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Development and present situation of utilization technology of Ventilation air methane (VAM) enrichment and utilization

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Abstract. As is known to all, the methane concentration in the ventilation air of coal mine is very low, which cannot be directly utilized, with a huge total amount of methane, resulting in significant greenhouse effect. Data show that China's annual greenhouse gas effect from methane released into the atmosphere from ventilation air methane (VAM) is about 200 million tons of carbon dioxide equivalent. Therefore, it is of great significance to study how to increase the concentration of methane economically and to make energy utilization. In particular, the Paris agreement put forward by the 21st conference of the parties to the United Nations framework convention on climate change recently requires the world to reach the peak of greenhouse gas emissions as soon as possible. The Chinese government has also made the commitment of reducing emissions from climate change. The only way for the coal industry to survive and develop is to popularize the technology of the scavenging gas concentration, destruction and utilization. This paper systematically summarizes the realization approach, technical objective and current situation of the utilization technology of VAM enrichment technology at home and abroad, and prospects its application prospect and new research direction.

1.Introduction

On November 12, 2014, the sino-us joint statement on climate change [1] jointly issued by China and the United States proposed that China plans to peak carbon dioxide emissions around 2030 and will strive to reach the peak as soon as possible, and plans to increase the proportion of non-fossil energy in primary energy consumption to about 20% by 2030. On November 30, 2015 to December 11, 2015, the Paris agreement passed in the contracting parties 21 times conference of the United Nations framework convention on climate change [2], proposed that the parties would strengthen the global response to the threat of climate change for controlling the global average temperatures rise from pre-industrial levels within 2 ℃, and strive to control the temperature within 1.5 ℃. In this context, China will face enormous pressure to reduce carbon emissions. The amount of methane released into the atmosphere from VAM each year in China is equivalent to the annual west-east gas transmission, and the greenhouse gas effect is about 200 million tons of carbon dioxide equivalent. Although the concentration of methane contained in VAM is very low and cannot be directly utilized, the total amount is extremely large, accounting for about 90% of the total methane of coal mine gas in China

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[3]. Therefore, it is of great significance to study how to improve the concentration of VAM and carry out energy utilization. In this paper, the way to realize the utilization technology of VAM enrichment, the technical target and the status quo of the implementation at home and abroad are discussed, and the application prospect of exhausted gas concentration utilization technology is prospected.

2. Objective and approach of utilization of VAM

2.1 Objective of VAM enrichment technology

There are three main methods to deal with VAM. Method 1 is to use VAM as auxiliary fuel, method 2 is to use VAM as main fuel [4], and method 3 is a biological filter method.

Among them, method 1 -- auxiliary fuel utilization method has no requirements for the concentration of VAM, and the technical application difficulty is relatively small. It is only applicable to the situation that the project is close to the ventilation shaft of coal mine, and the utilization amount of VAM accounts for a very low proportion of the ventilation air used in the whole coal industry. And method 3 -- biological filter technology is only a kind of tentative research, and this technology has problems such as low solubility of CH4 and long residence time of empty bed, which are currently in the laboratory research stage [5,6]. Therefore, methods 1 and 3 will not be introduced in detail.

Method 2 -- main fuel utilization method, which is the most important utilization technology to deal with spent wind, refers to the use of thermal regenerative oxidation (RTO) technology and catalytic lean combustion gas turbine power generation (CLCGTPG) technology for thermal energy utilization by increasing VAM to about 1% concentration through some way [7]. The reason for increasing the concentration of VAM is that the volume fraction of methane in VAM is too low (the concentration of VAM in most coal mines is less than 0.3%). If the technology of RTO and utilization is adopted for destruction treatment, only the self-thermal balance of the oxidation device can be maintained, and there is no excess available heat energy, which is difficult to achieve the economic return of the project. However, when using CLCGTPG technology, it is also necessary to increase the concentration of reactive wind to 1% to drive the generator rotor to generate electricity. Thermal regenerative oxidation technology and catalytic lean combustion gas turbine technology have been basically realized at present. How to appropriately increase the concentration of VAM has become an urgent and critical issue.

At present, the way to increase the concentration of VAM is mainly to mix coal mine methane (CMM) extraction from coal mine underground working face. According to the analysis of the existing application situation, this way will be limited to the flow and concentration fluctuation of CMM. In some cases, the amount of CMM cannot meet the requirements of the amount of methane for mixture, and even some coal mines have the situation of "no CMM available". All these factors cause obstacles to this application approach. Therefore, this paper mainly discusses how to increase the concentration of methane in VAM by technical means, and evaluates its application effect after enrichment. After the exhaust gas concentration reaches 1%, the VAM utilization technology equipment (such as RTO/ CLCGTPG) at the back end can be supplied. The technical roadmap is shown as follows.

1) Technical equipment for enrichment of VAM + technical equipment for RTO and thermal utilization

Collected from the mine ventilation shaft, through VAM enrichment equipment, up to about 1% of concentration of methane for RTO or regenerative catalytic oxidation device (RCO, another kind of RTO with catalytic layers), excess heat in the form of flue gas, which will be sent to the waste heat boiler for generating superheat steam/hot water for thermal utilization.

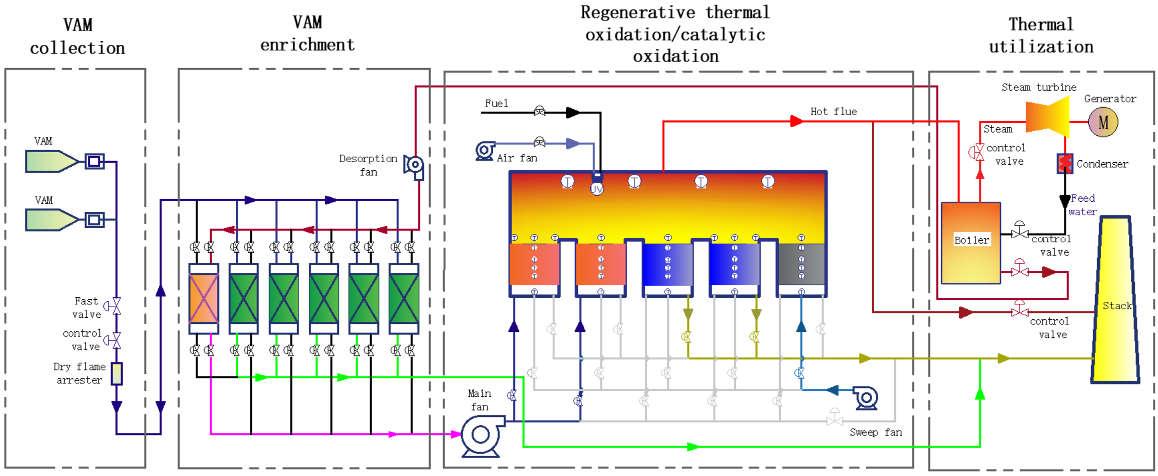

Fig.1 VAM enrichment device cooperated with RTO/RCO utilization system

2) Technical equipment for VAM enrichment + technical equipment for CLCGTPG

The VAM collected from the ventilation shaft of coal mine is increased to about 1% through the technical equipment of enrichment, and sent to the CLCGTPG system, which oxidizes methane in the catalytic combustion chamber, releases heat, and generates high-temperature flue gas impulse turbine for power generation. The process flow of the system is shown in figure 2:

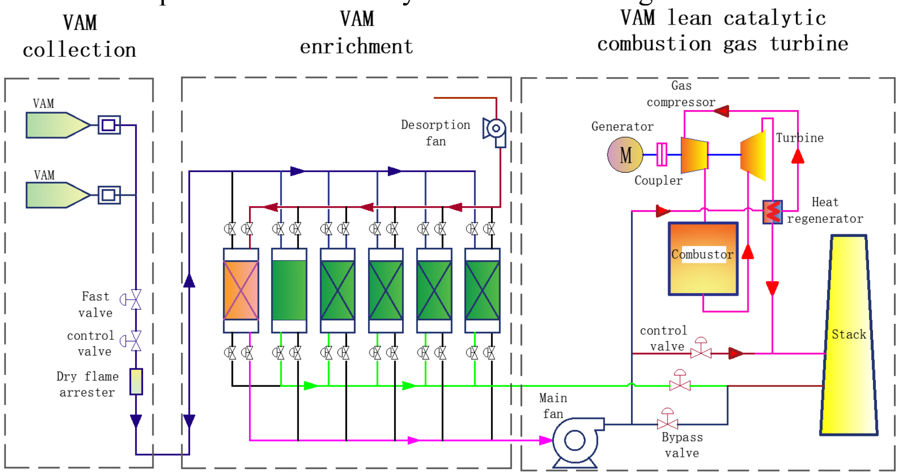

Fig.2 VAM enrichment device cooperated with lean-gas turbine system

2.2 The way of VAM enrichment technology

2.2.1 classification of technical approaches

With the increasing emphasis on energy conservation and emission reduction, more and more attention has been paid to the technology of methane enrichment and utilization in coal mine. At present, there are 5 common reference ways to improve the concentration of VAM: (1) cryogenic separation, (2) adsorption separation, (3) absorption, (4) membrane separation technology, (5) hydrate synthesis and separation.

Cryogenic separation technology has the advantages of high purity of product gas methane, stable and reliable operation, and so on. It is one of the important development directions of CMM separation and concentration enrichment in China. However, at the same time, this technology requires strict application conditions, such as low temperature conditions, high energy consumption, high investment, high operation cost and high operation requirements. Only in mass production can this technology be used to achieve economic benefits. The key problem to be solved by this technology is to reduce the energy consumption of the system and find the CMM source conditions that can meet the requirements of large-scale production.

The adsorption and separation methods include pressure swing adsorption (PSA) and temperature swing adsorption (TSA). At present, there are many research results in the field of methane enrichment in coal mine, and the technologies of PSA and vacuum swing adsorption (VSA) appear, because the technology has been used in other fields, with stable operation and safety guaranteed to a certain extent. However, PSA and VSA technology principle determines the booster adsorption energy consumption of this process is inevitable huge pressure, make its consumption of energy cannot balance the energy it generated. As a result, although quite a number of VAM enrichment research has been carried out, there still exists bottleneck problem in project economics. Moreover, the PSA or VSA technology for VAM is still in the primary stage, and no industrial test has been applied. TSA method refers to methane enrichment by changing the adsorption capacity of methane at different temperatures. The TSA technology has the disadvantages of long heating and cooling time and short life and the permeability coefficient affects osmotic quantity span of adsorbents under frequent thermal shock conditions, but its relatively low energy consumption and low thermal energy grade for desorption are easy to be obtained from the related process system, thus reducing the overall energy consumption index of the system. Therefore, TSA is not widely used in the field of methane enrichment. However, in the long run, TSA technology has a good application prospect for the enrichment of VAM, which has a large flow rate and low concentration.

Absorption method is to realize the separation of different gas components by using different solubility of different components in the same solvent. Absorption method for separation and purification of CO_2 has been widely used in industry, and the technology has been very mature. However, in terms of CH_4 separation and purification, although relevant studies have been conducted [8,9], no successful reports have been reported. Studies have shown that the selective absorption of CH_4 and N_2 by existing solvents is not high and the absorption amount is relatively small, resulting in poor separation and concentration effect of CH_4 by solvent absorption method. The applicability of this technique for extracting concentrated VAM is very limited.

Gas membrane separation technology is driven by using different permeability rate of components in the mixed gas membrane surface for separation. In recent years, in the industrial field, oxygen enrichment by membrane method and nitrogen enrichment by membrane method have been successively applied successfully, and it is possible to separate CH_4/N_2 by membrane separation technology. But the technology is used for gas separation to VAM has certain difficulty. The main components N_2, O_2 in VAM, with similar molecular dynamics radius and penetration of membrane to CH_4, which make it difficult to realize the separation. And pressure difference of the components on both sides of the membrane, the membrane area, and the permeability coefficient affects osmotic quantity; even, suction loss also can produce safety problems.

Hydrate synthesis and separation technology uses different pressure of gas component to produce hydrate and realizes separation of gas component by controlling temperature and pressure. Hydrate synthesis and separation method has the advantages of mild formation conditions, low energy consumption, small pressure loss, high separation efficiency and harmless to the environment. However, this technology is still in the preliminary stage of research and there is a great gap to practical application.

In addition, there are studies on the use of buoyancy to enhance the concentration of VAM, but Wang et al. believe that this technology is not practical feasibility [10].

2.2.2 comparative screening of technical approaches

Through the introduction of various technical approaches in 1.2.1, it is not difficult to conclude that adsorption and separation technology is more feasible than other technical approaches for the concentration of VAM, which is also consistent with the current research progress on the actual VAM enrichment technology. Therefore, this paper will focus on the most feasible enrichment technology of VAM--adsorption and separation technology research direction and related research progress.

3. Research direction of VAM enrichment technology

The existing technology of VAM enrichment technology mainly focuses on adsorption and separation. However, the technology of VAM enrichment technology is different from the existing technology of CMM enrichment. Due to the characteristics of large VAM flow and extremely low methane concentration, such as the use of the existing PSA technology, both the system design and the optimization of energy consumption index need to face severe challenges. The research direction of VAM enrichment technology includes the research of adsorption technology and preparation of adsorbent, and these studies are mainly laboratory studies, there is no industrial application of the research literature. Research on adsorption technology mainly includes the design of adsorber structure, switching control of adsorption/desorption process and optimization of energy consumption index of system operation [11,12]. Studies on adsorbents have been reported from the screening and preparation of adsorbents, carbonization and activation processes of adsorbents and performance testing of adsorbents [13,14].

4. Implementation status of VAM enrichment technology

At present, researches on the adsorption and concentration process of reactive gas mainly include VSA technology, PSA technology, and TSA technology. Most of them focus on the trial production, performance test and process test of adsorbent materials. The research institutions engaged in this field include Australian Federal Research Institute (CSIRO), University of Melbourne, Oxford Catalyst Group (Velocys) and Dalian University of Technology, Beijing University of Science and Technology, Tianjin University, etc.

American Velocys company (formerly known as Oxford Catalyst Group) carried out rapid TSA process for CMM research [15], a variety of different adsorption material has been carried out for selection, and used the mesoporous powdered activated carbon adsorption material, and gave simulation calculation of adsorption bed based on pore channel technology platform (MTP).

Thiruvenkatachari from Australia's federal research institute (CSIRO) used different groups of the activated carbon fiber and phenolic resin and other materials, prepared a honeycomb activated carbon fiber composite adsorbent (HMCFC)in the laboratory [16], and tested HMCFC adsorbent to simulate the adsorption characteristics of VAM with a concentration of 0.56%, with a result of reducing the VAM outlet concentration from 0.56% to 0.011%. The experimental results showed that the unit saturated adsorption capacity of methane for the group of materials in the dynamic adsorption process of HMCFC adsorbent is 2.7x10-4g /g. At the same time, the adsorption performance of HMCFC was compared with that of activated carbon and other adsorption materials, and it was believed that the experimental preparation of HMCFC adsorbent could double the adsorption capacity of methane. Through vacuum desorption, the concentration of VAM can be increased to 10 times. In addition, the research institute also studied and carried out experimental research on the VAM adsorption/desorption test system designed for the adsorption material [17].

As one of the research topic of ACARP project, Monash university's Paul a. Webley, carried out VAM adsorption enrichment research [18], the study of which says TSA and VSA of VAM are both feasible, and Using HYSYS software for vacuum adsorption of VAM process, as shown in figure 3,VAM was collected from the shaft of coal mine, sent to the adsorption separation plant by fan, and concentrated up to 1%, then sent to the RTO for oxidizing reaction with flue heat for thermal utilization of stem power generation. And the energy consumption index of the system is analyzed. The results showed that the TSA technology is more advantageous when the economy is considered, and it is suggested that the structure of the TSA device should be a honeycomb rotary adsorber.

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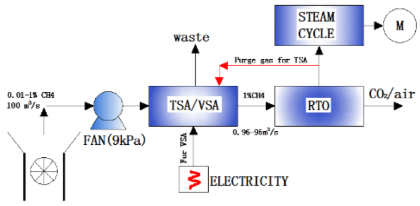

Fig.3 the system process simulation by HYSYS

Andrew Smith studied membrane separation technology and adsorption separation technology in VAM, and contrasted the two kinds of technology [19]. He thought that membrane separation technology is more feasible in the short term, and that of TSA technology is relatively low power consumption advantage makes the appeal for more research, and introduced that coal mining enterprises have been carrying out the plan to try in Germany.

An experimental study on ultra-low (CMM) with a concentration of 0.2%~1.5% was carried out by means of PSA [20], and the variable-pressure adsorption process circulated in two columnar devices, with 5A molecular sieve adsorbent loaded. The test results showed that the gas concentration of outlet of the adsorption column is the initial feed gas concentration of methane in 2 times when gas flow rate is 0.49 m^3/s. In addition, the application costs of PSA and membrane separation were analyzed and compared.

Jihan Kim et al., used molecular simulation method [21] to conduct laboratory research on adsorbent materials, and carried out systematic research on two different material systems -- liquid solvents (including ionic liquids) and nanostructured zeolites to capture methane. An adsorbent with zeolite structure was designed and its adsorption performance was tested for simulated exhaust methane with concentration of 1%. Zeolite structure suitable for absorbing exhaust methane (VAM) was named ZON and FER. However, at present, the research of these two materials is only limited to the laboratory design stage and has no practical application.

Ning, et al. using KOH impregnated liquid to modify activated carbon fiber adsorbent [22], and studied the adsorption performance of modified adsorbent on CH_4/N_2. She concluded that the adsorption ability of CH_4 by activated carbon and activated carbon fiber were greater than of N_2 in, and adsorption quantity stabilized gradually with the increase of pressure. The adsorption isotherm is the first type, which can be described by Langmuir adsorption equation.

Lei used $H_2/CH_4/N_2$ mixture gas to simulate VAM [23], measured adsorption breakthrough curve of five different commercial adsorbents in CH_4 and N_2, calculated CH_4 adsorption amount and CH_4/N_2 separation factor, selected adsorbent, and studied two tower PSA separation technology. The experimental results showed that the concentration of CH_4 in VAM can be increased from 0.503% to about 1.13% at a certain average pressure time.

Ouyang prepared coconut shell column-particle activated carbon adsorbent material with the CH_4/N_2 separation coefficient by 6.18 in laboratory [24]. CH_4/N_2 mixed gas was used to simulate the VAM, and studied the VSA enrichment of VAM. The test results showed that in the normal temperature 25℃, the adsorption pressure 0.2 MPa (absolute pressure) conditions, the VAM concentration could be enriched from 0.42% to 1.09%, with methane recovery of 88.5%.

Numerical simulation of separation and enrichment of VAM was carried out by Liu[25], He established a two-dimensional VAM flow, adsorption mass transfer mathematical model of adsorption bed with axial flow as the research target, simulated the process of VAM enrichment by the activated carbon, analyzed and the detailed flow field, distribution of concentration and the adsorption quantity within each cycle, optimized the recovery time, and compared different concentration of VAM.

Shenyang China coal engineering technology co., ltd. has applied for the patent technology for the enrichment of VAM with type of PSA [26]. The patented technology believes that it can increase the concentration of VAM from 0.1% to 0.7% to 2% to 4%. This patent mainly focuses on the control process of VAM enrichment process.

Sichuan DKT energy technology co., LTD has also applied for a patent of PSA process of methane [27], believing that its technology has a wide range of application, and the applicable concentration of methane can be as low as 0.5%.

Yang studied the influence of experimental parameters on the concentration improvement effect of VAM on a VSA test device [28]. The experimental device was a double-tower structure and the adsorbent was activated carbon. The effect of different process parameters on the methane volume fraction of product was studied by orthogonal experiment.

Zhang studied the method of PSA for enrichment of VAM [29], discussed the selection of adsorbent, the influence of the main operating conditions, conclude that half cycle, pressure equalizing, adsorption pressure and desorption pressure were the main operating conditions, and carried on the analysis of social, economic and environmental benefits.

Zhang studied the cyclic charging and vacuum extraction and discharge process of three-tower VSA device for VAM [30], and raised the methane concentration of VAM from 0.2% to 0.654%, with the methane recovery rate to 65%, at the condition of adsorption pressure 140kPa and desorption pressure 20kPa, respectively.

5. Summary and prospect

Based on the understanding of the technical approaches available for VAM enrichment and the research progress of adsorption and separation technology in the field of VAM, it is not difficult to conclude that the current research directions with more feasibility are VSA and TSA technology, especially TSA technology. When the TSA technology used for VAM enrichment, the consumed heat during the desorption process could be offered by the RTO device or a CLCGTPG system, with easy way to be obtained, which could improve the backend system of waste heat energy utilization efficiency, significantly reduce the energy consumption index of adsorption system, realize the maximization of the economic benefit of the overall project objectives.

Therefore, from the viewpoint of economics, the advantages of TSA are obvious. However, existing adsorbent materials have a small selective adsorption capacity for VAM, and the size of the TSA equipment is bound to be relatively large. In the short term, the operation economy of the equipment is still poor, and adsorbents with larger adsorption capacity and better heat resistance stability need to be developed.

In the long run, as the largest methane emission source in the coal industry, the government is bound to introduce relevant policies of destruction, utilization, carbon emission reduction subsidies and carbon trading for dealing with VAM. Improving the methane concentration of VAM through adsorption separation process, could make the VAM concentration suitable for the utilization of RTO or CLCGTPG system, solve the bottleneck problem of VAM utilization, offer stable gas source, and help the coal mines to better achieve the goal of energy conservation and emission reduction.

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