The Research Progress of the Enrichment of Ventilation Air Methane (VAM)

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Abstract: The concentration of ventilation air methane(VAM), exhausted from coal mine ventilation system, commonly is less than 0.5%(mostly below 0.3%), but the total emission amount is very large. According to the relevant data, The amount of VAM emitted annually into the atmosphere took up 80%~90% of the total emissions of China's coal mine annually[1]. Therefore, the utilization of VAM in energy conservation and environmental protection is of great significance through the enrichment technology. This paper summarized and prospected the technology progress of VAM enrichment.

1. Introduction

VAM, containing trace quantity methane gas, is discharged from coal mine ventilation system. According to the relevant data, The amount of VAM emitted annually into the atmosphere took up 80%~90% of the total emissions of China's coal mine annually. Other studies have indicated that methane's greenhouse effect is 21 times that of CO_2, and the capacity of damage to the ecological environment is enormous. The utilization of VAM through the enrichment technology is of great significance in energy conservation and environmental protection.

At present, the disposal of VAM is mainly through the technology of thermal reverse oxidization and catalytic lean burn gas turbine generation. However, the concentration of VAM, which is too low, mostly below 0.3%, and the VAM utilization technology, such as the way of thermal reverse oxidization, having no excess energy to use after the heat produced to sustain its own thermal balance, made it difficult to realize the VAM project's financial benefit. And if the technology of catalytic lean burn gas turbine generation is chosen for disposing VAM, the VAM concentration has also to be enriched from 0.2~0.3% to 1% or even higher for generation. Therefore, how to improve the concentration of VAM has become a key subject for VAM utilization economically. This paper summarized and prospected the technology of VAM enrichment, and carried out what have to be done in the following research.

2. General Situation of the VAM Enrichment

As a super low concentration methane gas, VAM's main component are air, and most of the components of air is nitrogen. So the separation of nitrogen and methane is the first goal for the enrichment of methane in the VAM, and many research documents were found making research on this area. At present, the main enrichment of VAM technology includes fluid beds enrichment technique, pressure swing adsorption(PSA) technique, membrane separation(MS) technique, temperature swing adsorption(TSA), and so on.

Lei Lichun[2] of Dalian University of Technology used a gas mixture from $H_2/CH_4/N_2$ to simulate VAM, tested the breakthrough curve of methane and nitrogen from 5 different commercial adsorbents, obtained these adsorbent's adsorbance capacity of methane and the separation coefficient of CH_4/N_2, and researched the VAM separation process in the two tower PSA adsorption devices.

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From the result of his experimental research, the concentration of VAM could be enriched from 0.503% to 1.79%.

Warmuzinski[3] researched ultra low concentration methane's PSA enrichment technology, with methane's concentration from 0.2%~1.5% (volume fraction) . The PSA process occurred in a two cylindrical device, in which 5A molecular sieves were piled up. When the velocity of the gas feed was 0.49m^3/s, the concentration of the obtained methane gas after the enrichment process is two times that of the previous gas.

Liu chi[4], from China Coal Engineering Technology Co., Ltd in Shenyang, opposed an patent about VAM enrichment through PSA technology, in which VAM's concentration can be improved to 2%~4% from 0.1%~0.7%. This patent paid more attention to the control system of the process, without any description of the performance of the adsorbents, which would influence the adsorption or desorption efficiency of the process.

Membrane separation(MS) technique is a method using the components' different transmission rates through the membrane by the same pressure to realise the goal of separation. Many research documents have reported the new structure module in the MS of methane/air mixture. But the MS process of large scale is still in development stage, especially the CH_4/N_2 system has not been reported in MS yet. The low selective permeability characteristic of membrane is the fundamental reason for the application of MS technology in the field of CH_4/N_2 separation[5]. Researching new high-selective membrane material and explore membrane process conditions are the key to the application of the MS technique in VAM enrichment[6].

For fluidized bed enrichment technology, Environmental C&C's Co., Ltd designed a fluidized bed concentrator which consisted of an absorber, a storage, a releaser and a set of transmission feeding system. Bed materials meant the adsorbents, and the common used adsorbents were activated carbon or zeolites. The methane in the VAM was adsorbed in the rising process, and fell into the bottom of the fluidized bed due to increased density when the adsorption saturation happened. Then it was collected to the storage and then be piped to the releaser. But this technology has not yet been reported in practical application[7].

In view of the defects of the ways of separation and enrichment of VAM above, China Coal Technology Engineering Group Chongqing Research Institute adopted temperature swing adsorption(TSA) mode to separate and enrich the VAM, offering stable and reliable gas source with the methane concentration of 1% for the VAM utilization apparatus, such as VAM oxidizer, or lean burn catalyst gas turbine generation. The technology of TSA for the VAM enrichment, usually included three processes—adsorption process in ambient temperature, desorption process by heating or in high temperature relatively and cooling process by cold wind blowing for regeneration. In the TSA process, the thermal energy exhausted in the desorption process was offered by the hot flue gas from the terminal of the VAM oxidization apparatus or from the export of the gas turbine. This kind of TSA process has some advantages, such as, the high efficiency of energy utilization, low investment cost, simple operation, and so on.

3. Research progress of the adsorbents for VAM enrichment

From the published literature we realized that for the VAM enrichment, the technique of adsorption separation was mainly employed, and many researches focused on the adsorbents preparation and its adsorption capacity.

Zhang Xiaohuan from East China University of Science and Technology[8], using a mixture gas of CH_4/N_2 to simulate low concentrate methane, researched on the key factor of the adsorption separation—adsorbents. He investigated the influential factors of CH_4/N_2 separation in the atmospheric pressure from the channel structure and the surface structure of the adsorbents. Through selecting molecular sieves and two series of active carbon adsorbents , he evaluated these materials' selective adsorption capacity of methane, and made some change to these adsorbents characteristics reasonably for improving the methane adsorption capacity. He used coconut carbonized shell materials to prepare some series of active carbon in different activation conditions and activation methods, and researched activation conditions' influence for the forming of active carbon. He discussed the best conditions of the methane enrichment process by experiment, mainly inspecting the influence by the adsorption temperature, adsorption pressure, and the flow of raw gas. Also, he gave research on the influence of vapor in the coal mine methane for the methane enrichment.

Qiao Zhijun[9] from Tianjin University have researched the preparation of rayon-based activated carbon fibers for methane adsorption. Through large amount of experiment data, He made a conclusion that the active carbon is the most effective methane adsorbents. Comparing three kind of active carbon structure—powder shaped, pellet shaped and active carbon fibers, he found that the contact area between active carbon fibers and adsorbates was biggest, with uniform adsorption process, short adsorption route, quick adsorption velocity and more suitable pore distribution for methane adsorption. So he believed that the active carbon fibers were the best suitable materials for methane adsorption.

A.A.Pribylov[10] studied the adsorption characteristics in different adsorbents, and observed the possibility of methane stored in the adsorption state.

Ramesh Thiruvenkatachari[11] from CSIRO considered several adsorbents' capacity for VAM adsorption, which is a series of monolithic honeycomb carbon fibers made by different types of carbon fibers. And he compared this adsorbents with pellet shaped active carbon on the adsorption capacity of VAM.

Jihan Kim[12] from Lawrence Berkeley Laboratory published an systematic studies on the methane capture effectiveness of two different materials systems, that is, liquid solvents(including ionic liquids) and nanoporous zeolites. His team screened of over 87000 zeolite structures led to the discovery of a handful of candidates that have sufficient methane sorption capacity, and two of the best candidates were named ZON and FER. But the two materials were still in the laboratory simulation step, with no actual application.

4. Conclusion and expectation

The methane concentration of VAM could reach 1% or even higher after enrichment process, and it could be used as gas source of the VAM thermal reverse flow oxidization or catalytic lean burn turbine apparatus. But the ways of MS echnique and PSA had some disadvantages, such as high operation cost which might exceed its financial benefits after enrichment, which made the projects became difficult to be carried out, districting its industrial application. Thus, the enrichment technique of MS technique and PSA technique should still make good effort on lowing the system operation energy cost, improving the process suitability, and so on.

Using the method of TSA for VAM enrichment, the process of its desorption would consume some amount of heat. But the heat could be provided by the hot flue gas from VAM oxidization apparatus followed up, or from export of the catalytic lean burn turbine. This utilization of the system's excess heat could decrease the TSA operation cost notably, and improve the energy utilization efficiency of the whole system. So in consideration of the financial aspect, TSA was better than MS technique and PSA separation technique.

In the long run, VAM emission reduction and utilization policy would be published imperatively, since VAM was the biggest methane emission sources of coal mines. Enriching the concentration of VAM by the way of TSA, and making the enriched VAM suitable for utilization of oxidization apparatus or catalytic lean burn turbine, would solve the bottleneck problem of the VAM utilization, offer stable gas source for VAM utilization apparatus, and have extensive application prospect.

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