Brief Analysis of Waste Gas Treatment Technology in Coal Chemical Wastewater Treatment System

Jiahui Wang

College of Mining and Coal of Inner Mongolia University of Science and Technology, Baotou, 014010, China

Keywords: Coal Chemical Wastewater; Waste Gas Treatment; VOCS; Membrane Gas Absorption

Abstract: VOCs and odors are volatilized from sewage to atmospheric environment in the process of sewage collection, storage and treatment in sewage treatment plants, and waste gas treatment should be carried out. Based on this, this paper analyzed the waste gas treatment process of coal chemical wastewater treatment system. Effective sealing and collection measures have been taken for the evaporating VOCS and the main links of odor generation to ensure that the exhaust gas meets the relevant standards after collection and treatment.

1. Introduction

The sewage treatment plant of coal chemical enterprises deals with the sewage from gasification plant, MTO plant and other production units [1]. The sewage contains raw materials, intermediate products and products brought by various upstream units. The composition of the sewage is very complex. The main pollutants are methanol, aromatic hydrocarbons, ammonia nitrogen, sulfide, sulfur-containing organic substances, etc [2]. Some materials are easy to volatilize, sulfur dioxide is the most common. Sulfur dioxide is one of the main air pollutants. Coal chemical enterprises in China generally use high sulfur coal, which produces a large amount of sulfur dioxide. Therefore, it is necessary to desulfurize the combustion tail gas. According to the requirements of the Comprehensive Treatment Plan for Volatile Organic Compounds in Petrochemical Industry, in the collection, storage and treatment of wastewater, waste liquor and waste residue, effective sealing and collection measures should be taken for the evaporated VOCS and the main links producing odor, so as to ensure that the waste gas after collection and treatment meets the requirements of relevant standards and prohibit dilution. In traditional desulfurization technology, packed column is usually used to absorb and remove SO2 through gas-liquid two-phase direct contact [3]. There are a series of problems in this way, such as flooding, ditch flow, foaming and entrainment of mist. In addition, particulates and impurities in waste gas enter the absorption liquid system directly, which also affects the purity of absorption liquid. In contrast, membrane gas absorption technology uses gas-liquid two-phase non-direct contact mode to avoid the above problems [4]. The essence of membrane gas absorption process is that the gas and liquid phases are separated on both sides of the membrane interface, and the gas to be absorbed passes through the membrane slightly. The pore diffuses to the side of the absorbent liquid to complete the gas removal and recovery. Because the membrane can provide huge gas-liquid contact area, fast mass transfer, and the gas-liquid two-phase flow path can be independently controlled, the membrane gas absorption technology has the advantages of high mass transfer efficiency, flexible operation conditions, easy integration of equipment, and low consumption of absorbent liquid. Series advantages.

2. Common Processes of Odor and VOCs Waste Gas Treatment in Sewage Treatment System

Direct combustion generally mixes fuel gas and odor fully at 700-950 C to achieve complete combustion, so that the final products are both CO2 and steam. Full combustion should be guaranteed when using this method, and partial oxidation may increase odor. Catalytic combustion method uses catalysts [5]. The mixture of odor and combustion gas oxidizes at 200-400 C to remove odor. The characteristics of catalytic combustion method are small unit volume, easy to

  DOI: 10.25236/acete.2019.009

solve the problem of material and thermal expansion, low operating temperature, fuel saving and no secondary pollution. The disadvantage is that it can only deal with low concentration odorous gas, catalyst is easy to poison and aging [6]. Chemical oxidation is the use of oxidants such as ozone, potassium permanganate, hypochlorite, chlorine and other substances to oxidize odorous substances into odorless or less odorous substances.

When the odorous substances can be dissolved by water or some substance's aqueous solution or organic solvent, the odorous substances can be removed by washing method [7]. The odorous substances with low olfactory threshold such as mercaptan and amine whose flow rate is more than 25 m3/min can be treated by liquid absorption method. Adsorption deodorization is a deodorization method with simple equipment and low power consumption. It is mainly used for deodorization of waste gas with low odor concentration [8]. The commonly used deodorizing adsorbents are activated carbon, ion exchange resin, sulfonation medium, molecular sieve, silica gel, activated alumina and so on. Biological method is the use of microbial metabolism activities to decompose odorous substances into odorless or less odorous substances. In the process of biological deodorization, odorous substances are decomposed by the following degradation processes: acid, phenol, formaldehyde and so on are decomposed into CO2 and H2O [9]; sulfur odor components are oxidized to sulfuric acid by the action of general bacteria and sulfur-oxidizing bacteria, and become the supply source of microorganisms; some nitrogen-based odorous components such as amines and ammonia become microorganisms. Some of the proteins that make up the protein are nitrite or nitric acid. Low temperature plasma technology has significant advantages in the treatment of gaseous pollutants. Photocatalytic oxidation of waste gas treatment is mainly through the high-energy UV ultraviolet radiation on oxygen in the air [10].

3. Waste Gas Treatment Technology of Coal Chemical Wastewater Treatment System

3.1. Process flow

Coal chemical waste gas is cooled down to below 50 C in the quench tower, and then enters the membrane absorption tower from bottom to top for desulfurization treatment. In the membrane absorption tower, the waste gas to be treated goes through the filament shell and the absorption liquid goes through the filament tube. The absorption liquid is pressurized into the membrane absorption tower through a water pump, and the gas is absorbed vertically through the membrane hole. At the end of the operation, ammonia and hydrogen peroxide are added to convert all ammonium bisulfite and ammonium sulfite existing in the system into ammonium sulfate. After the experiment, this part of the solution can be crystallized by evaporation into ammonium sulfate by-product [11].

The coal chemical waste gas used in the experiment comes from Claus tail gas of a coal chemical enterprise in Inner Mongolia. After cooling by quench tower, the flow rate, temperature and composition of the waste gas are continuously monitored. The basic situation is shown in Table 1.

Table 1 Basic situation of experimental exhaust gas

Project	Numerical Value	Project	Numerical Value
Flow(m3/h)	85~100	nitrogen oxide(mg/m3)	30~50
Import Waste Air Temperature(℃)	40~50	Hydrogen sulfide(mg/m3)	2~6
Import pressure(kPa)	6~11	Carbon dioxide(%)	13~15
sulfur dioxide(mg/m3)	1500~3500	Oxygen(%)	9~10

The effective component of the absorbent solution is ammonium sulfite at a certain concentration. After absorbing sulfur dioxide, it is converted to ammonium bisulfite. As shown in formula (1), ammonia water is added to restore ammonium bisulfite to ammonium sulfite. As shown in formula (2), in order to prevent the excessive concentration of ammonium sulfite in the absorbent solution, double sulfite is added. Oxygen water oxidizes part of ammonium sulfite to ammonium sulfate, as shown in equation (3), and maintains the equilibrium of absorbent concentration by adding deionized water:

$$(NH_4)_2SO_3 + SO_2 + H_2O = 2NH_4HSO_3 \quad (1)$$

$$\beta = \phi + \theta + \alpha + \psi - \frac{\pi}{2} \quad (2)$$

$$\beta = \phi + \theta + \alpha + \psi - \frac{\pi}{2} \quad (3)$$

3.2. Process parameters

The polypropylene hollow fiber membranes, membrane modules and membrane absorption towers used in this experiment are provided by Tianjin Blue Cross Technology Co., Ltd. The polypropylene membranes are hydrophobic porous membranes with an outer diameter of 450-550 um, a wall thickness of 50-70 um, an average pore diameter of 60-80 nm, a porosity of 52%-72%, and a gas flux of 2. 4-7.2m3/(m2.h) (0.01MPa) [12]. The filling rate of hollow fiber membrane module is 10%. The membrane absorber consists of several hollow fiber membrane modules. The gas-liquid two-phase flow pattern is adopted in the membrane absorber, and the gas-water two-phase flow rate can be controlled separately. The operation parameters: Membrane area/m232.7;Membrane Utility/(m3.m-2.h-1)2.6-3.0; Liquid-gas ratio / (L.m-3) 4.5-5.2. Among them, the membrane effect is the maximum amount of waste gas treatment per square meter when the sulfur dioxide in the tail gas after desulfurization treatment is less than 50mg/m3.

The experimental exhaust gas flow was converted by the mass flow data of the inlet and outlet. The concentration of SO2, gas composition and temperature were detected by ECOM multi-parameter gas analyzer, and the ammonia escape concentration was detected by Shenzhen Yuante SKY2000 ammonia analyzer.

3.3. Result of waste gas treatment

The desulfurization rates in the range of inlet gas concentration of 1500-2000mg/m3 and 3000-3500mg/m3 were tested respectively. From the test results, the concentration of sulfur dioxide in the tail gas was lower than 30mg/m3 after the treatment of low concentration waste gas, and the concentration of sulfur dioxide in the tail gas was lower than 30mg/m3 after the treatment of high concentration waste gas. The concentration of sulfur dioxide is lower than 50mg/m3, which is much lower than the limit in the Comprehensive Emission Standard of Atmospheric Pollutants (GB16297-1996). It shows the excellent desulfurization effect of the membrane absorber. After several hours of continuous operation, the membrane absorber can always maintain a low level of sulfur dioxide emission, indicating the device. The stability of continuous operation is good.

Ammonia escape is a problem to be overcome in traditional ammonia desulfurization technology. Because of direct gas-liquid contact, short gas-liquid contact time and low absorption efficiency, it is necessary to increase the pH and concentration of absorption solution to increase the absorption of sulfur dioxide. Because the dissociation constant of ammonia ion is 9.25, the increase of pH makes the absorption solution more efficient. The increase of the proportion of free ammonia provides favorable conditions for ammonia escape. Unlike the traditional process, the gas-liquid contact is not direct and the gas-liquid two-phase contact time is long in the process of membrane gas absorption, which can appropriately reduce the pH of absorption liquid and achieve the goal of reducing ammonia escape. When the pH range of absorption liquid is between 5.0 and 6.5, ammonia escapes. The concentration of ammonia is always below 10mg/m3, which indicates that the combination of membrane gas absorption and ammonia desulfurization technology can not only maintain high desulfurization efficiency, but also control ammonia escape well.

The absorbent liquid obtained after the experiment was collected and sent to the third-party testing institution, Chemical Analysis and Detection Center, for component analysis. According to the test results, the absorbent liquid after the experiment of ammonia desulfurization by membrane absorption tower was clarified liquid, its pH value was 5.30, and the content of ammonium sulfate was 28.44%. 2.88 mg/L nitrate, 56 mg/L chloride and 65.45 mg/L calcium.

Chloride and calcium mainly come from softening water provided by the factory. White powder ammonium sulfate crystalline salt is obtained by evaporating and crystallizing the absorbent solution. According to the national standard GB535-1995, the content of nitrogen is 21.2%, which is better than the national first-class standard of ammonium sulfate. This shows that the membrane gas absorption-ammonia desulfurization method is superior to the national first-class standard of ammonium sulfate. The absorbent solution after desulfurization produced by the technology can be used as a reserve solution for salt production and has the potential to produce by-products of ammonium sulfate.

Table 2 Contrastive analysis results

project	Traditional ammonia method	Membrane Gas Absorption Method
Gas handling capacity(m^3/h)	50	85~100
Sulfur dioxide concentration(mg/m^3)	2400	1500~3500
Liquid gas ratio(L/m^3)	4	4.5~5.2
Absorbent concentration(%)	1	0.5~1
Hand sanitizer pH	6.0	5.0~6.
Desulphurization rate(%)	96.2	98.3~100
Ammonia escape(mg/m^3)	14.3	0~7.76

Selected the traditional ammonia desulfurization experiment report similar to the scale of this experiment, compared the key parameters of membrane gas absorption-ammonia desulfurization technology and traditional ammonia desulfurization technology, such as operation parameters, desulfurization rate, ammonia escape amount, and made a comparative analysis of the technical advantages of the two processes,the results are shown in table 2. Through the comparison, it can be seen that the membrane gas absorption-ammonia method. Desulfurization technology is still superior to traditional ammonia process in terms of desulfurization rate and ammonia escape rate when the gas treatment capacity is about twice as much as that of traditional ammonia process and the concentration of sulfur dioxide in the intake gas is higher. It is especially noteworthy that the gases used in the literature are simulated flue gas with single composition and interference factors (such as water vapor and other acidic gases). The results of this experiment are more close to the actual industrial application effect of this technology. In terms of temperature, the membrane gas absorption-ammonia desulfurization technology needs to cool the high temperature gas due to the influence of the membrane material itself. If it is replaced by the hydrophobic membrane material which can withstand high temperature. Material (such as PTFE) can reduce the energy consumption and investment cost of cooling treatment.

4. Conclusion

The air pollution caused by the waste gas of coal chemical wastewater treatment system is very serious. This research combines membrane gas absorption technology with ammonia desulfurization technology, and tests the actual operation effect of this technology through desulfurization treatment of coal chemical waste gas. The experimental results show that the membrane gas absorption-ammonia desulfurization technology has excellent desulfurization efficiency and low ammonia escape, which makes up for the shortcomings of traditional ammonia desulfurization technology, and also makes up for the shortcomings of traditional ammonia desulfurization technology. It can produce high purity salt-making reserve liquid, which can be used for upgrading the traditional ammonia desulfurization technology, and has the potential to undertake desulfurization treatment of coal chemical waste gas independently.

References

[1] achkov V R, akusheva E A. Processing of chemical waste in coke production at OAO EVRAZ NTMK. Coke and Chemistry, 2015 58 624-226.

[2] one. Chemical engineering: Waste gas makes liquid fuel. Nature, 2016, 531(7594) 278-278.

[3] lga Bičáková, Straka P . Co-pyrolysis of waste tire/coal mixtures for smokeless fuel, maltenes and hydrogen-rich gas production. Energy Conversion and Management, 2016, 116:203-213.

[4] aisso M , Roussel P , Auwer C D , et al. Evidence of Trivalent Am Substitution into U3O8. Inorganic Chemistry, 2016, 55(20):10438-10444.

[5] uang N , Zhu Y B , Meng D J . Novel Sorbents and their Sorptive Properties for Mercury Emissions Control of Coal-Fired Flue Gas. Advanced Materials Research, 2015, 1088:332-336.

[6] ason M W , Joel J P , Amy M G . Clostridium ljungdahlii: A Review of the Development of an Industrial Biocatalyst. Current Biotechnology, 2016, 5(1):54-70.

[7] ernández-Naveira, ánxela, Veiga, María C, Kennes C. H-B-E (hexanol-butanol-ethanol) fermentation for the production of higher alcohols from syngas/waste gas. Journal of Chemical Technology & Biotechnology, 2017, 92(4):712-731.

[8] uan T , Lu P , Feng Q , et al. Review on Shale Gas Produced Water Chemical Characteristics and Treatment Techniques. Nature Environment & Pollution Technology, 2015, 47(29):161-163.

[9] azzella A , Errico M , Spiga D . CO2 uptake capacity of coal fly ash: Influence of pressure and temperature on direct gas-solid carbonation. Journal of Environmental Chemical Engineering, 2016, 4(4):4120.

[10] órdoba, Patricia. Status of Flue Gas Desulphurisation (FGD) systems from coal-fired power plants: Overview of the physic-chemical control processes of wet limestone FGDs. Fuel, 2015, 144:274-286.