

## Development of Dissolved Methane Sensor for Methane Leakage Monitoring

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For the future methane hydrate production in Japan a methane sensor will be used for leakage monitoring to sense change in the concentration in seawater. The requirements are: use in great depth, long-term deployment, real-time monitoring and quick response.

A commercially produced dissolved methane sensor (known as the METS sensor from Franatech GmbH (Germany)) provides the basis to satisfy such requirements. Research for development the sensor for that purpose has been conducted since 2004. This paper summarizes the methodologies of development and the specifications of the resulting prototype.

First, in the presented study, as a result of improvement of the mechanical structure of the METS sensor, the response time to dissolved methane concentration changes has been successfully shortened. Also as a result of enlargement of the membrane, the sensor output has been more stabilized through reduction of the influence of water turbulence. Thus, utilization as a methane leakage alarm sensor is now promising. Additionally, the influence of the water flow rate before the membrane was evaluated with the objective of looking for solution for reducing the resistance of boundary layer that influences the response time. Now, the METS sensor has been equipped with a water pump which can supply a constant flow-rate water in order to have a constant response time.

Second, a methodology for the reduction of dissolved oxygen dependability has been established, since the dissolved methane concentration obtained by the METS sensor depends under circumstances on dissolved oxygen in the seawater. Therefore, the METS sensor could be deployed in the future at sites where the oxygen level varies with time, as well as at different locations with differing levels. In the course of the development, the behavior of the semi-conductor detector was evaluated systemically by varying both dissolved methane and oxygen concentrations. From the evaluation, a new formula for calculating dissolved methane concentration is established in order to reduce the dissolved oxygen dependability.

Finally, two new methodologies (pre-aging process and self-calibration function) to allow the METS sensor to use for long-term monitoring have been established. One critical reason of the instability of the METS sensor is due to the behavior of the semi-conductor detector. Typically, in continuous use, after burning-in, the resistance of the detector to a constant methane concentration increases within 2 to 6 weeks, then stabilizes. To compensate this, a pre-aging process has been established. Since the existence of oxygen inside semi-conductor causes instabilities of the semi-conductor performance, the semi-conductor detector is left in a gas-tight chamber filling with nitrogen in order to deplete oxygen existing inside semi-conductor before assembling. For this, the METS sensor can be used without instability due to the semi-conductor's characteristics. In addition to the pre-aging process, the self-calibration function has been established. In case that the sensor output becomes unstable in long-term deployment, the semi-conductor detector built in the METS sensor is heated at a specific temperature, and then the characteristic of the semi-conductor detector will recover to the initial one.

Though that process, an improved METS sensor to satisfy the above mentioned requirements was made as a prototype. It is now waiting for performance verification in an actual sea where dissolved methane is highly concentrated.

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