CONTINUOUS IMPROVEMENT AND DE-BOTTLENECKING OF EXISTING ASU ASSETS VIA FRONT-END RETROFITS

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The front-end of an air separation unit (ASU) removes trace impurities from the air to prevent operating and safety problems. A plant audit may show the front-end has become a bottleneck on ASU production, power, and / or operability. New developments in front-end purification technology such as advanced adsorbents, improved regeneration processes, and better process control can remove these bottlenecks and improve ASU safety. These developments can readily be retrofitted into existing plants. The considerations of which type of retrofit is best for a given application are discussed. Several real examples and actual benefits are presented.

BACKGROUND & EXISTING TECHNOLOGY

Prior to the cryogenic distillation in an air separation unit (ASU), the feed air to the cold box is pre-treated by the "front-end" equipment, which removes trace impurities that can cause safety hazards or operating problems. Hydrocarbons (HC) are flammable or reactive if concentrated with oxygen or enriched air; acetylene (C_2H_2) is a significant safety hazard in this regard. Carbon dioxide (CO_2), water (H_2O), and nitrous oxide (N_2O) will freeze out in the cryogenic plant; they will precipitate into solids that will plug exchanger passages, as well as cause dry boiling and HC build-up in reboilers [1, 2, 3].

Many front-end systems in existing ASUs employ one of three mature technologies to pre-treat the feed air: Thermal Swing Adsorption (TSA) [4, 5, 6, 7], Pressure Swing Adsorption (PSA) [8, 9, 10, 11, 12, 13], or Reversing Heat Exchangers (REVEX). Figure 1 presents a typical two-bed adsorption system flowsheet. Each vessel is filled with one or more granular adsorbents. One bed is online, adsorbing impurities until it reaches its capacity for them. At the same time, the other bed is being regenerated, undergoing clean-up to remove the impurities. Regeneration includes (1) depressurization to purge pressure (typically near ambient pressure), venting the gas to atmosphere; (2) regeneration by dry, clean gas; and (3) repressurization to feed pressure (typically 5 bara or greater) with clean product gas from the other online bed. In TSA, the regeneration gas is externally heated to improve the removal of impurities; in PSA, the regeneration gas is not heated. Beds in a TSA system stay online for about two to eight hours, while PSA beds stay online for about fifteen minutes. TSAs typically use alumina as the adsorbent to remove H_2O and sodium-X

(NaX, also known as 13X) to remove other impurities, while PSAs typically use alumina to remove all impurities of interest. TSAs and PSAs completely remove C_2H_2 so it does not enter the cryogenic section of the ASU.

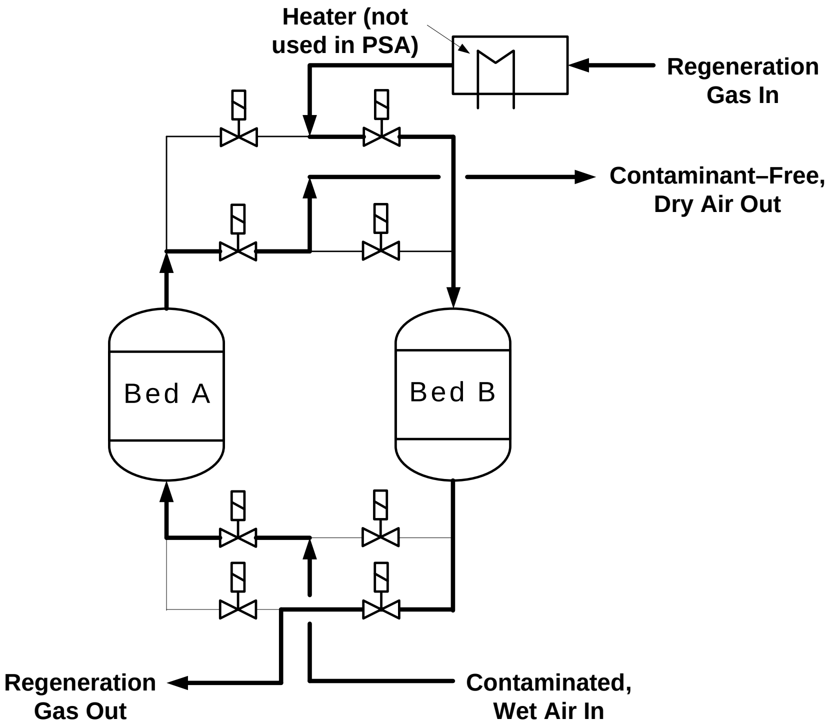

Figure 1 Two-Bed Adsorption System Flowsheet

While TSA and PSA systems are widely and successfully used in the front-end of new ASUs, they may constrain a particular facility for one of several reasons:

- <u>Throughput</u>: The overall ASU production may be limited by the TSA or PSA due to loss in adsorbent capacity over time; because the product demand has increased beyond the TSA or PSA's capability; or because an increase in gas velocity will fluidise the adsorbent, leading to dusting.
- <u>Heater Power</u>: In TSA, the regeneration heater's instantaneous or time-average power consumption may be too high. Alternatively, high time-of-day power charges may cause significant costs if heater operation is not optimized.
- <u>Switch Losses</u>: The short onstream times in PSAs require the beds to be repressurized very quickly from purge to feed pressure. This steals air from the feed to the coldbox, reducing coldbox performance. The pressurization air ("switch loss") is lost to the process and thus increases the ASU power consumption.
- <u>N_2O</u>: Older designs did not remove N_2O. It accumulates in downflow reboilers, requiring more frequent defrost [1].

Air Products' retrofits of TSA and PSA systems have eliminated these constraints.

Figure 2 shows a simple REVEX front-end flowsheet. Impurities from the air are frozen out on the surface of the main heat exchanger as the air cools down to cryogenic temperatures, getting its heat from warming waste gas. To avoid plugging the exchanger, after several minutes the air and waste nitrogen passages are switched. This waste nitrogen vaporizes the accumulated ice, frozen CO_2, and other impurities, all of which are vented.

REVEX systems are rarely used in new ASUs. Those that still exist can operate successfully, but often face challenges:

- <u>Leaks</u>: Frequent thermal cycling can cause leaks to develop in exchanger passages. These leaks need to be plugged and this leads to increased pressure drop and downtime, and ultimately to shorter exchanger life.
- <u>Plant Stability</u>: Switching the exchangers every seven to eight minutes sends flow and pressure disturbances to the ASU. These disturbances cause continual variations in O_2 and N_2 purity and they reduce argon production.
- <u>Large Waste Flow</u>: Clean-up of the REVEX system requires 40 – 50% of the inlet air. If the clean-up required less air, this extra air could be made into saleable product, or used for other means (e.g., cooling the air into the front-end).
- <u>Acetylene</u>: C_2H_2 is not frozen out in the reversing exchangers and thus enters the cryogenic section of the ASU. This presents significant safety issues that are covered in other publications [1, 2, 3].

At Air Products, changing from REVEX to adsorption-based systems has eliminated these challenges.

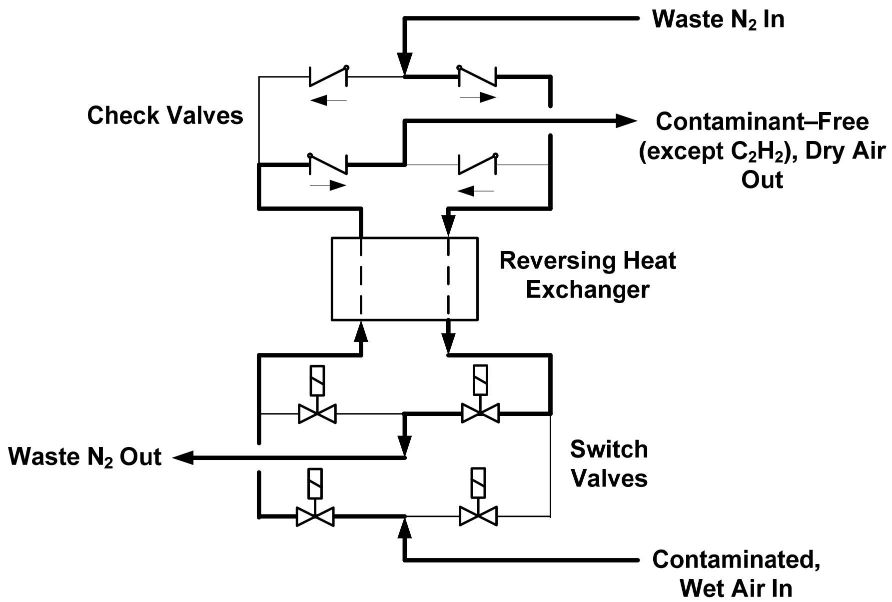

Figure 2 Reversing Heat Exchanger Flowsheet

IMPROVED ADSORBENT AND REGENERATION TECHNOLOGIES

Continuous enhancements in adsorbent technology and in the methods of regenerating adsorbent beds enable the improvement of existing ASU front-ends. Newer, improved adsorbents with up to 80% greater capacity for impurities are available, so the same volume of adsorbent can remove more impurities. These improved adsorbents can allow greater air flow through the adsorber beds, help optimize regeneration power consumption, and / or improve the adsorption of specific impurities. Examples of improved adsorbents include:

- <u>Base-treated alumina</u> [14]: The alumina typically used in PSAs is treated with potassium carbonate (K_2CO_3), increasing the alumina's capacity for CO_2.
- <u>High H_2O Capacity desiccants</u>: Alternative desiccants with higher capacity than alumina for H_2O can be used in TSAs.
- <u>High CO_2 Capacity NaX</u> [15]: The NaX materials used in TSAs to remove CO_2 can be made with less or no binder material, or with different formulations to increase capacity relative to standard NaX products.

- Calcium-X (CaX) [16, 17]: CaX has higher capacity for N_2O than NaX, which may be utilized in TSA systems.

Table 1 summarizes these newer adsorbents and their opportunities to improve the front-end.

Table 1 Improved Adsorbent Technologies to Retrofit Existing ASU Front-Ends

Adsorption Cycle / Component Removal	Standard Adsorbent	Improved Adsorbent	Improvement Opportunities
PSA	Alumina	Alumina Treated with K_2CO_3	increased front-end throughput
TSA—H_2O Removal	Alumina	Higher H_2O Capacity Desiccants	increased front-end throughput
TSA—CO_2, HC, and N_2O Removal	NaX	Higher CO_2 Capacity NaX	increased front-end throughput
		CaX	increased front-end throughput, higher N_2O removal

Advanced technologies to regenerate existing adsorbent beds allow the ASU to operate with lower power consumption, and in some cases enable increased front-end throughput. Historically, TSAs have been regenerated by passing a large heat pulse through the bed. In many older systems, the heater energy supplied is much greater than that theoretically required to desorb the impurities. This extra energy exits the bed as a high-temperature waste gas. To reduce energy consumption, the TSA can be retrofit into a Thermal Pressure Swing Adsorption (TPSA) system [18, 19]. In TPSA, the heater supplies less energy during regeneration, and the heat energy is consumed inside the bed with none wasted to vent. Because the degree of regeneration is less than a TSA, the TPSA onstream time is shorter.

PSA systems require frequent repressurization from purge to feed pressure. A PSA system can be converted to Thermally Enhanced PSA (TEPSA) [18, 20]. A small heater is installed to deliver a short ~70 °C heat pulse during regeneration. This small amount of heat greatly increases the bed capacity, and significantly extends the onstream time. While the heater requires additional power, the overall ASU power consumption decreases because the longer onstream time requires fewer repressurizations, reducing the switch losses.

Any adsorption-based regeneration cycle may be used to replace REVEX front-ends. This reduces the frequency of switching, extending the exchangers' useful life and facilitating more stable operation. All the adsorption cycles remove C_2H_2, eliminating its safety and operational challenges. And TSAs, TPSAs, and TEPSAs require less waste flow for regeneration, making air available for other purposes. Table 2 summarizes how advanced adsorbent cycles may improve the ASU's front-end.

Table 2 Improved Regeneration Cycles to Retrofit Existing ASU Front-Ends

Original Cycle	Improved Cycle	Improvement Opportunities
PSA	Thermally Enhanced PSA (TEPSA)	decreased regeneration energy & waste flow, increased front-end throughput
TSA	Thermal Pressure Swing Adsorption (TPSA)	decreased regeneration energy & waste flow
REVEX	any adsorption cycle	safer and more reliable operation, decreased waste flow if TSA, TPSA, or TEPSA

IDENTIFYING THE BOTTLENECK AND PLANNING THE RETROFIT

Before any retrofit to the ASU is considered, it is prudent to conduct an overall plant audit. The audit confirms that all aspects of the facility have been optimized. For example, can air flow through a TSA front-end be increased simply by decreasing the onstream time? The audit also assesses how far all elements of the plant are from their limits. E.g., retrofitting a TSA to process 10% more air may require an upgrade to the main air compressor (MAC) as well. These issues are best addressed during a winter performance test when flow rates can most easily be maximized. To maximize return on investment, any retrofit to the ASU's front-end should not exceed the limits of other equipment that will not be upgraded.

Typical adsorption-based front-end retrofits include actions such as removing and installing new adsorbent, installing heaters and instrumentation, and / or modifying existing control systems. This work can generally be arranged to take less than one week to complete, and to be performed when convenient. In cases where REVEX front-ends are being replaced with adsorption-based systems, much of the necessary work can be conducted while the ASU is on-line, with a short outage required only for the final tie-ins.

INCREASING FRONT-END THROUGHPUT

Situations may arise where higher product flows are desired and can be accommodated by other equipment, but the existing front-end cannot remove more impurities. If increased product flows require more air flow, one must modify the front-end to remove the extra impurities which will cause issues in the ASU.

Using improved adsorbents in PSA or TSA front-ends can allow the front-end to accept higher air flow while also accepting the increase in impurities that must be removed. For PSA applications, a proprietary alumina treated with a K_2CO_3 solution is available. This treatment increases CO_2 removal versus standard alumina. Air Products' experience is that a PSA using this improved alumina may process at least 10% higher air flows.

While traditional TSAs use alumina to remove H_2O and standard NaX to remove the bulk of the CO_2, different and newer adsorbent materials can remove larger quantities of these impurities. Such adsorbents include improved desiccants for H_2O removal, and proprietary advanced NaX for CO_2 removal. At an ASU in Europe, Air Products replaced an existing alumina / NaX TSA bed with better desiccant and NaX materials. This allowed TSA throughput to be increased by 13%, making more O_2 product available to the market.

Air flow through existing PSAs can also be increased by changing the system to run the proprietary TEPSA cycle. This modification involves replacing at least 15% of the alumina with NaX, installing a small regeneration heater, and making control system modifications. Air Products has employed this PSA-to-TEPSA retrofit at five ASUs in Europe and the United States; using TEPSA allowed front-end throughput to be increased by up to 20%.

In Air Products' typical experience, when the extra front-end throughput was converted to more product, the modest capital investments had payback periods of one year or less.

REDUCING FRONT-END POWER CONSUMPTION

Reduced ASU power consumption is a desired, ongoing efficiency improvement, especially with recent increases in power costs. Changes to the regeneration cycle of existing ASU front-ends can reduce power consumption.

Retrofitting a TSA to the patented TPSA cycle reduces average power consumption during regeneration, and may reduce peak power consumption as well. A TSA-to-TPSA retrofit may require a partial or complete adsorbent re-load, as it is important that enough alumina be loaded in the bed to accommodate the impact of the reduced regeneration energy. The TPSA also requires control system modifications to maintain regeneration energy at a minimum. Air Products retrofit an existing TSA in the United States to run TPSA; the average heater power consumption was about 40% lower in TPSA mode.

In the PSA-to-TEPSA retrofit, the decrease in MAC power consumption during the repressurization step of the TEPSA cycle is greater than the increase in power required to run the regeneration heaters. In the ASUs where Air Products performed PSA-to-TEPSA retrofits, the overall ASU power per unit of product decreased by up to 2%.

IMPROVING FRONT-END OPERABILITY, RELIABILITY, AND/OR SAFETY

Replacing a REVEX system with an adsorption-based front-end can eliminate the need to replace the reversing exchangers, and solves many operating and safety problems. Installing an adsorption system requires much less downtime than is needed to replace the exchangers. Removing and installing new exchangers can require a three-to-four week outage, but only a few days are needed to make the piping tie-ins for the adsorption unit. Because the REVEX will still be the main heat exchanger to cool the air to cryogenic temperatures, this retrofit can only be performed if the MAC can accommodate the typical 0.2 – 0.5 bar increase in head pressure caused by pressure drop across the adsorption system. And because the exchangers have a finite life in reversing service, this retrofit should be performed proactively so the exchangers still function after the adsorption system is installed. Globally, Air Products has upgraded about fifteen REVEX systems to adsorption-based front-ends.

A different operability improvement may be achieved with the implementation of TPSA regeneration discussed previously. Compared to TSA regeneration, TPSA can require less waste gas flow while still consuming less power. This makes more waste gas available, either for better chilling of the feed to the adsorbers or for use as more product if the columns can accommodate. Reduced waste flow also decreases backpressure in the ASU, allowing a lower MAC discharge pressure and more efficient ASU operation.

Improvement can also be made in the area of safety by replacing NaX with CaX in a TSA or TPSA. This proprietary change increases the front-end's retention of N_2O without sacrificing the CO_2 capacity of the bed. Air Products performed this type of retrofit in the TSA of a large ASU in the United States. In addition to increasing the safety level of the ASU, downtime was reduced so that 0.5% more O_2 was produced.

CONCLUSION

A plant audit of an existing ASU can demonstrate which areas of the plant are bottlenecks on production, power, operability, and / or safety. If the front-end is a bottleneck, retrofitting it can successfully remove its restrictions. Air Products has developed advanced adsorbent and regeneration technologies to improve the front-end, and has proven these technologies to make thirty existing ASUs safer, more operable, and more profitable.

REFERENCES

1. “Safe Operation of Reboilers / Condensers in Air Separation Plants”, EIGA IGC Document 65/99/E (1999).
2. Schmidt, W., Kovak, K., Licht, W. Feldman, S., “Managing Trace Contaminants in Cryogenic Air Separation”, AIChE Spring Meeting (2000).
3. Schmidt, W., “Reboiler / Condenser Safety”, EIGA Production Safety Symposium (2006).
4. Theobald, A., "Air Purification Thermal Swing Adsorption", U.S. Patent 4,372,764 (1983).
5. Gemmingen, "Design of Adsorptive Dryers in Air Separation Plants", Linde Reports on Science and Technology, (1994) 54.
6. Grenier, M., "Process and Apparatus for Purifying Air to be Distilled by Adsorption”, U.S. Patent 5,137,548 (1992).
7. Kerry, F., "Front-End for Air Separation Plants—The Cold Facts", Chem. Eng. Progress (August 1991) 48 – 54.
8. Skarstrom, C., "Use of Adsorption Phenomena in Automated Plant-Type Gas Analyzers", Ann. N.Y. Acad. Sci. (1959) 72 752.
9. Skarstrom, C., "Method and Apparatus for Fractionating Gaseous Mixtures by Adsorption", U.S. Patent 2,944,627 (1960).
10. Skarstrom, C., "Heatless Fractionation of Gases Over Solid Adsorbents", N.N.L1(ed), CRC Press, Cleveland, OH (1972).
11. White, D., "Practical Aspects of Air Purification by PSA", AIChE Symo Ser, No. 264, 84.
12. White, D., "The Pressure Swing Adsorption Process", AIChE Spring National Meeting (1988) New Orleans.
13. Kalbassi, M., Golden, T., “Advanced Pressure Swing Adsorption (PSA) Air Purification Systems”, Int. Inst. Ref. MUST 96 (1996) 159.
14. Golden, T., Taylor, F., Wang, A., Kalbassi, M., “Base Treated Alumina in Pressure Swing Adsorption”, U.S. Patent 5,656,064 (1997).
15. Golden, T., Taylor, F., Malik, N., Raiswell, C., Salter, E., "Process for Reducing the Level of Carbon Dioxide in a Gaseous Mixture", U.S. Patent 6,506,236 B2 (2003).
16. Golden, T., Taylor, F., Johnson, L., Malik, N., Raiswell, C., “Purification of Air”, U.S. Patent 6,106,593 (2000).
17. Kalbassi, M., Raiswell, C., Golden, T., Taylor, F., “Improving ASU Safety with Front End Adsorption of N_2O”, GPA Conference (2004).
18. Kalbassi, M., Golden, T. “Thermal Adsorptive Processes for Air Pre-Purification”, Cryogenics (2000).
19. Kalbassi, M., Golden, T., “Purification of Gases Using Solid Adsorbents”, U.S. Patent 5,855,650 (1999).
20. Kalbassi, M., Golden, T., “Purification of Gases Using Solid Adsorbents”, U.S. Patent 5,614,000 (1997).