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Research Paper

Waste heat recovery method for the air pre-purification system of an air separation unit

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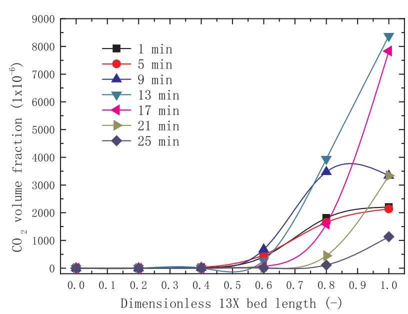
HIGHLIGHTS

- The three-bed temperature swing adsorption air pre-purification unit was proposed.
- The partition theory was proposed, and the 13× molecular sieve was divided into four zones.
- The waste heat recovery from the heat-blowing stage was verified via experiment.
- The maximum saving energy of the three-bed TSA recovery strategy was up to 51.1%.
- The regenerative heat mass transfers of the three- and two-bed were distinguished.

GRAPHICAL ABSTRACT

Regeneration gas CO_2 concentration distribution along the bed in the heat blowing process by pure nitrogen desorption. The regeneration time t_R is from 1 min to 5 min, and the regeneration partition zone III (Re-adsorption Area) is not formed. The CO_2 concentration curve has no significant peak, and the CO_2 regeneration rate slows down at this point. In 5–9 min: the regeneration mass partition zone is basically formed, the CO_2 regeneration rate of speed increases, the CO_2 concentration curve reaches a peak. In 9–17 min: the regeneration zones III and IV gradually disappear, the CO_2 breakthrough curve reaches a peak, and the volume fraction is 9250×10^{-6}. In 17–25 min: the value of the CO_2 concentration peak decreases, and the volume fraction of CO_2 becomes 1064×10^{-6}. When t_R exceeds 25 min, the CO_2 that remains in the 13× molecular sieve bed is completely precipitated and discharged from the absorber.



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ABSTRACT

A novel three-bed temperature swing adsorber was built to recover low-temperature waste heat from heat- and cold-blowing stages in a double molecular sieve of an air pre-purification system. The regenerative mass transfer in the adsorption bed was divided, and the temperature and concentration breakthrough curves of the adsorber regenerator were obtained via an experiment. Experimental results show that the relationship between the starting point and the energy of waste heat recovery is parabolic. However, energy saving reached the peak at 52.5% when the starting point of heat recovery was 23 min; this result would yield additional H_2O and CO_2 into the bed, thereby affecting the purification effect of the absorbers. The starting time of exhaust gas recycling for limit waste heat recovery strategy was 26 min, which resulted in 51.1% energy savings by recycling different stages of regeneration exhaust. The starting time of exhaust gas recycling for the optimal heat recovery strategy was 29 min, in which energy saving reached 46.5%. The starting time of exhaust gas recycling for the best regeneration strategy was 35 min, which generated energy saving of 29.8%.

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1. Introduction

The iron and steel industry is not only the pillar industry but also the focus of energy-saving emission reduction work in China. The global production of crude steel has reached 1.6228 billion tons in 2016. The International Iron and Steel Institute has estimated that 100 million tons of billets produce an average of 19,000 tons of CO_2 emissions. The CO_2 emissions of the global steel industry reached 308,000 tons. The Chinese crude steel output in 2016 accounted for 48% worldwide, whereas the CO_2 emissions of Chinese steel industry accounted for approximately 12% of the total global CO_2 emissions. The energy consumption of the Chinese steel industry accounted for approximately 15% of the total energy consumption in China. The remaining heat recovery ratio must be further improved to decrease CO_2 emissions effectively.

Oxygen, nitrogen, and argon gases required in steel production are generally supplied by air separation equipment. In China, the electricity consumption of air separation units (ASUs) in steel enterprises account for approximately 15–20% of the total electricity consumption of the entire iron and steel industry. Air separation methods can be mainly classified into cryogenic method, pressure swing adsorption (PSA), membrane separation, and chemical separation [1,2]. Cryogenic method is the cheapest and most widely applied method in the steel industry.

Air pre-purification system is an essential part of cryogenic air separation for the removal of H_2O, CO_2, hydrocarbons, and other impurities in air, as well as the prevention of impurities from blocking the pipeline and guarantee of the safe operation of ASUs [3]. The volumes of water vapor and CO_2, which are required to enter the air separation distillation unit, are less than 1×10^{-7} and 1×10^{-6}, respectively [4]. Most industrial air pre-purification adsorption methods use temperature swing adsorption (TSA) and PSA [5]. TSA air pre-purification is the earliest and most technologically sophisticated adsorption process. More than 90% of the air pre-purification processes in China currently use this method. Energy consumption in TSA mainly occurs at the heat-blowing stage. This process must blow 170 °C waste nitrogen, i.e the mixture of nitrogen and a small amount of argon, into the absorbers for 25 min. The method of heating waste nitrogen is divided into electric heating and high-temperature steam heating. The electricity consumption for heating accounts for approximately 11% of the total electricity consumption in ASUs [6], which is equivalent to 1.6–2.2% of the total electricity consumption of the iron and steel industry in China.

In an air pre-purification system, the adsorber passes through five stages, namely, adsorption, pressure relief, heat blowing, cold blowing, and pressure increase. A large number of exhausts with temperature of 40–120 °C and contain CO_2, hydrocarbons, and nitrogen-polluted water vapor are directly discharged into the atmosphere. Zhang proposed a new three-adsorber TSA process, which transported exhaust gas with waste heat into the adsorber for analysis, to recover the aforementioned part of exhaust heat [7–10]. This approach could accomplish analytical waste heat recycling, however it will bring more H_2O and CO_2 into the absorber bed to affect the desorption effect. In addition, the difference of desorption effect for multi-component mixture gas consisting of H_2O and CO_2 and waste nitrogen is not obtained. Especially the starting point and the energy of the waste heat recovery is not given.

Several researchers have studied multi-component gas below the critical temperature of the adsorption equilibrium theory on the basis of the assumption of saturated liquid-phase adsorption, which was proposed to predict multi-component adsorption equilibrium models and methods. However, these theories or models have not been widely verified due to the lack of reliable experimental data on multi-component gas adsorption equilibrium. The prediction of different existing theoretical models has several limitations and different scopes. Only several of the binary components have generated relatively satisfactory results; however, they generally have large deviation from the experimental data. Large deviations have been observed, especially for mixture gases with weakly adsorbed components. Ruthven, Yang, and Do introduced the multi-component adsorption equilibrium theory in their monograph [11–14]. Several researchers have determined that when the partial pressure of CO_2 is low, small amounts of moisture can promote the adsorption of CO_2 in molecular sieve [15–18]. Although these studies have significant reference values, the analysis of multi-component gas partition and the characteristics of multi-component gases have yet to be investigated.

The recovery and use of low-temperature waste heat from desorption of molecular sieves are the starting points of this work. In this paper the concentration profiles of CO_2, H_2O and the temperature profile of the bed show that the mass transfer of H_2O and CO_2 in the regeneration process of 13X molecular sieve bed is creatively partitioned along the bed length. The partition theory to divide the 13X molecular sieve into four zones, instead of the traditional three areas, was proposed. The waste heat recovery from the heat blowing stage was verified by experiment. The influences of regenerating heat and mass transfer of 13X molecular sieve during the regeneration of tail gas and their difference with the regeneration of double adsorbers were investigated together with the purification experiment of three adsorbers. The experiment proves that the feasibility and energy-saving capability of the pre-heat recovery of the regenerated tail gas can be used to provide theoretical and experimental support for the final realization of three-adsorber air pre-purification system. The results of this study can be applied not only in China but also in the adsorption/desorption process of molecular sieves in USA, Europe, and the UK.

2. Adsorption, regeneration, regeneration zone districts, and mass transfer analysis of pure nitrogen

Suppose that CO_2 is adsorbed sufficiently by the 13X molecular sieve bed in the adsorption process of the air pre-purification system and appears in the complete mass transfer zone. The temperature and flow rate of the regeneration gas are appropriate during the regeneration, the bed is sufficiently long, and the regeneration gas moves from the top to the bottom of the bed when the regeneration process stabilizes. The dimensionless length distribution of the CO_2 concentration and the temperature along the bed during the regeneration process are shown in Fig. 1(a) and (b), respectively. From the figure, the regeneration gas flows from left to right, and the mass and heat transfers during the regeneration process are considerably more complex than in the adsorption process. The regeneration process is not a simple inverse process of adsorption because of its unique characteristics and laws.

The 13X molecular sieve was partitioned into four regions along the dimensionless length bed according to the distribution of CO_2 concentration waves and inflection point of the curve. The analysis and research on the mass transfer, heat transfer characteristics, and variation of each zone of the regeneration process were also conducted.

Zone I (CO_2 regeneration Complete Area): Regeneration of the 13X molecular sieve bed is substantially complete. No CO_2 is present in the bed and regeneration gas. The temperature of the bed and regeneration gas reaches 170 °C.

Zone II (CO_2 regeneration area): The 13X molecular sieve bed is in the regeneration phase. In this case, the CO_2 concentration along the longitudinal direction of the bed gradually increases and reaches a peak at point B. According to the 13X molecular sieve adsorption isotherms of CO_2, the CO_2 concentration, relative pressure P_B, and temperature T_B of the regeneration gas reach a dynamic equilibrium with the adsorption amount of CO_2 in the bed.

Zone III (Re-adsorption area): Given that the temperature of the regeneration gas decreases along the bed, the bed continues to absorb a certain amount of CO_2. The concentration and temperature of CO_2 decrease to point C and stop.

Zone IV (Balance area/area to be regenerated): The bed zone in this area is not involved in the regeneration process. The concentration of CO_2 in the regeneration gas and its adsorption in the bed reach a