Taylor & Francis
Taylor & Francis Group

Compressed Air and Gas Purification and Fractionation for High Purity Applications by Improved PSA Processes

Donald H. White, Jr.

Donaldson Company, Inc., Bloomington, Minnesota, USA

Abstract: An objective of this paper is to review the purity requirements for clean air and gases used in industrial and laboratory applications. Also described are the principles applied in the design of regenerative pressure swing adsorption systems to meet the most recent process requirements. Methods developed to reduce the energy consumption of the pressure swing process are described.

Keywords: Adsorption, adsorbents, air purification, gas purification, pressure swing adsorption

INTRODUCTION

The pressure swing adsorption processes for the continuous and regenerative purification of air and gases have been well established since the discovery of the basic process over fifty years ago. Recent advances in the adsorption process have resulted in improved separation efficiencies and lower energy consumption.

PURITY REQUIREMENTS

Purity requirements for clean, dry air have become more stringent in recent years to meet the increased demands of industry and laboratories (1). Thirty years ago, pure air was required to have a moisture dew point of $-40°C$ or lower and less than 1 ppmv hydrocarbon content

Address correspondence to Donald H. White, Jr. Donaldson Company, Inc., Bloomington, Minnesota, 55430, USA. E-mail: don.white@donaldson.com

(as methane). The levels were gradually lowered to $-76°C$ dew point and less than 0.5 ppmv total hydrocarbon content. With advances in technology, the purity requirements were reduced to less than 1 ppbv for semiconductor photolithography applications, fuel cell development, automobile emissions testing, pharmaceutical manufacturing, and other critical applications. Recently, the manufacturers of lithographic systems have required extremely dry air, less than $-96°C$ dew point, and contamination levels lower than 1 pptv. In addition to the removal of water vapor and hydrocarbons, pure air is defined as being free of acid forming gases such as hydrogen sulfide, sulfur dioxide and nitrogen oxides, and free of base gases such as ammonia.

Contaminants are very detrimental in many areas where compressed air is used (2). In breathing air systems, contaminants are an irritant in the human respiratory system and can even be a health hazard. In pharmaceutical manufacturing processes, products are subject to contamination by the compressed air used in conveying and mixing solutions. In lithographic systems, the optical lenses are clouded by the adsorption of hydrocarbons and the surfaces are permanently etched by acid forming gases and ammonia even at low concentration levels (3). In automobile emission testing, dilution air contains more contaminant from the environmental than is present in the exhaust system of the engine making it difficult to accurately measure the exhaust concentration levels (4,5). In fuel cell systems, development has been affected by contamination in the oxidant stream that coats and often corrodes the membrane electrode assemblies rendering them permanently impaired (6). Also in fuel cell systems, biogas from anaerobic digesters used as fuel contains large quantities of carbon dioxide that smother the reactor degrading the power generation and hydrogen sulfide that corrodes the electrodes (7).

PRESSURE SWING ADSORPTION

Pressure Swing Adsorption (PSA) systems have served a major part in compressed air and gas purification. Invented by Dr. Charles Skarstrom in the 1950s, PSA was readily applied to both air and gas purification, and to air fractionation in the generation of both oxygen and nitrogen (8). Dr. Skarstrom used the earliest PSA systems in his laboratory at Esso to operate laboratory gas analyzers. His discoveries formed the basis for the design of PSA systems (9).

The design and operating characteristics of PSA systems have been well established over the years since Dr. Skarstrom's discovery of the process (10). When properly sized and operated, the PSA process yields a very stable, constant outlet product purity level (11). The first principle

in the design of a PSA system is the retention of the heat of adsorption within the adsorbent bed. The PSA system consists of two or more adsorption towers that are connected together with valves so that one tower is on-stream purifying or fractionating the contaminated gas stream while the other tower is sequestered by valves to regenerate the contaminated tower adsorbent. A PSA system designed to purify 0.15 kg/sec of compressed air is illustrated in Fig. 1. During the purification phase of the process, heat is evolved from the change in phase of the contaminant vapors as they are adsorbed and this energy must be retained in the tower to desorb the contaminant during the regeneration phase. Clean, dry purge air is used to convey the heat into the contaminated regions of the adsorbent bed and to sweep the desorbed gases out of the bed.

The temperature elevation resulting from the adsorption of contaminant vapors is determined from an energy balance around the mass transfer zone in the adsorbent bed (10).

$$\Delta T = [(\Delta X \ H) - (q/w)]/[c_{po} - c_{pa}(X_i/Y)] \tag{1}$$

Figure 1. Pressure swing adsorption system.

The adsorbent bed length downstream of the mass transfer zone needed to retain the heat of adsorption within the bed based on a 5% temperature elevation is determined by the Anzelius equation for heat transfer in a packed bed (10).

$$L = (w\ c_{po}/A)[1.48/(U\ a) + t_a/(c_{pa}\rho_a) + 2\sqrt{1.48t_a/(U\ a\ c_{pa}\rho_a)}] \quad (2)$$

The purge needed to convey the desorbed contaminant vapors out of the adsorbent chamber during regeneration and to maintain the pressure swing adsorption process is determined by a mass balance equation about the adsorption bed based on nearly isothermal conditions (10).

$$w_p(\text{minimum}) = 1.15\,w(t_a/t_p)(p_p/p_a) \quad (3)$$

The effluent purity is determined by an analysis of the adsorption front formed in the adsorbent bed for a single contaminant system (10).

$$X_o = 1.02 \times 10^{-4} X_i^2 v^2 t_a^3\ (\rho_o/\rho_a)/[Y\ k\ a\ L^2 R^2\ (1 - p_p/p_a)] \quad (4)$$

$$\text{Where } \overline{Y} = (1/\Delta X)\int Y\ dX \quad (\text{from } X = X_i \text{ to } X = X_o)$$

$$R = \text{Purge ratio,}\ w_p(\text{actual})/w_p(\text{minimum})$$

The presence of coadsorbing contaminants accelerates the advance of the mass transfer front in the adsorbent bed and degrades the quality of the effluent product (12).

Many adsorbents have been used in PSA systems including activated alumina, molecular sieve, silica gel and activated carbon (13). Activated alumina has been shown to have the highest capacity for water vapor and lowest effluent contamination at very low concentration levels. Molecular sieve has greater capacity at elevated temperature than activated alumina. Silica gel has the highest capacity for contaminants at moderate concentrations. The choice of adsorbent is dependent on the contaminants present, their concentrations, operating temperature, effluent purity required and other factors.

Originally, it was common practice to operate a PSA system with a single adsorbent to achieve the purity levels needed for industry and laboratories. As the purity requirements became more stringent, two or more PSA units were connected in series, each with a different adsorbent, to achieve low concentration levels. Each PSA unit would consume 20% to 25% purge, and the overall system could use 40% to 60% of the inlet flow to achieve the purity levels required. This is a very costly and energy intensive method of obtaining high purity air.

It has been shown that a single PSA unit with the proper layered filling of absorbents will achieve the lowest possible effluent concentration levels with the least amount of purge gas consumption. The approach of using a blended, layered adsorbent bed yields the best product purity at lowest energy usage (14).

The most beneficial PSA adsorbent bed for air and gas purification has been found to consist of 13X molecular sieve installed at the inlet end of the bed followed by activated alumina, a catalyst layer and a final adsorbent layer. 13X molecular sieve is very effective at coadsorbing water vapor, hydrocarbon gases, acid forming gases and basic gases. The crystalline micropore size of 7.4 Å in the 13X molecular sieve adsorbent allows for the concurrent adsorption of multiple contaminants (15,16). After removing the bulk of the contaminant vapors, the gas passes through an activated alumina layer to affect the adsorption of the removing trace contaminants. The catalyst is used in the third stage of the adsorbent bed to convert carbon monoxide to carbon dioxide because adsorbent affinity for carbon dioxide is much greater than for carbon monoxide. Carulite manufactured by the Carus Chemical Co., an admixture of manganese dioxide and copper oxide, has been found to be a very effective catalyst at ambient temperatures. The catalyst is also effective at reacting low molecular weight contaminant gases that elude capture by molecular sieve and alumina. Downstream of the catalyst layer, a final layer of activated carbon can be used to adsorb products from the catalyst layer and to remove residual contaminants that have evaded capture upstream (17).

A further development has been found in the use of a natural zeolite in the final layer of the adsorbent bed in place of activated carbon (18). Clinoptilolite is particularly effective in this region of the bed. Having very small micropores, approximately 3.5 angstrom diameter, clinoptilolite is very effective in removing difficult to adsorb contaminants such as trace ammonia gas and other low molecular weight contaminants. Further, it is about 33% more dense than synthetic adsorbents and has a very high volumetric heat capacity. Clinoptilolite is highly effective at retaining the heat of adsorption within the adsorbent bed. Improved heat capacity afforded by the zeolite layer results in a reduction in the overall size of the adsorbent bed, less heat loss from the system, and reduced purge requirements to maintain the process. The improvement in the process reduces the energy consumption in the purification system.

DISCUSSION OF RESULTS

A pressure swing adsorption system designed to purify 0.004 kg/sec of air to a level of less than 1 ppbv hydrocarbon content was recently tested in the emissions laboratory at the University of Minnesota. Effluent air samples were extracted in Tenax™ and Carbotrap sampling tubes, and the clean air was analyzed by thermal desorption-gas chromatography-mass spectroscopy. The results indicated less than 1.0 ppbv hydrocarbon content (5).

A second pressure swing adsorption system with layered adsorbent beds designed to provide pure air containing less than 1 ppbv volatile organic compounds (VOC's) was tested in the High Purity Products laboratory at Donaldson, Bloomington campus. It was found to contain undetectable VOC's, less than 1 ppbv, when the effluent was tested with a RAE Systems photoionization gas detector model ppbRAE Plus. The effluent water vapor content was found to have a dew point below $-73°C$ when tested with a GE Panametrics Moisture Target Series 5 hygrometer.

ENERGY SAVING CONTROLS

Microprocessors used in Programmable Logic Controllers provide large system energy savings by sensing the system operating conditions and altering the PSA functions to reduce purge consumption. Purge savings of over 30% are commonly realized through the use of intelligent controls (19). The PLC can sense system pressures, temperatures, flow rates and contaminant concentration levels to determine the most energy efficient operating conditions and alter the purge flow and cycle time to achieve the best performance at lowest operating cost.

Energy savings in the operation of a pressure swing adsorption system are obtained through the use of a single PSA unit designed for low velocity through the adsorbent bed and piping system, and through the use of a PLC to most effectively control the operation and conserve purge air in regeneration of the adsorbent beds. Power consumption is calculated on the basis of the thermodynamic equation for polytropic compression (10).

$$P = (287\, T_i w/\beta)[(p_o/p_i)^\beta - 1]/\eta \text{ watts} \qquad (5)$$

At a product discharge flow rate of 0.0334 kg/sec and 7 bar g discharge pressure, a power reduction of 530 watts is realized by decreasing the pressure loss from 0.75 bar differential to 0.25 bar, and a power savings of 640 watts is realized by reducing the purge flow 30% by the use of clinoptilolite in the adsorbent bed to retain the heat of adsorption and a PLC to control the operation of the system.

CONCLUSIONS

Improvements in the pressure swing adsorption process have resulted in cleaner, purer compressed air and gases, and the energy required to operate the PSA system has been significantly reduced. Layered adsorbent beds in the regenerable towers of the PSA system have been found to be effective in the separation of multiple contaminants including water vapor, hydrocarbon gases, volatile organic compounds, and caustic gases. Newly developed electrical control systems have reduced the operating costs of pressure swing adsorption systems resulting in large energy savings.

RECOMMENDATIONS

Further improvements in the pressure swing process are expected with the development of improved physical adsorbents and new system control methods. Future developments in higher capacity adsorbents with higher volumetric heat capacities will further improve the process. Developments in control systems that respond to contaminant vapors and gases will further reduce the energy consumption and operating costs.

NOTATION

a	adsorbent granule specific surface area, m^2/m^3
A	cross sectional area of adsorbent bed, m^2
c_{pa}	specific heat of adsorbent, J/kg-K
c_{po}	specific heat of gas, J/kg-K
H	heat of adsorption, J/kg of adsorbate
k	adsorbent overall mass transfer coefficient, m/sec
L	adsorbent bed length, m
n	polytropic compression exponent
N	number of compressor stages with intercooling
p	compressor inlet pressure, Pa
p_a	adsorption pressure, Pa
p_i	compressor suction pressure, Pa
p_o	compressor discharge pressure, Pa
p_p	regeneration purge pressure, Pa
P	compressor power, watts
q	vessel heat loss rate, J/sec
T	temperature, K
T_i	compressor inlet temperature, K

t_a adsorption time per NEMA cycle, seconds
t_p regeneration purging time per NEMA cycle, seconds
U   adsorbent overall heat transfer coefficient, watts/m^2-K
v   fluid superficial velocity through adsorbent bed, m/sec
w   inlet gas mass flow rate, kg/sec
w_p purge gas mass flow rate, kg/sec
X_i contaminant inlet concentration, kg adsorbate/kg gas
X_o outlet contaminant concentration, kg adsorbate/kg gas
Y   adsorbent equilibrium capacity, kg adsorbate/kg adsorbent
β (n-1)/(n N)
η motor Efficiency x compressor Efficiency
ρ_a adsorbent density, kg/m^3
ρ_o gas density in adsorbent bed at elevated pressure, kg/m^3
ΔX change in contaminant concentration, kg/kg

REFERENCES

1. White, D.; Heinrici, C. (2004) *What is Clean, Dry Air?*; Compressed Air and Gas Institute Technical Article, TAP 106.
2. Dallas, A.J.; Bellefeuille, C.; Arends, D.; Grafe, T. (1997) Pushing Chemical Filtration Technology towards the Future: Low Concentrations. Proceedings of the 10th Annual Technical Conference of the American Filtration and Separations Society, Minneapolis, MN, April, 1997, *Advances in Filtration and Separation Technology*, E.R. Baumann and L. Weisert, Eds, Vol. 11, 285.
3. Vigil, J.C.; Barrick, M.W.; Grafe, T. (1995) Contamination control for processing DUV chemically amplified photoresists. *SPIE.*, *2438*: 626.
4. Sun, E.I.; McMahon, W.N.; Peterson, D.; Wong, J.; Stenersen, E.; Dallas, A.J. (2005) Evaluation of an Enhanced Constant Volume Sampling System and a Bag Mini Diluter for Near Zero Exhaust Emission Testing. SAE International paper number 2005-01-0684.
5. Swanson, J.; Kittelson, D.; Dallas, A.J. (2007) An Alternative Method for Generating Ultra-Clean Dilution Air for Engine Emissions Measurements. SAE International paper number 2007-01-1111.
6. Moore, J.M.; Adcock, P.L.; Lakeman, J.B.; Mepsted, G.O. (2000) The Effects of Battlefield Contaminants On PEMFC Performance. Journal of Power Sources, Elsevier, 85, 254.
7. Sundareshwar, A. (2007) Purification of Digester Gas Using a Pressure Swing Adsorber. Master's Thesis, University of Minnesota, Department of Bioproducts and Biosystems Engineering, P. Goodrich, Advisor.
8. Skarstrom, C.W. (1960) Method and Apparatus for Fractionating Gaseous Mixtures by Adsorption. U.S. Patent 2,944,627, July 12.
9. Skarstrom, C.W. (1972). Heatless Fractionation of Gases over Solid Adsorbents. *Recent Developments in Separation Science*, Li, N.N., ed.; CRC Press: Cleveland, OH, Vol. II, 95–106.

10. White, D.H.; Barkley, P.G. (1989) The design of pressure swing adsorption systems. *Chemical Engineering Progress*, Jan. 25.
11. Ruthven, D.M.; Farooq, S.; Knaebel, K.S. (1994) *Pressure Swing Adsorption*; VCH Publishers, Inc.: New York, N.Y.
12. White, D. (1988) Practical aspects of air purification by pressure swing adsorption. Adsorption and Ion Exchange: Fundamentals and Applications, *AIChE Symposium Series*, *264* (84): 129.
13. White, D.; Heinrici, C. (2004) Sorbents for Air and Gas Purification. Compressed Air and Gas Institute Technical Article, TAP 104.
14. White, D.H. (2007) High Purity Air and Gas Fractionation System. U.S. Patent 7,306,658 B2, Dec. 11.
15. Yang, R.T. (2003) *Adsorbents: Fundamentals and Applications*; John Wiley & Sons, Inc.: Hoboken, N.J.
16. Valenzuela, D.P.; Myers, A.L. (1989) *Adsorption Equilibrium Data Handbook*; Prentice Hall: Englewood Cliffs, N.J.
17. Jonas, L.A.; White, D.H. (1995) Sorbing Apparatus with Guard Bed. U.S. Patent 5,443,623, Aug. 22.
18. White, D.H.; Weber, B.; McGill, B. (2006) Sorption Systems with Naturally Occurring Zeolite. Provisional Patent Application Serial No. 60/820,420, July 26.
19. White, D.; Weber, B. (2004) *The Adsorption Dryer Process*. Compressed Air and Gas Institute Technical Article, TAP 105.