Air separation

carbon dioxide removal by adsorption

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The process described is applicable to air-separation plants using conventional shell-and-tube heat exchangers. In two ways it meets the demands of today for removing carbon dioxide: first, it eliminates caustic scrubbing (which until recently was the normal method of removing carbon dioxide from the air to be separated in air-separation plants using conventional, continuously operating shell-and-tube heat exchangers); second, it offers the highest degree of safety for air-separation plants as far as dangerous accumulations of hydrocarbons in the cold box are concerned.

Both improvements are realized by this removal, just above the dew point, of the carbon dioxide, and also the hydrocarbons such as acetylene by means of adsorption, for example, with silica gel. Two interchangeable adsorbers are used. Before the ad-sorber in use is exhausted, it is exchanged for one that is freshly regenerated, regeneration being effected by allowing a gas which is free of CO_2 to flow through the adsorber. This may be done at the temperature of adsorption, or by simultaneously warming up the adsorber to ambient temperature.

Application of process

The practical application of this process in a medium-pressure air-separation plant is described in Figure 1. Air is compressed to about 14-18 kg./sq. cm. (200-250 lb./sq. in.), during summer months 16-20 kg./sq. cm. (225-280 lb./sq. in.), and then dried in interchangeable activated alumina adsorbers. The dried air is then cooled down in the exchangers A, B, and C to nearly the
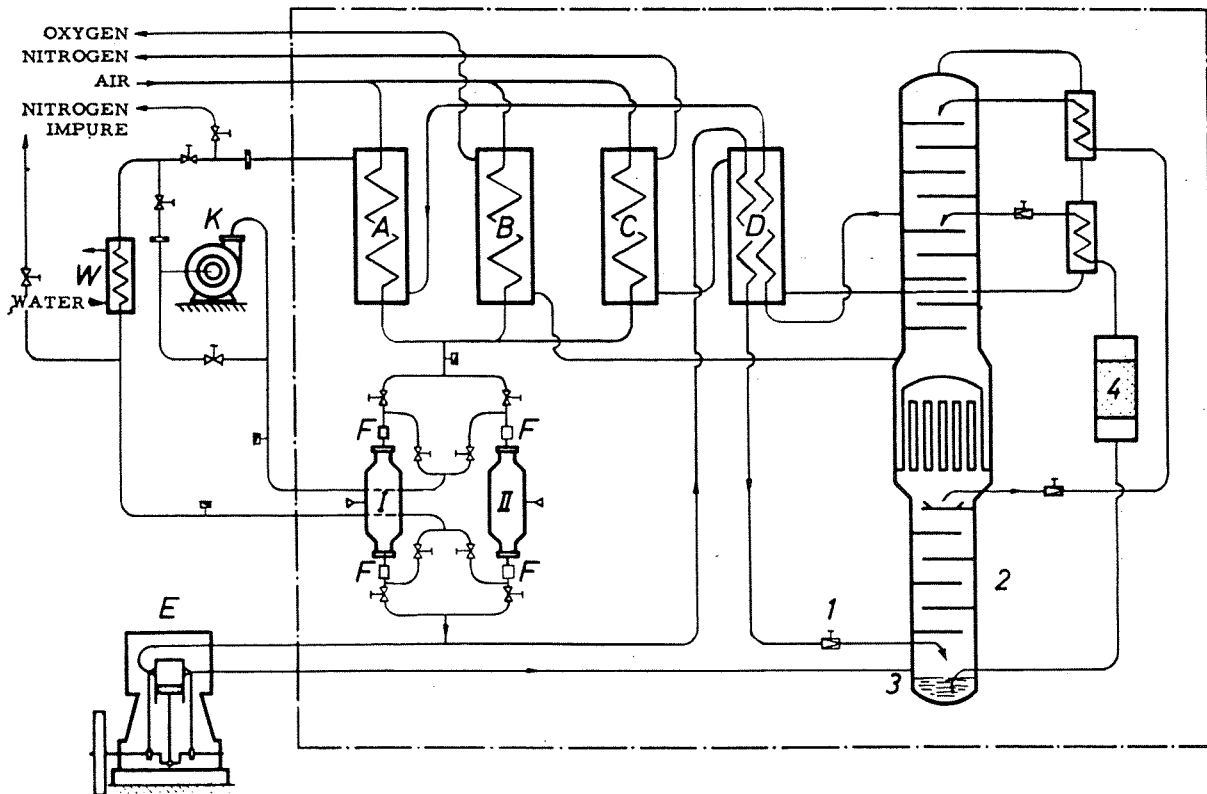
Schematic of application of this process in a medium-pressure air separation plant.

Air separation

continued

dew point of the carbon dioxide, against the separation products—impure nitrogen, pure oxygen, and pure nitrogen. After this, carbon dioxide and hydrocarbons (for instance, acetylene) are removed in the interchangeable silica gel adsorbers I and II. A part of the air so purified is expanded in the expansion engine E in the performance of work, the rest is liquefied in exchanger D in exchange with pure and impure nitrogen. Then it is expanded in the expansion valve 1 into the pressure column 2. The exhaust of the expansion engine enters the pressure column at the low end at 3. The air is separated in a two-stage rectification and the separation products are warmed up in the usual way. For safety's sake the acetylene adsorber 4 was not eliminated in the first plant.

The CO_2 adsorbers are cylindrical vessels with reducers at the ends for smaller flanges made of stainless steel, the wall thickness being designed to withstand the start-up pressure of 50 atm. (700 lb./sq. in.). They are solidly packed with silica gel. Filters F prevent gel dust from reaching the expansion engine or the expansion valve. The adsorber is sized to keep the CO_2 content of the purified air mostly below 0.5 p.p.m. over the service period of the adsorber. Air purified with caustic contains somewhat more CO_2, i. e., 1-3 p.p.m. CO_2.

Processing procedure

To monitor the process of saturation, an analysis line is attached at the lower third of the adsorber. Air from this point bubbles through test tubes, one filled with water, one with barium hydroxide. If the barium hydroxide water clouds, the end of the service period within a few hours is indicated, and the adsorber has to be changed. Usually switching to the second, previously regenerated adsorber is done after a 24-hr. service.

To regenerate the adsorber, either at elevated temperature or at the temperature of adsorption, a dry gas which is free of CO_2 is sent through the adsorber. Since nitrogen and oxygen as main products are not available, only the impure nitrogen fraction can be used in the plant described here.

This fraction is too small to warm up the valves, the gel filling, and the vessels of the adsorbers from operating to ambient temperature if used only once. Therefore, the recycle

blower K is used which sucks cold regenerating gas from the adsorber through the heater W and feeds it back to the adsorber at a temperature of 20 to 40° C. The cycle is continuously "flushed" with the impure nitrogen fraction. The cycle warms up the adsorber system and desorbs the carbon dioxide. In 24 hr., 18 cu. ft. CO_2 are adsorbed from 1250 std. cu. ft./min. of air.
The cycle contains:

at −51 °C. after 1.25 hr. 8% CO_2
−18 °C. after 2 hr. 0.8% CO_2
and +20 °C. after 3 hr. 0.1% CO_2.

In order to remove CO_2 completely from the adsorber, especially from the end at the outlet, the blower is stopped in the last phase, and, for one hour, only the fraction of impure nitrogen, which is free of CO_2, is fed to the adsorber at a temperature of +20° C.

To cool down the adsorber to the operating temperature 15 to 18 hr. are now still available. The outlet valve is opened and a small flow of precooled air then flows parallel to the adsorber in operation and cools down the adsorber just regenerated. This small partial side stream is freed of CO_2 by the comparatively large amount of gel. Downstream of the adsorber it joins the main stream. The cooling-down is completed after about 10 hr., regeneration and cooling-down together taking about 15 hr. The refrigeration necessary for cooling-down is thus distributed over many hours and the additional demand of refrigeration is hardly felt. The adsorber should be heated to a higher temperature than +20° C., for instance, to +100° C. in longer intervals in order to remove water which may have possibly entered the adsorber and is adsorbed. Practical operation has shown that occasional saturation with water vapor could be reversed by repeated application of the ordinary desorption process (+20° C.).

Purification and safety

The efficiency of the purification is such that after a 14-month operation with warm regeneration circuit there were no signs which would have indicated the necessity of deriming the plant.

In the CO_2 adsorbers, hydrocarbons such as acetylene are also retained down to a small fraction of their initial concentration, even under severe conditions. There are two reasons for this excellent purification effect of the warm-desorbed adsorbers: first, carbon dioxide is present in air in far higher concentration than

hydrocarbons. The adsorbers are sized for the carbon dioxide and desorbed daily, i. e., after a comparatively short period. Second, the silica gel adsorbs, for instance, acetylene much more than carbon dioxide. Acetylene even displaces carbon dioxide from gel with the result that the adsorbers are of tremendous size if one considers only acetylene. The same is true for hydrocarbons of higher molecular weight, alcohols, ketones, and similar compounds. The conditions are almost the same for C_4, C_3, and C_2 hydrocarbons, but not for methane. However, methane is comparatively harmless in an air-separation plant. NO together with its product of oxidation NO_2 is also retained in the adsorber. It is probably safe to say that no system of air separation for the production of gaseous oxygen has a higher degree of safety against damaging effects of air pollution, than the system described here. The degree of safety is at least the same as in liquid-oxygen-producing plants.

It would be possible to regenerate the adsorber without additional cold loss, and projected plant modifications will make use of this step. For this purpose the cold, impure nitrogen fraction will be sent through the saturated, cold adsorber in the opposite direction to the air. The gas picks up carbon dioxide from the silica gel. As much carbon dioxide as the gas has carried away may again be adsorbed from the air in the next period. The air outlet end of the adsorber is completely purified from carbon dioxide which, in the following adsorption period assures practically complete removal of carbon dioxide from air. This has been proven by extended research studies in an industrial tonnage oxygen plant. Acetylene concentrations behind the adsorbers will be slightly' higher than with warm desorbed adsorbers, but these traces are removed in the acetylene adsorber 4. The service period of the cold-desorbed adsorbers will be shorter, for instance, 3 to 4 hr. It then pays to have automatic switching. In designing the heat exchanger A it is necessary to interrupt the impure nitrogen flow at the temperature of the adsorbers, and to pipe the impure nitrogen to the adsorber and back to heat exchanger A, where the nitrogen-carbon dioxide mixture is further warmed up to ambient temperature. The blower-circuit K is then omitted. Automatic switching frees operators from changing the adsorbers. This should be of greater importance than saving the small cold losses involved with warm desorbing.   # #