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A Type of Optical Hydrogen Sulfurous Gas Sensor Based on Surface Plasma Resonance

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Abstract: With the development of society and the improvement of people's awareness of environmental safety, the problem of real-time on-line detection on the composition of hazardous gas has become the focus of people's attention. Traditional testing technology is usually based on the non-optical detection, such as point type sensor which uses electrochemical and semiconductor technology. Although these sensors can achieve enough low detection limit, but these detection methods are easy to be effected by other gas components crossed sensitive and sensitive membrane surface contamination and other unfavorable factors, and its response is slow, repeatable utilization rate is low, service life is short, is difficult to achieve real-time online monitoring. It is very difficult to use the traditional non-optical fiber gas sensor to carry out distributed real-time detection if performing detection on poisonous and pernicious gas in special environment. The gas detector based on optical fiber technology is now being used in many application fields such as environmental safety and industrial process monitoring. Compared with other technologies, the optical hydrogen sulfurous gas sensor based on surface plasma resonance is more reliable, the system operation cost is lower and the real-time performance is better.

Keywords: Hydrogen sulfurous gas, optical sensor, concentration detecte, surface plasma resonance.

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1. INTRODUCTION

Hydrogen sulfide (H2S) gases are common by-products of industrial processes, especially in the petrochemical industry[1-2]. Hydrogen sulfideis a colorless combustible gas with the odor of rotten eggs. Its explosion limit: lower limit 4.3% Vol (volume percentage ratio) and upper limit 40.0% Vol. Hydrogen sulfide is also a highly toxic gas, even minute amount of gas, the harm to human body is serious. Its toxicity is 5-6 times that of CO, and it is a nerve agent that strongly stimulates nerves. When exposed to extremely high concentrations of hydrogen sulfide, the human body may die like an electric shock, falling to the ground in a flash, just like being shocked. Although the human nose is very sensitive to H2S gas, the person's sense of smell can quickly become paralyzed even in the case of low concentration. Therefore, the olfactory sense cannot provide reliable warning of hydrogen sulfide gas concentration in the environment [3] .

In recent years, with the continuous exploitation and use of petroleum and natural gas, the accidents of well blowout and gas poisoning and explosion occur frequently. On December 23, 2003, a huge explosion of hydrogen sulfide in Kaixian County, Chongqing Province, which is resulting in 243 deaths, 2,142 hospitalizations, more than 90,000 people were evacuated, and direct economic losses amounted to 64.3231 million yuan. On March 22, 1998, the serious accident of hydrogen sulfide string-layer poisoning occurred in hot spring No. 4 well of Sichuan Petroleum Administration Bureau, resulting in 11 dead, 13 poisoned and one burned. On September 28, 1993, a hydrogen sulfide poisoning accident occurred in No.48 well of North China Oil Field, Zhaoxian County, Shijiazhuang City, resulting in 7 people died, 24 people were moderately poisoned and over 440 were mildly poisoned, meanwhile 226 thousands of nearby villagers were evacuated. On April 20, 2010, 11 people were killed and 17 were injured in a well blowout explosion at Mississippi canyon252-01 well of British Petroleum located in Gulf of Mexico. From the above large hydrogen sulfide poisoning accidents, we can see that the rapid and reliable detection of hydrogen sulfide is particularly important in the petrochemical industry. Hydrogen sulfide is also a strong corrosive gas, which poses a threat to the safety of equipment [4]. In petrochemical industry, because gas leakage has the characteristics of fast diffusion rate and large influence range, higher requirements are put forward for the sensitivity, reaction speed and monitoring range of detection instruments. At present, most of the commonly used monitoring devices in the industrial environment are point-type instruments based on semiconductor or electrochemical principles, which generally have the disadvantages of slow reaction speed, easy aging of sensitive components, small monitoring range, etc. and the current technology cannot fully meet the needs of large-scale field hydrogen sulfide concentration monitoring and safety warning.

2. KINDS OF OPTICAL FIBER GAS SENSORS

Compared with other optical type gas detection method, the main advantages of optical fiber gas test mainly reflect in the following aspects: first, because the optical sensor uses light transmission information while the optical fiber is one kind of transmission medium with high insulation and stable chemical properties, so the optical as sensor has electromagnetic interference resistance, electric insulation, corrosion resistance and other advantages. Secondly, because the optical fiber has light weight, small volume and flexible characteristics and other features, the optical fiber gas sensor can be made into small size, different shapes of the probe which can be used in small and special occasions. In addition, the optical fiber sensor is easy to reuse and form a network, and the optical fiber sensor network can be constituted by corresponding devices and technologies to realize multi-point distributed detection. Therefore, the optical sensor has a great advantage in gas monitoring under special circumstances[5-8].

Optical fiber gas sensor is proposed in 80s of last century. Currently, the typical optical fiber gas sensors are mainly spectrum absorption type optical fiber gas sensor, fluorescence optical fiber gas sensor, interferometric optical sensor, micro lens type optical fiber gas sensor, evanescent wave field type optical type gas sensor, optical fiber grating sensor and the surface plasma resonance gas sensors.

Spectral absorption optical fiber gas sensor belongs to optical fiber gas sensor, which uses gas chamber as its sensing element. Each kind of gas has an inherent absorption spectrum. When the emission spectrum of light source is consistent with the absorption spectrum of the gas, the concentration of gas can be measured by measuring the absorption intensity of the spectrum.

There is a relationship between the concentration of some gases to be measured and their corresponding fluorescence radiation. By using this characteristic, a fluorescence fiber gas sensor can be made. The lifetime and intensity of fluorescent radiation can be changed according to the concentration of gas to be measured. In practical application, the higher the wavelength spacing between radiation and excitation is the better. Therefore, the lower cost wavelength filter can be applied to the output terminal. Fluorescence optical fiber gas sensor is limited by the fluorescence of gas to be measured or produced by the fluorescent dye. At present, it is mainly used for the detection of gas such as oxygen and acetylene.

Interferometric optical fiber gas sensor is used earlier; whose basic structure is a Mach Zehnder interferometer Interferometric optical fiber gas sensor has high detection accuracy, but its structure is complex, easy to be affected by many factors, and has no reuse capability.

The optical fiber micro lens type gas sensor is a sensor formed by coating a metal film on optical fiber end surface. Its structure and manufacturing process is simple, which only requires evaporation and plating film on multi-mode fiber end with advantages of low cost and easy to use. However, it is only suitable for point measurement with limited reuse capacity. Moreover, its sensitivity and response time interfere with each other and cannot be optimized independently.

The principle of optical fiber-evanescent wave field gas sensor is that when light travels in optical fiber, evanescent wave is generated between the coating layer of optical fiber and the fiber cladding or core layer. Mode losses are generated by guided waves propagating in the optical fiber, and the instantaneous value of gas concentration variation can be obtained by detecting the relationship between loss and refractive index . The sensitivity of optical fiber-evanescent wave field gas sensor is relatively high, but the disadvantage is that the response speed is slow.

The operating principle for the gas sensor of Fiber Bragg Grating (FBG) is that the additional Bragg wavelength drift will occur when the gas acts on a sensor grating coated with a metal film. Therefore, the concentration of gas can be reflected by optical wavelength analysis of reflected light. As the gas sensor of fiber Bragg grating is greatly affected by temperature and mechanical stress, the corresponding treatment method should be adopted to eliminate other factors affecting Bragg wavelength change during practical use.

3. OPTICAL FIBER SURFACE PLASMA RESONANCE GAS SENSOR

Optical fiber surface plasma resonance (SPR) gas sensor is a kind of sensor which uses the surface plasma resonance of sensitive film to detect the change of gas concentration. The sensor has the following advantages: good real-time, wide range and high signal-noise. With the development of optical fiber technology and many unique advantages of optical fiber, it has become a new hot spot in the field of SPR sensor research. However, at present, there are still some defects in the manufacturing process of optical fiber SPR sensor (especially the preparation of sensitive films), which is limited to the laboratory stage and cannot be commercialized[9-12].

At present, the optical fiber sensing method for hydrogen sulfide gas is mainly adopted at domestic and overseas, including: Tang Donglin, Wang Ying, Zhang Xiaodong, Li Jun, etc. of Southwest Petroleum University have designed an infrared absorption spectrum hydrogen sulfide sensor based on differential absorption detection.Yu Dianqiang and Dong Jinting of Sheng Li Oilfield Exploration and Design Research Institute have designed a hydrogen sulfide detection system for natural gas desulfurization based on laser absorption spectroscopy; Wang Nana and Yu Zhenhong of Jiangnan University have studied the absorption theory and detection technology of hydrogen sulfide gas by near-infrared spectrum selection using distributed feedback semiconductor laser light source; According to the near-infrared absorption theory of gas and the Lambert-Beer law, Wu Bingbing and Dai Jizhi of University of Electronic Science and Technology have used the differential spectral absorption detection technology of narrow-band light source to detect hydrogen sulfide gas. Wang Peipei, Qiao Xueguang, Jia Zhen’an, Wang Junfeng, etc. of xi 'an University of Petroleum have studied the Raman scattering characteristics of hydrogen sulfide gas, and have detected the hydrogen sulfide gas using the broadband light source spectral absorption detection technology. Chen W and Boucher D of Binhai University in France have designed a hydrogen sulfide gas sensor based on tunable diode laser absorption spectrum. Ralf P, David M, et al. from the Baltic Sea institute in Germany have proposed a method to measure the content of hydrogen sulfide in the Baltic Sea using in situ absorption spectroscopy. Alessandra N, Marco P et al. of the technical university of Turin, Italy, have designed a new type of optical fiber sensor for hydrogen sulfide gas and other sulfide detection based on the change of light absorption in the sulfide atmosphere.

Through literature retrieval, other types of optical fiber hydrogen sulfide sensors have only a few references, including: Zhao Fen,Feng Wenlin etc. from Chongqing University of Technology have conducted mechanism analysis and preliminary experimental study on fluorescence quenching hydrogen sulfide sensor using Zn:Eu^{2+} gas-sensitive film. Tang

Donglin and Ke Zhijun of Southwest Petroleum University have made the evanescent field spectroscopic absorption fiber by chemical etching method, and have studied the influence of sensing fiber with different power ratios of evanescent field on sensitivity and stability of hydrogen sulfide concentration detection. The Gupta B team of Indian Institute of Technology has studied ZnO, ITO, and Cu/ZnO hydrogen sulfide sensitive films for fiber SPR sensors.

4. CONCLUSION

In recent years, the United States, Japan, France, Britain and other countries in terms of optical fiber gas sensor research is more active, many domestic universities and research institutes have done many basic theory and experimental researches, forming a more effective detection method, but due to problems of technology and process, etc., it remains to be further research in the current conditions.

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