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Some Issues in Operating Adsorption Prepurification Systems for Cryogenic Air Separation

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ABSTRACT

The paper outlines the operational aspects of a typical prepurification unit associated with a cryogenic air separation plant. The factors which may cause loss of performance are discussed. These include adsorbent degradation, feed impurity levels, moisture ingress, and regeneration aspects. Understanding these factors should improve the efficiency of the system.

INTRODUCTION

Air purification prior to its low temperature liquefaction or processing is an important step in the technology of cryogenic air separation. The purification step involves the removal of minor impurities such as water vapor, carbon dioxide, and potentially dangerous hydrocarbons. Although the air separation industry has employed several different methods to purify the air, the ability of adsorption-based systems to efficiently and economically remove the desired impurities have made them the most favored process option for air prepurification. In our previous publication (1), we discussed some of the main elements of the design philosophy employed in designing adsorption-based prepurification units (PPU). In this paper we discuss some of the operating issues associated with PPU operation.

With the increasing use of PPU on air separation plants, the operating experience has continued to grow. For example, some of the operational

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problems encountered over the years have ranged from those occurring simply as a result of lack of understanding of the fundamental adsorption process to those involving mechanical aspects of the adsorber vessel design. While the effect of some of the operating parameters (e.g., temperature, pressure, regeneration conditions, etc.) is generally understood, little or no information is available in the open literature on other important aspects such as the nature and causes of adsorbent degradation. The primary aim of this paper is to discuss some of the PPU aspects hitherto not fully understood and to show how PPU performance can be maximized by developing a deeper understanding of these issues.

ADSORBENT DEGRADATION

With the increasing number of PPU requiring large quantities of adsorbents, the useful service life of an adsorbent has become an important issue. There is little or no information available in the literature on adsorbent degradation, particularly in PPU application and how this can be minimized.

The two known mechanisms of sieve degradation in PPU application are hydrothermal degradation and the liquid water degradation. The basic nature of PPU operation makes the adsorbent extremely vulnerable to both types of degradation. For example, even in normal operation of PPU, conditions which may lead to hydrothermal degradation (i.e., high temperature-high humidity) exist in the bed. Liquid water carry over on the beds has also occurred in the past. These mechanisms of molecular sieve degradation were investigated in BOC's laboratory, and the resulting effect on CO_2 adsorption was measured.

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Hydrothermal Degradation

Hydrothermal degradation was simulated by regenerating an adsorber bed containing 13X molecular sieve using saturated air at atmospheric pressure and 200°C. The direction of regeneration was from top to bottom, i.e., downward. The bed showed about 60% loss in its adsorption capacity for CO_2. Samples of molecular sieve were taken from various locations in the bed. The samples were analyzed in a microbalance for their static CO_2 equilibrium capacity and their x-ray crystallinity. Figure 1(a) shows the CO_2 capacity of the degraded samples collected from different bed lengths. The figure reveals:

- Virtually negligible CO_2 capacity of the samples collected from the regeneration outlet region (top end of the bed)

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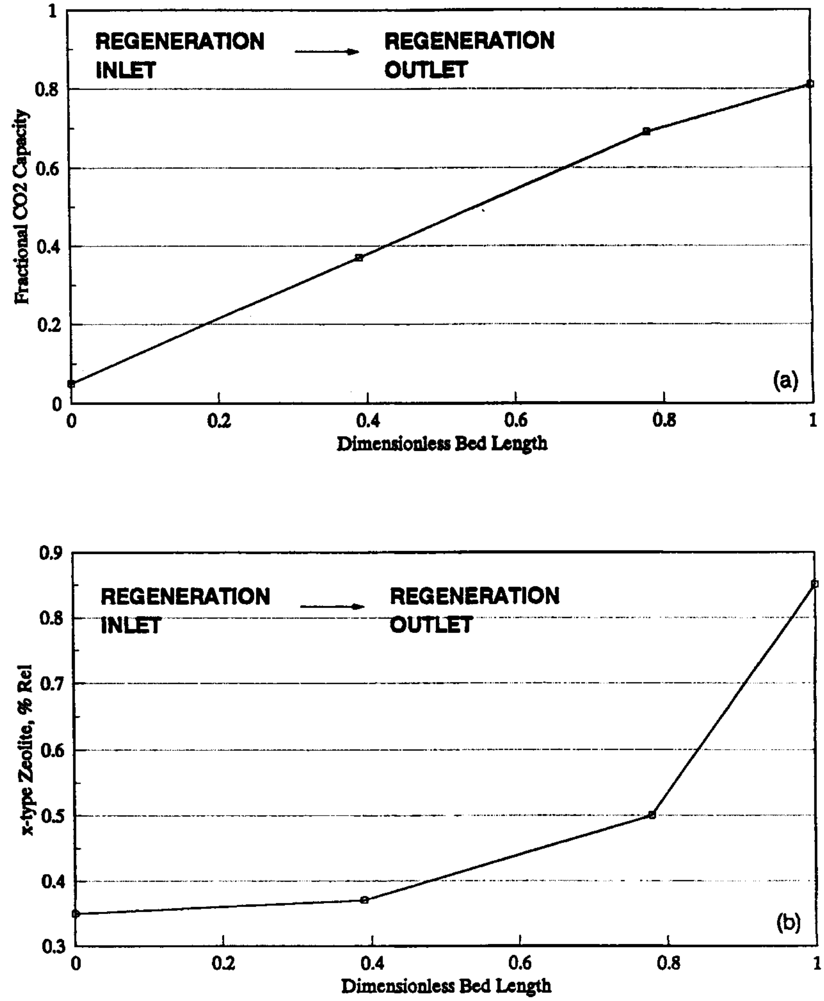

FIG. 1 (a) Capacity of hydrothermally degraded sieve. (b) X-ray crystallinity of hydrothermally degraded sieve.

- Slightly better capacity of the sieve located in the bottom area (regeneration inlet) of the bed; however, even these values are below the expected or reference values
- The capacities of the samples collected from intermediate positions in the bed were between the two limits set by the top and bottom samples

The above findings suggest that the loss in capacity of the sieve is progressive from top to bottom of the bed. The x-ray crystallinity data plotted in Fig. 1(b) confirm that the sieve suffered hydrothermal degradation progressively from top to bottom of the bed. The precursor to hydrothermal degradation appears to be the presence of high temperature/high humidity environments. There is now increasing evidence in the literature that hydrothermal degradation of sieve (particularly 13X type) could occur when it is heated to even moderate temperatures (about 200°C) in the presence of moisture. The results of Ruthven's (2) accelerated aging study of several different commercial samples of 4A and 13X sieves are shown in Fig. 2. Each sample was subjected to 725 2-hour cycles during which it was repeatedly saturated with water at room temperature and regenerated at 260°C. It can be seen from the figure that

- The deterioration is generally more severe for 13X
- Out of three samples of 13X tested, two showed about 27% reduction in equilibrium capacity

Another characteristic of the hydrothermally degraded sieve is that it may still continue to show good capacity for water even when its capacity

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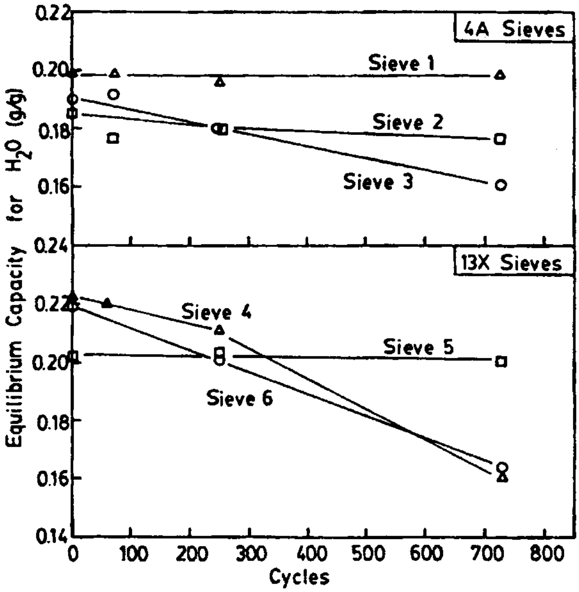

FIG. 2 Results of accelerated aging tests carried out with six different commercial molecular sieve adsorbents (4A and 13X) from Ruthven (2).

to adsorb CO_2 has virtually been lost. This is the reason why hydrothermal degradation is perhaps not as critical in dryer application as in PPU applications. Even in PPU applications, in an all-molecular-sieve bed for example, such degradation is expected in the water removal zone. However, as long as the degradation is confined to the water removal zone, it is unlikely to cause PPU underperformance.

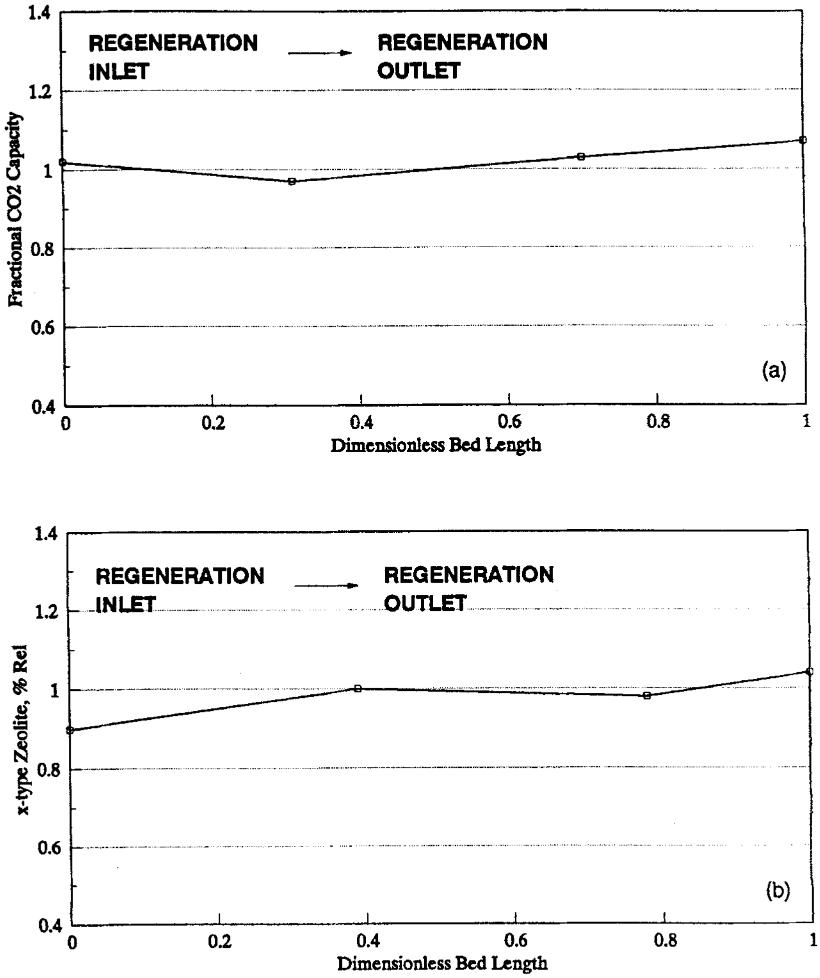

FIG. 3 (a) Capacity of liquid-water-degraded sieve. (b) X-ray crystallinity of liquid-water-degraded sieve.

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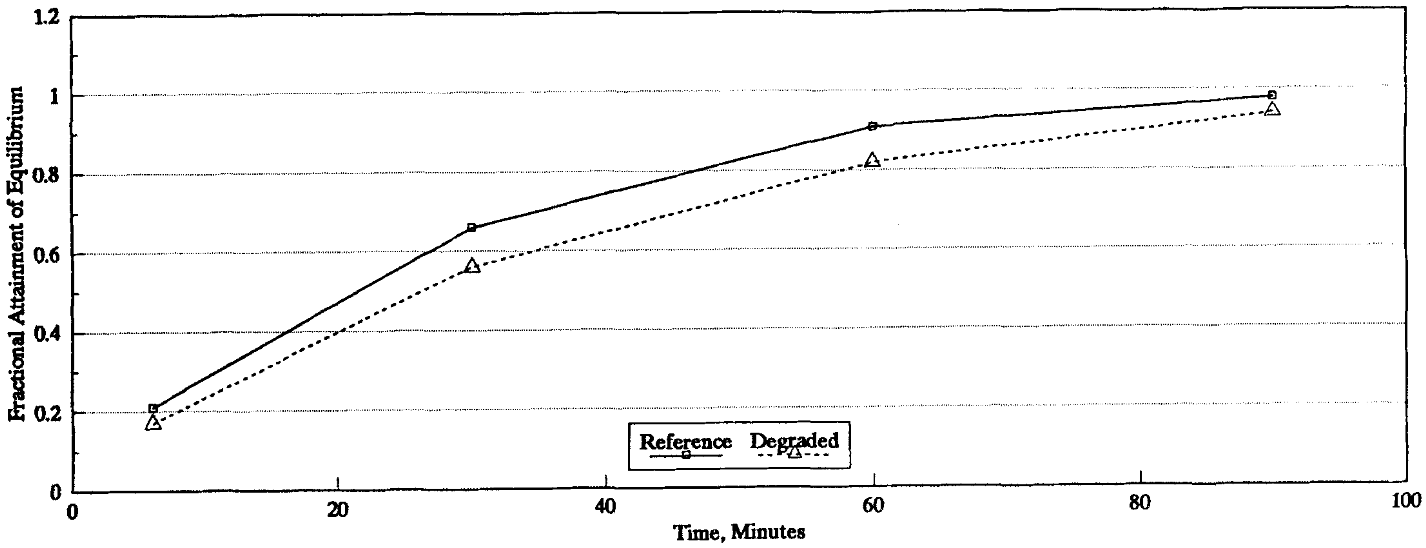

FIG. 4 CO_2 uptake by liquid-water-degraded sieve.

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Liquid Water Degradation

The liquid water degradation was studied by partially flooding the adsorber vessel with liquid water followed by draining of the water. The bed was first dried using dry nitrogen at low temperatures (70–100°C) and subsequently with nitrogen at high temperatures (200–275°C). The performance of the bed declined by about 35%.

Samples of molecular sieve were collected from different locations in the bed and analyzed for their CO_2 capacities. The results are plotted in Figs. 3(a) and 3(b). As can be seen, all the samples have CO_2 capacities about the same as the reference sample. The x-ray crystallinity data also suggests no evidence of hydrothermal degradation. Further tests revealed that the water-degraded samples were significantly slower than the reference sample in terms of their rates of CO_2 uptakes. As can be seen in Fig. 4, the degraded sample is about 24% slower than the reference sample after 6 minutes of adsorption. It is important to mention here that the residence time of air in a typical PPU bed is about 8–10 seconds. The slow uptake of CO_2 basically indicates that the material affected by liquid water will exhibit longer mass transfer zones than the normal or reference material, thus reducing the effective CO_2 capacity. To summarize, the degradation of 13X-type molecular sieve due to liquid water contact appears to be caused by increasing the mass transfer zone lengths of the sieve for CO_2 which could be the destruction of the internal microstructure of molecular sieve due to its contact with water.

ELEVATED FEED IMPURITY LEVELS

PPU designs generally assume the feed concentration of CO_2 to be 300–500 vpm. Small fluctuations from the design CO_2 concentration (i.e., ±20 vpm) generally do not pose any problem since the design margin provided should be adequate to cover this. However, if the CO_2 concentration is significantly higher (i.e., by 50 vpm or more), then this could affect the PPU performance.

The CO_2 content of air can fluctuate depending on the location of the plant. However, a major source of CO_2 is the regeneration vent, particularly during the period when the adsorbed CO_2 is being desorbed. The data of CO_2 measurement around the regeneration vent are shown in Fig. 5 over a period of 4 hours. The figure shows that after about an hour into the adsorption cycle, the CO_2 concentration in the area surrounding the regeneration vent starts to increase and peaks at over 1000 vpm. The CO_2 concentration remains high for a period of about 70–80 minutes before coming back to its normal value of about 360 vpm. Further analysis of

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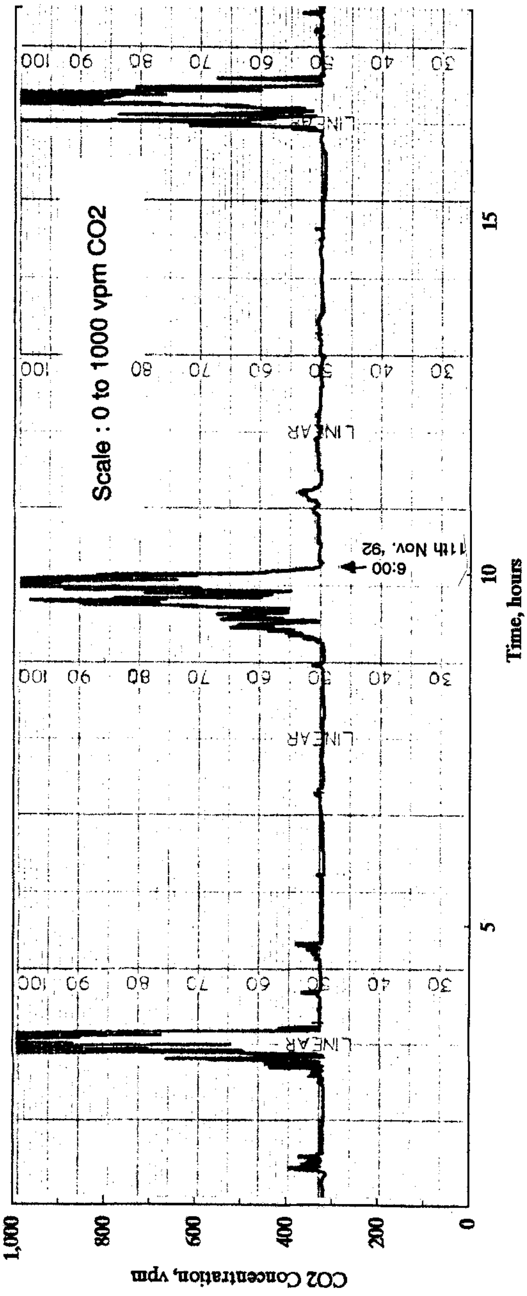

FIG. 5 CO_2 concentration in the area surrounding the regeneration vent.

the data suggests that the high CO_2 concentration occurs when the other bed is about 45 minutes into the heating cycle, the time at which most of the CO_2 is being desorbed and the vent regeneration gas can be expected to have high CO_2 concentration. For example, consider adsorption of CO_2 at 350 vpm in an airflow of 30,000 sm^3/h for a period of 6 hours. During regeneration, this amount of CO_2 is desorbed in about 1.5 hours using a regeneration flow of about 15% of the airflow. The CO_2 concentration in the regeneration flow during this period can be expected to be as high as 9500 vpm. Clearly, if the locations of the regeneration vent and the air intake of the plant are close enough or if there is the right wind direction, it is possible that the CO_2 concentration in the feed air would increase to a very high value, affecting the PPU performance.

If the regeneration heater is a natural gas fired heater and if the flue gas stack, though it may be at a higher elevation, is not very far from the air filters, the possibility of increased CO_2 levels due to stack emissions also needs to be considered. CO_2, being heavier than air, would tend to settle down and could increase its concentration in the area surrounding the air filters. The effect could be severe if there is no wind to diffuse it. However, if the flue gas is the principle source of CO_2 in the feed air, then the CO_2 concentration in the feed air should show an increase soon after the heater came on stream.

In both cases, attempts should be made to locate the CO_2 vent as far away from air intake as possible.

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MOISTURE INGRESS

In normal PPU operation, regeneration is always countercurrent to adsorption. The sieve located in the adsorption outlet region is therefore not expected to contain any moisture. The water removal zone in a PPU bed is located near the adsorption inlet. There are then only two main reasons for water ingress to the adsorption outlet region.

1. Contamination of regeneration gas with moisture. The effect would be twofold and cumulative, i.e., during the heating period the sieve will be subjected to high humidity high temperature conditions, and during the cooling cycle moisture adsorption on the sieve would occur, causing higher moisture levels in the subsequent regeneration step while at the same time reducing adsorption efficiency.
2. Bed depressurization in the direction of adsorption. The extent and length of the water front would depend on velocities during depressurization. However, results of our preliminary tests provide some evidence that PPUs using cocurrent depressurization would be more vulnerable to hydrothermal degradation.

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UNDERSTANDING REGENERATION

The regeneration behavior of beds is generally investigated by recording and analyzing the bed inlet and outlet temperature history during regeneration. The first objective is to confirm the adequacy of the regeneration step during normal PPU operation. The purpose of subsequent analysis of the data is to reduce the regeneration heat input while studying its effect on PPU performance.

Figure 6 shows a typical bed inlet and outlet temperature profile during regeneration with 130 minutes of heating and 180 minutes cooling. The bed outlet temperature profile in the figure clearly shows the presence of both CO_2 and water plateaus. The bed outlet temperature reached a peak value of about 138°C during the regeneration step (the bed inlet temperature during regeneration was 160°C). Regeneration temperature profiles shown in Fig. 7 indicate a different behavior. While the bed inlet temperature profile looks similar to the inlet profile of Fig. 6, the bed outlet temperature profile is different in that it shows three plateaus. The additional plateau is located between the normal CO_2 and water plateaus.

The presence of a third adsorbable component in the feed air can manifest itself in the form of an additional plateau if present in sufficient concentration. Since the additional plateau in Fig. 7 is located between the CO_2 and water plateaus, it can be argued that the plateau represents a

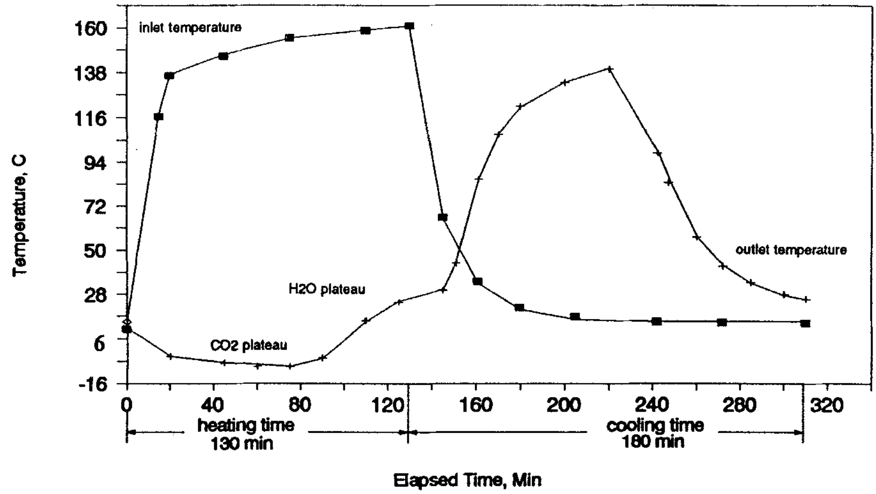

FIG. 6 Normal regeneration behavior.

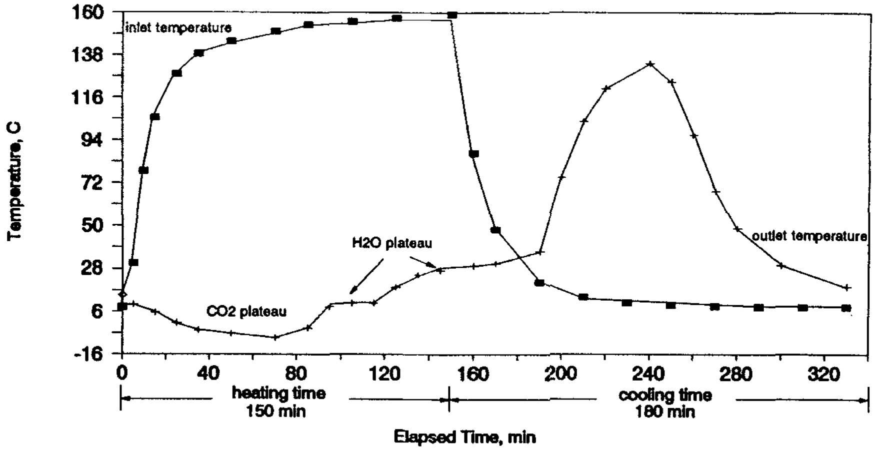

FIG. 7 Three-plateau regeneration behavior.

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component which is adsorbed between the CO_2 and water zones of the bed. However, an analysis of the feed air in this case did not reveal a high concentration of any other impurities, i.e., other than CO_2 and water.

The most satisfactory explanation of the presence of the third plateau is low temperature desorption of moisture before its normal regeneration. Since the regeneration stream flows in the opposite direction to the feed stream, the hot gas initially contacts adsorbent containing CO_2. It has been shown [Basmadjian (3)] that for a single trace component being desorbed into a hot purge stream, the temperature profile adopts the form of two temperature fronts, with the temperature of the leading front in the 38–50°C range. As the leading front advances through the bed, it reaches the water zone and causes water desorption at 38–50°C. Due to the desorption process, it splits once again into two temperature fronts with the leading front temperature at about 0–5°C. The leading front advances out of the bed, and the exit regeneration temperature remains at this temperature for a short period. This is the first plateau observed in the regeneration profile, and it is termed the CO_2 plateau.

The highest temperature front gradually advances as the CO_2 is desorbed until it arrives at the water zone (CO_2 desorption is complete). Here it merges with the intermediate front and desorbs water at higher temperature. This is accompanied by a rise in the exit temperature to a new plateau in the 25–35°C range. This plateau is termed the water plateau.

Usually the highest temperature front and the intermediate front are very close and merge before any appreciable water desorption occurs at the intermediate temperature. In such a case, only two plateaus are observed (Fig. 6). However, if there is a significant time difference between the two fronts, then appreciable water desorption occurs at the intermediate temperature and an additional plateau is observed in the outlet temperature profile (Fig. 7). The significant time difference between the fronts could occur due to longer adsorption time, for example.

CONCLUSIONS

There appear to be two mechanisms of sieve degradation with different effects on sieve properties. Hydrothermal degradation causes a severe decline in the CO_2 equilibrium capacity, which in turn results in a loss of PPU performance. Liquid water contamination in the absence of high temperatures, on the other hand, seems to have no effect on the CO_2 equilibrium capacity but seems to increase the mass transfer zone lengths.

The CO_2 concentration in the area surrounding the regeneration vent could be high during the period when the adsorbed CO_2 is being desorbed, leading to a significant reduction in bed capacity.

Moisture ingress in the adsorption outlet region could occur if the regeneration gas is contaminated or if cocurrent depressurization is employed. There is a potential risk of damaging the sieve due to hydrothermal degradation. The three plateau regeneration behavior can be attributed to a low temperature water regeneration front prior to normal regeneration.

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