employed in this ORP sensor) sensor was installed in the nose-cone tip of the AUV (Figure 3). Furthermore, two acoustic doppler current profiler/doppler velocity loggers and the side-scan sonar were also equipped.



Fig. 2. In-situ pH/pCO2 sensor



Fig. 3. AUV installed with chemical sensors

#### 2.4. Towing multi-layer monitoring system

After the identification of  $CO_2$  leakage points following the detection of leakage of the sequestered  $CO_2$ , a long-term monitoring of the issuing and the diffusive behavior of the leaked  $CO_2$  is necessary. The multi-layer towing monitoring system (MLTMS) was developed in order to conduct periodic monitoring of the diffusive behavior of leaked  $CO_2$  [2]. This system can observe the issuing and dissolution behavior of leaked  $CO_2$  by collecting the reliable data in real time, which is accomplished by using a research vessel to tow a towing line equipped with multiple observation instruments, such as the above mentioned pH/pCO<sub>2</sub> sensor, a depth sensor and a sub-navigation device. Figure 4 shows a schematic drawing of the MLTMS. To minimize acoustic noise from the observation ship, a submersible towing unit equipped with a super short baseline (SSBL) sub-sea navigation system transducer, is kept it away from the ship. This method improved much the precision of the sub-navigation, so enabling to use a general-purpose work ship in the observation. In operation at sea, several data transponders with in-situ chemical sensors are installed on the towing line attached to the towing unit (the sinker at the end of the line weights about 2 tons). The MLTMS consists of the following devices (Figure 4).

1. Submersible towing unit (data/position receiver)

A submersible towing unit, equipped with an SSBL transducer, SSBL system, compass, clinometer, pressure gauge and sea anchor, is towed below the sea surface by a research vessel, and performs acoustic communication with the underwater transponders. The data from each transponder are forwarded to a host CPU on the ship through a wireless modem on the surface unit.

2. Transponder unit (data/position transmitter)

Through acoustic communication with the towing unit, in-situ data such as water depth, pH,  $pCO_2$  and position are transmitted to the submersible towing unit. A deep-sea camera and water sampler can be attached to the unit and controlled via the transponder.

3. Onboard control unit (data/position display and sampling/camera controller).

The onboard control unit consists of a host CPU, an operating software, a differential-GPS and a wireless modem. Using the data forwarded from the submersible towing unit, the underwater position, water depth and in-situ measurement data collected by each underwater transponder are displayed, and ON/OFF control commands for the deep-sea camera and water sampler are to be transmitted from on board.

## 2.5. Seafloor-mounted automatic elevator

In a long-term continuous monitoring of the diffusive behavior of leaked  $CO_2$  at the seafloor, it is important to obtain continuous observation data, both temporally and spatially. The seafloor-mounted automatic elevator was developed to monitor a spatiotemporal change of pH and pCO<sub>2</sub> in seawater in case the CO<sub>2</sub> leakage were detected [2]. Photographs in Figure 5 represent the overview of the automatic elevator (a), and the close view of the observation buoy (b) and the sea winch (c). The observation buoy with the pH/pCO<sub>2</sub> sensor and the depth sensor is attached on the top of a cable to be winded by the sea winch, where the length of the cable is 300 meters at maximum. The winch lets out the cable to a preset length at a preset time, and then the buoy ascends. Thereafter, when the winch rolls in the cable, the buoy descends. The in-situ sensors conduct the continuous measurements of each parameter during ascent and descent of the buoy. The series of action can be repeated, following the prefixed schedule which is to be programmed through an onboard PC. In this way, a continuous monitoring of diffusive behavior of leaked  $CO_2$  is possible by installing the autonomous elevator on the seafloor of the suspected area or detected point of  $CO_2$  leakage.



Fig. 4. Schematic drawing of TMLMS.



Fig. 5. Seafloor-mounted automatic elevator. (a: Overview of automatic elevator, b: Observation buoy ( $pH/pCO_2$  and depth sensors are installed inside of the buoy), c: Sea winch)

## 3. Proposal of strategy for detecting and monitoring of CO<sub>2</sub> leakage in sub-seabed CCS

Combining the developed and introduced equipment presented in this paper, the detailed procedure for the detection and monitoring of  $CO_2$  leakage in sub-seabed CCS can be proposed as follows.

- 1. CO<sub>2</sub> leakage is detected with the multiple seafloor-mounted acoustic tomography transponders covering a wide area of seafloor on the seabed CO<sub>2</sub> storage region.
- If CO<sub>2</sub> leakage from a seafloor is detected, the automatic mapping could be performed with the AUV equipped with an in-situ pH/pCO<sub>2</sub> sensor and a side-scan sonar, thereby, narrowing the leakage point.
- 3. After narrowing the leakage point, the exact leakage site could be located through the visual observation with an conventional remotely operated vehicle (ROV), thus establishing the space and time extension of the  $CO_2$  leakage.
- 4. After identifying the leakage point, the issuing and diffusive behavior of the CO<sub>2</sub> leakage could be observed and monitored. The periodic observations are recommendable for focused surveillance of the behavior of leaked CO<sub>2</sub> near the leakage point. The diffusive behavior of leaked CO<sub>2</sub> is periodically monitored by using ROV and TMLMS.
- 5. The continuous observation is applicable to a long-term monitoring of the changes in issuing and diffusive behavior of  $CO_2$  leakage near the leakage point. The diffusive behavior of leaked  $CO_2$  is monitored continuously with the automatic elevator mounted on the seafloor.

The outline of the steps of detecting and monitoring  $CO_2$  leakage in sub-seabed CCS is illustrated in Figure 6. By applying some or all the observation technologies presented in this paper, the  $CO_2$  leakage in a sub-seabed CCS can be identified and monitored reliably, and the diffusive behavior of the  $CO_2$  can be monitored in the marine environment. Such technologies for detection and monitoring of  $CO_2$  leakage will be vital in development and implement of the sub-seabed CCS technology.



Fig. 6. Strategy for detection and monitoring of CO2 leakage in sub-seabed CCS. (Numbers correspond to those in Chapter 3)

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