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EDITED BY
Anna Stoppato,
University of Padua, Italy

REVIEWED BY
Sukru Merey,
Batman University, Türkiye
Yanghui Li,
Dalian University of Technology, China

*CORRESPONDENCE
Shuangxing Liu,
shuangxing_liu@outlook.com

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A review on the methane emission detection during offshore natural gas hydrate production

Shuangxing Liu[1]*, Ming Xue[1], Xiangyu Cui[1] and Wenzheng Peng[1,2]

[1]State Key Laboratory of Petroleum Pollution Control, CNPC Research Institute of Safety and Environmental Technology, Beijing, China, [2]China University of Petroleum Beijing, Beijing, China

Due to the high energy density, large potential reserves and only release CO_2 and water after combustion, natural gas hydrate (NGH) is considered as the most likely new clean energy source to replace traditional fossil energy (crude oil, natural gas, *etc.*). However, unlike the exploitation of traditional fossil energy, the essence of natural gas hydrate exploitation is to induce the production of methane by artificially decompose the natural gas hydrate and to simultaneously collect the generated methane. Because of the uncontrollable decomposition, the methane percolation and the gas collection efficiency, methane emission is inevitably occurred during natural gas hydrate exploitation, which could significantly affect the environmental friendliness of natural gas hydrate. In this review, the methane emission detection was divided into three interfaces: Seafloor and sediment, seawater, atmosphere. Meanwhile, according the summary and analysis of existing methane emission detection technologies and devices, it was concluded that the existing detection technologies can identify and quantify the methane emission and amount in the three interfaces, although the accuracy is different. For natural gas hydrate exploitation, quantifying the environmental impact of methane emission and predicting the diffusion path of methane, especially the methane diffusion in strata and seawater, should be the focus of subsequent research.

KEYWORDS

natural gas hydrate, offshore, methane, detection, monitoring system

1 Introduction

As the demand of energy kept increasing and the environmental pollution became more serious, fossil energy, including oil, coal, and natural gas were unable to meet the requirements of energy amount and environment protection. Therefore, the development of clean-alternative energy attracted much attention in recent years (Khare et al., 2016; Olabi, 2017; Liu L. et al., 2019). However, common renewable energies, including wind energy, solar energy, biomass energy, nuclear energy and ocean energy were constrained by geographic conditions, infrastructure or politician issues (Twidell and Weir, 2015; Bhattacharya et al., 2016; Quaschning, 2016). More importantly, the capacity and growth rate of renewable energies were much lower than the increase in energy consumption according to the report published by International Energy Agency (IEA) (IEA, 2019).

Natural gas hydrate (NGH) is an ice-like crystalline compound formed by natural gas (mostly methane) molecules and water molecules (Pearson et al., 1983; Li et al., 2012a; Zhao et al., 2015; Khan et al., 2016). Since the crystal structure and unit cell of NGH were determined and published by Claussen and Von Stachelberg in 1949 (Claussen, 1951a; Claussen, 1951b), the research on the physical and chemical properties of NGH continues. Commonly, the empirical formula of NGH can be expressed as $(CH_4)_8(H_2O)_{46}$ (Dharmawardhana et al., 1980; Stackelberg, 1949; Clennell et al., 1999; Takeyaa et al., 2006; Li et al., 2012b), the crystal structure of NGH was considered to be in three types (sI, sII and sH) (Tse, 1990; Matsumoto et al., 2000; Kumar et al., 2008). Since the naturally-produced NGH was detected in the permafrost of northern Siberia, Messoyakha oilfield in 1965 (Hitchon, 1974; Makogon and Omelchenko, 2013), significant amount of NGH reservoirs have been discovered and exploited worldwide (Dickens et al., 1997; Collett, 1999; Shukla et al., 2019). Although NGH is considered to be an efficient and clean energy, the methane escaping into the seawater and air during production can seriously impact on the environment (Yang L. et al., 2019). Due to its molecule structure, methane is one of the most potent greenhouse gases (GHGs) (Holmes et al., 2017; Krapivina et al., 2017; Tutak and Brodny, 2017). Therefore, only by preventing or reducing the methane emissions during the production of NGH can NGH truly become a clean energy.

Currently, many reviews were conducted by different researchers and groups over the world, including the investigation of NGH's fundamental properties (e.g. structure, composition, formation and decomposition) (Kvenvolden, 1995; Bavoh et al., 2019; Lijith et al., 2019; Yang M. et al., 2019), the exploration and production of NGH reservoirs (Lee et al., 2011; Li et al., 2016; Acharya et al., 2019; Ke et al., 2019; Li et al., 2019), the utilization and potential of NGH (Kvenvolden and Lorenson, 2001; Koh and Sloan, 2007; Demirbas et al., 2016). Meanwhile, as the development of NGH production pilot worldwide, many researchers have studied the environmental impact of NGH exploration and production (Liu S. et al., 2019; Riley et al., 2018; Stanković et al., 2017; Kvenvolden and Barnard, 1982; Ye et al., 2018. However, few reviews on the study of methane emission detection during the exploitation of NGH reservoirs. Therefore, in this review, we summarized and strived to review holistically the studies and progresses on methane emission detection during NGH production process from the following aspects, including current issues, seafloor and sediment detection, seawater detection, atmosphere detection, and challenges. We hope to provide more information of how methane emitted from NGH and how to detection the methane emission during NGH production. Moreover, we also put forward some suggestions on the establishment of methane emission monitoring system and on the methods for methane emission reduction during NGH production.

2 Existing issues

2.1 Environmental risks during NGH production

Environmental impact is a potential risk which cannot be ignored during the production of NGH. Firstly, the dissociation of NGH could lead to significant drilling risks, resulting in gas leakage, blowout, collapse, wellbore instability or failure (Islam, 1991). Since the decomposition of hydrate is endothermic process and its formation is exothermic process, the temperature gradient in the wellbore and formation could change significantly during the production process, which could possibly lead to stability reduction. Meanwhile, the CH_4 concentration in pore water increases as the NGH decomposition process proceeds, which led to an increase in sulphur content and increase the equipment corrosion risk (Song et al., 2016). Secondly, the dissociation of NGH deposits could trigger large underwater landslides on continental margins, which could destroy offshore mining equipment, endanger the lives of operators, and pose a hazard to coastal areas (Locat and Lee, 2002; Collett et al., 2014). Besides, the uncontrollable dissociation of NGH could cause methane emission and significantly impact on the atmospheric environment. The atmospheric record of ice cores during the Pleistocene suggests that the increase of CH_4 in the atmosphere is mainly due to the release of NGH by dissociation (Maslin et al., 2004; Sun et al., 2019).

In essence, the NGH production was to artificially induce the decomposition of the NGH (e.g., hot water injection, pressure reduction, chemical injection, direct grinding, *etc.*), and then collect the methane generated during decomposition process. Therefore, the stability of NGH layers would be reduced while the production proceeds (Maslin et al., 2010). Meanwhile, since the hydrate layer and sediment were integrated in structure at NGH reservoirs, the decrease of stability of hydrate layer will lead to the decrease of structural strength of sediment layer, resulting in the deformation of seafloor and the occurrence of major disasters such as submarine landslides, methane escape, earthquakes and tsunamis.

2.2 Limitation of current monitoring system

With the development of research and the progress on technologies/equipment, many countries engaged in NGH research and exploration had carried out field test production, including Canada, United States, Japan and China (Li et al., 2018) (Table 1).

In these field tests, environmental monitoring had been attached great importance, and monitoring systems suitable for each test`s production characteristics have been established (Figure 1). Atmospheric component monitoring, wellbore leakage monitoring, underwater sensors, underwater/submarine robots, non-contact detection and other technologies were applied and validated in these field tests.

During 2011 to 2017, the China Geological Survey (CGS) launched a filed trial of NGH production at Shenhu area, South China Sea. In this field test, new submarine technologies, such as swath bathymetry, three-dimensional seismic data, side-scan sonar, and AUVs (He et al., 2018), as well as numerical simulation tools (Shi et al., 2019), were utilized for the establishment of a "four-in-one" (atmosphere, seawater column, seafloor and underground) comprehensive environmental monitoring system Figure 1A (Li et al., 2018; ye et al., 2018).

In 2008, the Gulf of Mexico Hydrates Research Consortium designed and implemented the Monitoring Station/Seafloor Observatory (MS-SFO) (Majumdar and Cook, 2018; Moore et al., 2022), which was a seafloor observatory network with the purpose of monitoring gas hydrate-bearing sediment dynamics the Woolsey Mound in MC118. The seafloor observatory consists of seismic-acoustic receiving arrays, geochemical arrays in bottom water column and upper sediments, micro-biologic sensors, and s series of arrays: Horizontal Line Array (HLA), Vertical Line Array (VLA), Chimney Sampler Array (CSA), Pore-fluid Array (PFA), and Benthic Boundary Line Array (BBLA), *etc.*

Japan`s Research Consortium for Methane Hydrate Resources conducted a series of studies to develop environmental monitoring technologies for the NGH production field test since 2001. Besides, these technologies, which mainly included sensors (e.g., methane sensors, seafloor deformation sensors, biosensors), integrated environmental monitoring system, and auxiliary devices (e.g., power system, electric cables, *etc.*), were applied and verified in the world's first depressurization method to exploit offshore NGH

TABLE 1 NGH production field tests.

Year	Location	Method	Duration	Amount/ m^3	Remark
2002	Mackenzie Delta, Canada	Heating	5 d	516	The world's first field test of offshore NGH exploitation, in order to test technical feasibility and investigate potential environmental risks
2007	Mackenzie Delta, Canada	Depressurization	12.5 h	830	
2008	Mackenzie Delta, Canada	Depressurization	6 d	13,000	
2011	Permafrost area of Qilian Mountains, Qinghai, China	Depressurization, Heating	101 h	95	A field test of onshore NGH exploitation in plateau area, meant to investigate the feasibility of large-scale exploitation and evaluate the value of hydrate resources
2016	Permafrost area of Qilian Mountains, Qinghai, China	Depressurization	23 d	1,078	
2012	North Slope of Alaska, United States	CO_2 replacement, Depressurization	30 d	24,000	Close to existing oil and gas producing areas, to verify the feasibility and safety of permafrost hydrate exploitation
2013	Nankai trough, Japan	Depressurization	6 d	119,000	Cooperated with Canada, the world's first field test for large-scale production, and the first multi-interface monitoring system was established
2017	Nankai trough, Japan	Depressurization	12 d	35,000	
2017	Nankai trough, Japan	Depressurization	24 d	200,000	
2017	Shenhu area of South China Sea, China	Formation fluid extraction	60 d	309,000	The largest field test of offshore NGH exploitation in scale and output so far, meant to verify the safety and controllability under large-scale exploitation scenario. It was the preliminary preparation for commercial exploitation
2020	Shenhu area of South China Sea, China	Depressurization	30 d	860,000	

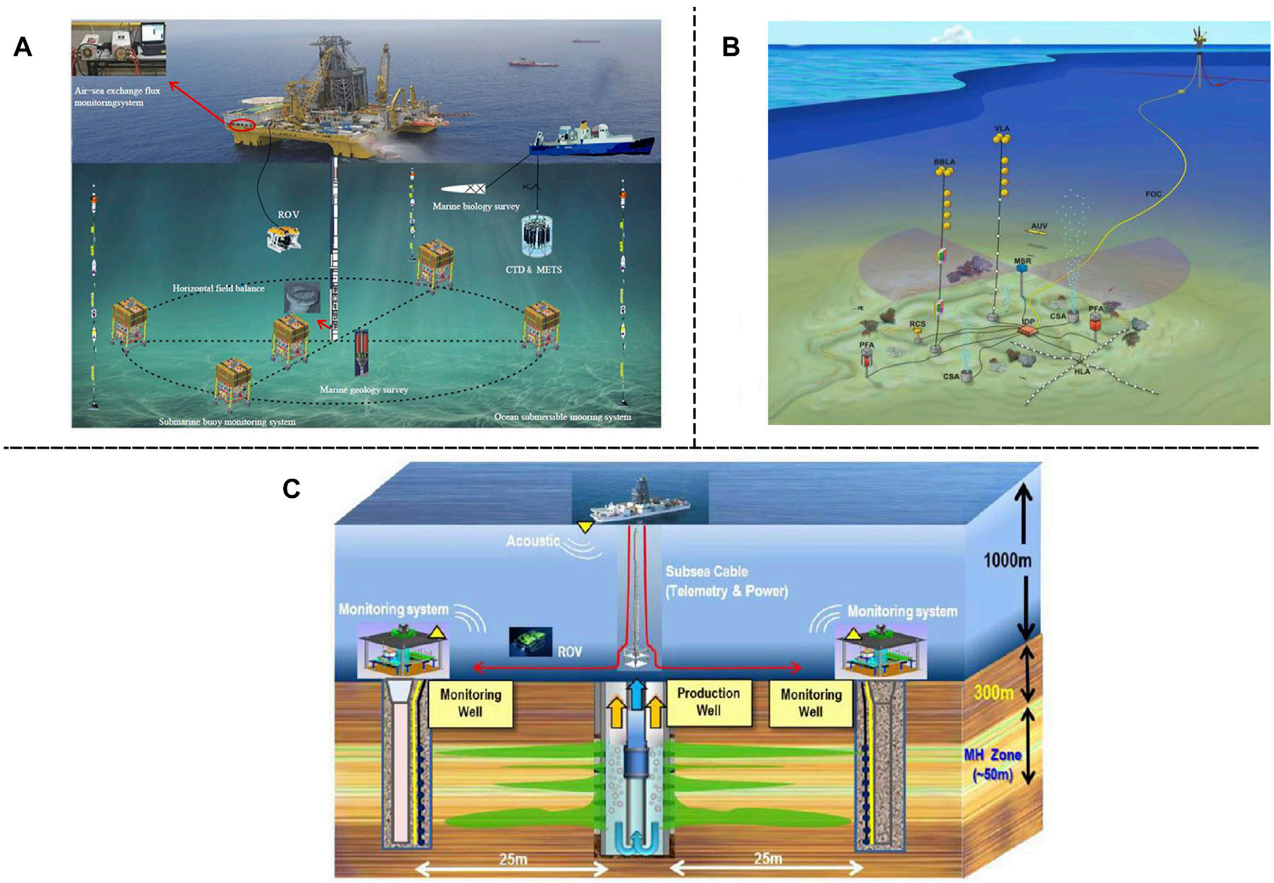

FIGURE 1
Current monitoring systems for NGH field test. Image **(A)** "Four-in-one" environmental monitoring system employed during South China Sea NGH production field test in 2017 (Li et al., 2018). Image **(B)** illustration of the seafloor observatory at the Woolsey Mound (Mississippi Canyon Lease Block 118, MC118) in 2012 (Macelloni et al., 2012). Image **(C)** production and monitoring systems at Nankai Trough in 2013 (Chee et al., 2014).

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TABLE 2 Detection methods for seafloor and sediment.

Method	Mechanism	Advantages	Disadvantages	Application	Optimization
Non-explosive seismic reflection	Using non-explosive elements to produce non-pulsed waves, which are received by the detector	Environmental friendly, continuous and real-time monitoring of both formation and gaseous methane	Small detection depth, bad resistance to disturbance	Nankai trough, Japan	Enhance the anti-jamming ability of detector
Underwater optical observation	Using optical equipment to directly observe the surface of hydrate or sediment	Intuitive, fast, continuous	Unable to quantify the amount of gas emitted and analyze the composition of the gas	Mackenzie Delta, Canada	Enhance the resolution and observation range
				Nankai trough, Japan	
				Shenhu area of South China Sea, China	
Sub-bottom profiler	Send sound waves underwater and receive feedback	High resolution, wide range and continuous monitoring	Unable to detect gaseous methane	None	Enhance the resolution

reservoir in 2013, Nankai trough, Japan (Fujii et al., 2015; Yamamoto, 2015).

In NGH production field tests to date, rigorous monitoring systems had been deployed and no large-scale methane leakage had been reported. However, due to the greater hazards of geological disasters, the focus of monitoring systems was on the changes of sediment stability and formation structure. The methane leakage detection and monitoring were realized by placing sensors in seawater at different depths. This method shown the advantages of low cost, accurate data, short response time and strong reliability, but it also shown a small monitoring range and significantly affected by seawater flow. Therefore, continuously developments on new monitoring technologies for different monitoring scenarios were still necessary, to achieve methane emission detection over a wider area.

3 Methane emission detection technologies

In the process of NGH production, methane exists in three layers: the seafloor and sedimentary layer, seawater, and atmosphere. Since the occurrence state of methane, media, type of disturbance, temperature and pressure conditions in these three scenarios are significantly different, the methane emissions detection techniques need to be selected according to the differences in utilization scenarios.

3.1 Seafloor and sediment

In seafloor and sediments, free gaseous methane exists in porous media composed of argillaceous silt, the contact detection methods are not feasible. Meanwhile, since the muddy silty sand layer existence in deep water, and compared with onshore strata, the muddy silty layer has the characteristics of weak cementation and low strength, which makes conventional geophysical detection methods unable to be applied. Due to their characteristics, sound wave detection, seismic reflection, underwater optical observation and other technologies shown the ability to complete the detection of subsea and sedimentary methane emissions (Table 2).

3.1.1 Non-explosive seismic reflection

Seismic reflection technology had developed as a method to image subsurface structures, especially in the oil and gas exploitation industries. It is possible to identify sedimentary structures from the reflection configuration and faults by offsetting the reflections on the seismic reflection profiles (Tsuru et al., 2018). Commonly, explosives were utilized as the energy sources to generate pulse waves with high sound pressure. However, the high sound pressure generated by explosive (more than 160 dB in the frequency range below 400 Hz) could cause serious damage to aquatic mammals and fish and threaten their lives (Hatakeyama et al., 1997). In this situation, non-explosive energy sources, including underwater speaker (UWS), low-power air gun, electrical transmitter and mechanical shock were utilized on marine geological prospecting. These non-explosive sources generate non-pulse waves (electrical transmitter could generate both pulse and non-pulse waves) with low sound pressure over a certain period of time (lower than 130 dB in the frequency range of 100–1,000 Hz) (IAGC, 2002), and it is possible to conduct seismic surveys with a relatively low environmental impact on marine ecosystems.

Since offshore NGH layers are usually shallowly buried and the overlying layers are not as dense as onshore strata, high-resolution structural profiles could be obtained using non-pulsed waves, and the differences in wave velocities in different regions can be obtained to determine the accumulation of gaseous methane. These studies had been confirmed in a study by Japanese researchers (Tsuru et al., 2019). Non-explosive source detection could be used as a safe and low environmental impact detection method to continuously and real-time detect the accumulation and distribution of gaseous methane in seafloor and sedimentary layers.

3.1.2 Underwater optical observation

Unlike onshore reservoirs, offshore NGH reservoirs are covered with seawater, which is transparent and makes direct observation with optical equipment possible. The keys to underwater optical observation is optical receiver. Since the light propagation is more complex in a seawater environment, the light received by the optical receiver has three parts: the imaging beam reflected from the target, absorbed by the water medium and lost by scattering; the backscattered light between the light source and the target affects the specific illumination of the image; the forward scattered light formed by the small scattering angle between the target and the receiver, which can directly affect the detail resolution of the target.

Therefore, the research focus of underwater optical observation is to reduce the influence of strong scattering effect and fast absorption power attenuation characteristics of water medium on underwater communication, imaging and target detection.

At present, several underwater optical observation technologies had been applied in practice and achieved good working results: 1) Synchronous scanning imaging, is the synchronization of the scanning beam (continuous laser) and the receiving line of sight, using the principle that the backscattered light intensity of water decreases rapidly relative to the central axis. This technique uses collimating beam point scanning and narrow field of view tracking receiving of highly sensitive detectors based on photomultiplier tubes (Liu, 1999). This technique could effectively improve the signal-to-noise ratio and the action range of imaging. 2) Range gating technique, is to use pulsed laser and gating camera to separate the scattered light at different distances from the reflected light of the target, in order to make the radiation pulse reflected from the observed target reach the camera and image within the same time when the camera gating works (Busck and Heiselberg, 2004; Tu et al., 2021). This method is very useful for solving the backscattering problem caused by suspended particles in seawater. 3) Polarization imaging technique, is to improve the resolution of imaging by using the polarization characteristics of reflected light and backscattered light of objects (Boer et al., 1998; Kong et al., 2020). This technique could improve the specific illumination and resolution by adjusting the ratio of reflected and scattered light energy. 4) Underwater laser three-dimensional imaging technique, is to measure the round-trip time between the transmitter and the target, and recover the distance image of the original target (Schulein and Javidi, 2010).

Underwater optical observation technologies could rapidly, continuously and intuitively observe the upper surface of NGH layer and sedimentary layer, and provide early warning for gas leakage and fracture production, but it cannot quantify the amount of gas escape and obtain gas components.

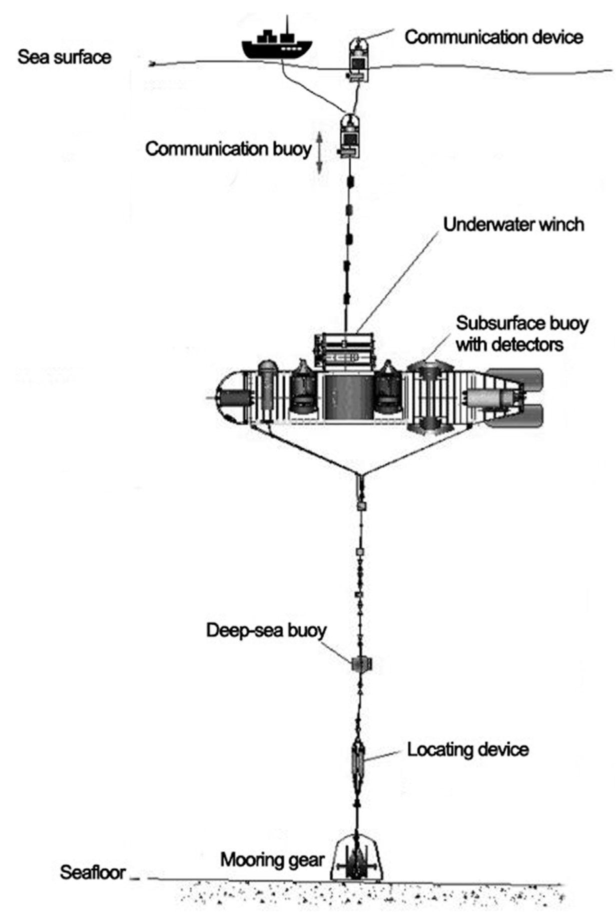

FIGURE 2
Schematic diagram of subsurface buoy with sensors (Xu, 2017).

3.1.3 Sub-bottom profiler

Sub-bottom Profiler, also known as shallow seismic profiler, is to detect the profile structure of shallow bottom strata by transmitting sound waves and receiving reflected sound waves. It is an improved device based on ultra-broadband submarine profiler, which displays the strata at the bottom of oceans, rivers and lakes. Combined with geological interpretation, it can detect the geological structure below the water bottom. The instrument has high performance in formation resolution and formation penetration depth, and can choose any combination of sweep signals to design and adjust working parameters in real time, as well as to measure bedrock depth and thickness in offshore oilfield drilling (Yang et al., 2021). Therefore, it is a widely used instrument in Marine geological survey, geophysical exploration and ocean engineering, ocean observation, seabed resources exploration and development, waterway harbor engineering, seabed pipeline laying (Li et al., 2021).

Due to its mechanism and characteristics, although the sub-bottom profiler had been utilized to detect the structure of sedimentary layer and cannot directly detect the distribution of gaseous methane, it can continuously detect the structural changes of sedimentary layer and hydrate layer, and monitor the formation and development of cracks in real time, and to predict the methane escape channels of gaseous methane based on the change of sediment structure and pore distribution. Therefore, although this technology cannot directly detect methane distribution, it can provide data support for monitoring and control of methane escape through real-time detection of potential methane leakage channels.

3.2 Seawater

The traditional method for detecting methane gas in seawater was to collect water samples with a water sampler, and to obtain the dissolved gas in the laboratory through gas-liquid distribution and purging, then analyze the content of methane in seawater by gas chromatography. Although these analytical methods was mature enough after decades of continuous utilization and improvement, it may cause sample contamination, mixing and dissolved gas escape during the sampling process, and degassing and isotope fractionation of samples in deeper waters, which may cause errors in the test results.

The *in situ* detection technologies of seawater dissolved gas could be used for underwater real-time and *in situ* high-resolution observation. The *in situ* detector can be placed in the subsurface buoy at different depths for continuous monitoring, and can be integrated with other chemical and physical sensors to realize continuous and real-time underwater observation (Figure 2). It provided a new observation method for detecting the abnormal

TABLE 3 Detection methods for seawater.

Method	Mechanism	Advantages	Disadvantages	Application	Optimization
Electrochemical sensor	Different components have different electrical signals on the surface of semiconductor components	High accuracy, low cost	Low durability, small detection range, unable to quantify the amount of gas emitted	Mackenzie Delta, Canada	Enhance the durability
				Nankai trough, Japan	
				Shenhu area of South China Sea, China	
Optical measurement method	Different substances have different absorption spectra	High accuracy, can analyze material composition	Unable to quantify the amount of gas emitted, small detection range, high cost and low durability	Shenhu area of South China Sea, China	Reduce cost
Mass spectrometry	Different compounds ionize to produce charged particles with different masses	High accuracy, can analyze material composition	High cost, small detection range and low durability	None	Reduce cost
Biosensor	Different components have different electrical signals	High accuracy	Low durability, small detection range, high cost	None	Enhance the durability

concentration of methane in seawater, discovering new gas hydrate occurrence areas, and deeply understanding the effect of gas hydrate seepage on global climate change and global carbon cycle (Table 3).

Currently, most *in situ* seawater methane detectors are designed on "sampler-analyzer" principle: the high-pressure seawater enters into the instrument through the ballast tank inlet, and forms the seawater at constant pressure through the decompression and flow stabilization device; the gas in the seawater separated through the gas-liquid separation device, and quantitatively sent to the analysis device for testing and output electrical signal. Commonly, samplers include membrane degassing device, decompression shunt devices, *etc.*, and analyzers include electrochemical monitoring, optical analysis, mass spectrometry and biosensors.

3.2.1 Electrochemical sensor

The electrochemical sensor usually uses the semiconductor probe (Garcial and Masson, 2004) in the detection cavity to detect the gas passing through the gas-liquid separation membrane, and outputs the voltage signal, and uses the signal change to reflect the measured gas concentration (Fukasawa et al., 2008). The content of CH_4 was measured by the electrochemical reaction between CH_4 and adsorbed oxygen under the heating voltage on the surface of the semiconductor material SnO_2, which caused the change of electrical conductivity.

The first commercially available SnO_2-sensing underwater CH_4 sensor (METS) was produced by Capsum in 1999 (Garcial and Masson, 2004). A polydimethylsiloxane (PDMS) membrane was installed under the protective shell to separate dissolved gases from seawater and was supported by a metal sintered plate. The standard METS sensor has a detection range of 10 to 4,000 nmol/L, a maximum operating water depth of 2000 m, and a typical response time of 1–30 min (Di et al., 2014). combined METS sensor and CTD sensor to design an *in situ* on-line gas flow measurement (GFM) device. The concentration range of CH_4 was 50–20 μmol/L and the resolution was less than 10 nmol/L. Anchored over hydrocarbon seps in the northern South China Sea, the device was used for 19 days of *in situ* measurements to obtain real-time data on gas flow and dissolved CH_4 concentrations. Because of the significant lag of METS sensors in the variation of dissolved CH_4 concentration, the data need to be corrected.

At present, electrochemical sensors based on semiconductor gas sensitive materials had been widely used in various industries because of their advantages of high precision, low price and small size. However, in the future, it is still necessary to shorten the response time of the instrument, expand the detection range and improve the accuracy of the direction of development and research.

3.2.2 Optical measurement method

The optical measurement methods have the characteristics of non-destructive, fast and high precision, including infrared absorption spectroscopy, fading wave and Raman spectrum.

Infrared absorption spectroscopy, is to irradiate molecules by infrared light at a certain frequency, if the vibration frequency of a group in the molecule is consistent with the external infrared radiation frequency, the energy of light is transferred to the molecule through the change of molecular dipole moment, the group will absorb infrared light of a certain frequency, resulting in a vibration transition. The infrared absorption spectra of the sample can be obtained by recording the molecular absorption of infrared light with instruments. The wavelength, intensity and shape of the absorption peaks in the spectra can be used to judge the groups in the molecules and analyze the structure of the molecules.

The fading wave generated by infrared light at the interface between the waveguide material and its coating can be used to detect the concentration of gas, which is another method of infrared spectroscopy applied to the detection of dissolved gas in seawater (Pejcic et al., 2007). When the light incident from the optically dense medium to the optically sparse medium, if the incident angle was greater than the critical Angle, the phenomenon of total reflection will be generated. The light wave generated along the parallel direction of the critical surface is the fading wave, and its amplitude decreases exponentially with the distance from the critical surface (Yuan et al., 2020). The sensor based on fading wave has the advantages of high sensitivity, simple design and small size, which is conducive to the realization of sensor miniaturization.

Raman spectroscopy is a fast, non-contact and non-destructive molecular vibration spectroscopy technique, which can reflect the internal energy level structure of molecules (Brewer et al., 2004). The principle is: in the process of molecular vibration, polar group vibration, molecular asymmetrical vibration leads to molecular

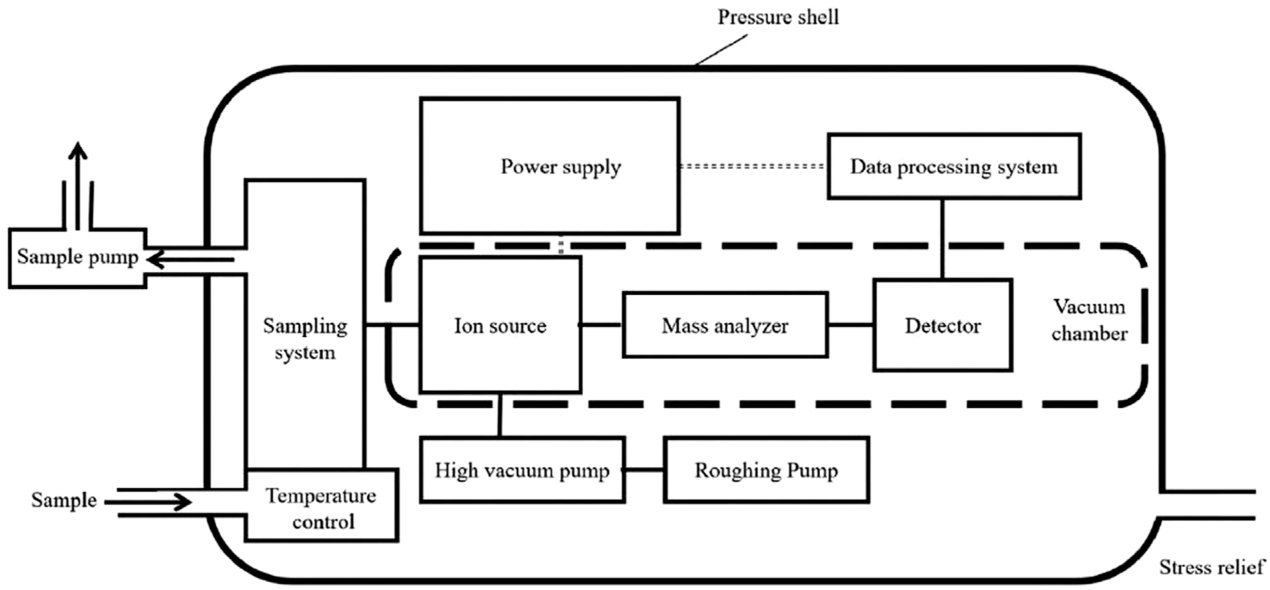

FIGURE 3
Schematic diagram of underwater mass spectrometry system (Gao et al., 2022).

dipole moment changes, produce infrared activity; The non-polar group vibration and the full symmetric vibration of the molecule change the molecular polarizability and produce Raman activity (White et al., 2006). Raman spectra of molecules of different substances may have similar peak positions, but the intensity of the peak is significantly different. The intensity of the peak reflects a large amount of information about molecular structure, so the research on molecular structure mainly focuses on the intensity analysis of the peak (Hester et al., 2007; White, 2009). A unique advantage of Raman spectroscopy in *in situ* geochemical exploration of the ocean is its ability to measure solid, liquid and gas phases, which greatly expanding its application.

Although the optical measurement methods commonly have high precision and can analyze the gas components in real time. However, limited by the mechanism of optical detection and light wave transmission, the optical measurement method cannot realize quantitative detection, and the detection range in water is much smaller than that on land. Meanwhile, due to the high precision of optical detection equipment, this method has high cost and poor durability.

3.2.3 Underwater mass spectrometry

Underwater mass spectrometry (UMS) is a method for qualitative and quantitative analysis of the mass and strength of material ions (Maher et al., 2015). Gaseous molecules lose an electron after being bombarded by a certain energy electron flow and become positively charged ions. Under the comprehensive action of electric field and magnetic field, these ions are collected by the detector and recorded into a spectrum according to the mass charge ratio (m/z), forming a mass spectrum (Camilli et al., 2010; Gentz and Schlüter, 2012). Applying the analytical function of mass spectrometry to the *in situ* detection of dissolved substances in Marine water is an important progress in the study of marine chemistry. UMS have been widely used in the study of water chemistry. Current UMS are based on membrane injection mass spectrometry (MIMS) technology, which allows gases and small volatile organic molecules to enter the mass spectrometer directly by using a hydrophobic semi-permeable membrane and applying a vacuum on one side. Some UMS devices are set up on mobile platforms to generate two/three-dimensional maps of chemical concentrations in water bodies (Camilli and Duryea, 2009), while others have been developed to detect *in situ* isotope ratios and pore water (Bell et al., 2012). The mass spectrometry method has the advantages of short response time, high sensitivity and strong specificity, which can provide the information of elements, structure and isotope of a large number of chemical substances, and can be used to identify some unknown compounds.

Even though UMS has many advantages, due to its complex structure and high precision requirements (Figure 3), the UMS has the disadvantages of high manufacturing and maintenance cost, poor durability and small effective range, which limits the application of this technique. The current UMS technology is still immature, the main goal of related research is to achieve high precision and stable detection of multi-component gas under low power consumption condition.

3.2.4 Biosensor

Biosensor is a sensor technology that integrates biotechnology and electronic technology. It converts biochemical reaction into electrical signal by using the principle of biochemistry and electrochemical reaction. Through the processing and detection of electrical signal, the measured substance and its concentration can be measured. Damgaard (Damgaard and Revsbech, 1997) embedded the cultured methane oxidizing bacteria in the oxygen storage sac and the permeable membrane oxygen sensing probe. The oxidation degree of the oxidizing bacteria changed with the change of methane concentration, and the concentration of dissolved methane gas could be measured indirectly by detecting the change of oxygen consumption. The results of seawater experiments of the biomethane sensor show that the measurement response time is 20s, the methane detection range is 50–100 mol/L, and the sensitivity is up to 5 mol/L (Damgaard et al., 2001).

Although biosensors have the ability to detect dissolved gas, they can only be applied in some specific environments because the physiological state of microorganisms is affected by temperature and pH. Its high detection limit and inability to detect isotopes also limit its wide application.

3.3 Atmosphere

Due to the limited application scenarios, atmospheric methane detection during offshore NGH production cannot be carried out by traditional point detection methods, such as catalytic combustion, semiconductor sensors, gas chromatography, *etc.* A large-scale monitoring device should be placed on offshore platform, monitoring ship, aircraft or even satellite for regional monitoring. Among all the large-scale monitoring technologies, absorption spectrum technology is the most feasible and most widely used. With the development of research and technology, satellite monitoring had become the main technology for atmospheric methane monitoring, The mechanism of the methane monitoring satellite is to estimate the total amount of methane through the spectral absorption of methane at different wavelength positions. The range of remote sensing detection is the methane amount in the column space from the satellite to the ground (Buchwitz et al., 2017). The devices used on the satellite are generally solar backscatter instruments and thermal emitters, while the solar backscatter instruments commonly were used to measure the total amount of methane and the thermal emitters were used to measure the amount of methane in the upper atmosphere. The size range of satellite remote sensing pixels is about 4–50 km^2 (Conley et al., 2016). The satellites currently in use operate mainly in sun-synchronous orbits, but isolated missions require remote sensing satellites to be placed in geostationary orbits, which continuously monitor only a fixed area. Generally speaking, methane remote sensing satellites can be used to estimate the total amount of methane in a certain limited area, but the detection accuracy cannot reach the level of specific equipment.

So far, there are 11 methane monitoring satellites in operation around the world, which can achieve real-time monitoring of abnormal methane emissions around the world. However, due to the limitations of monitoring accuracy, data inversion accuracy and anti-disturbance capability, satellite methane monitoring still needs to be further optimized.

4 Conclusion

At present, the most serious environmental threat to gas hydrate production is the methane emission caused by uncontrolled decomposition. In this study, three scenarios in which methane exists in the process of NGH production were put forward: seafloor and sediment, seawater, and atmosphere. Besides, the methane monitoring technologies applicable to the three scenarios were summarized and analyzed, aiming at a complete and full description of the advantages and disadvantages of existing methane monitoring technologies, and providing new ideas and directions for the development of methane monitoring technologies. The main conclusions are as follows.

(1) In terms of technology, the durability, response time and limit of detection of the sensors still need to be improved, and the accuracy, resolution and continuity of the optical detection means have shortcomings. In addition, it is also a way to improve detection capability by combining detection techniques of different mechanisms to cover each other's shortcomings.
(2) In terms of methodology, the effectiveness of the monitoring system could be improved by optimizing its composition and location. Analyzing the NGH distribution and sediment characteristics based on the preliminary exploration and hydrological data, and carry out numerical simulation to predict the methane leakage characteristics in the early stage, and select the detection method and monitoring point based on the numerical simulation results.
(3) In terms of science, research on the environmental impact of methane emission during NGH production should be strengthened to clarify the impact of methane emissions on marine ecology and greenhouse effect. On this basis, targeted methods to control methane emissions or eliminate the negative effects of methane should be developed.

Author contributions

SL contributed to conception and design of the study and wrote the first draft of the manuscript, MX and XC wrote sections of the manuscript, WP participated in part of the literature research. All authors contributed to manuscript revision, read, and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

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