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Gas Mixture Fractionation to Produce Two High Purity Products by Pressure Swing Adsorption

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Abstract

Pressure swing adsorption processes have been traditionally used to produce one high purity gas stream from a gas mixture. One of the most common uses of this technology is in the production of ultrahigh purity hydrogen from various gas streams such as steam methane reformer (SMR) off-gas. However, many of these gas streams contain a second gas in sufficiently high concentrations, e.g., carbon dioxide in SMR off-gas, that the recovery of this secondary gas stream along with the primary product is extremely desirable. A new pressure swing adsorption (PSA) process, GEMINI-8, has been developed at Air Products and Chemicals, Inc., to achieve this goal. Process cycle steps for the GEMINI-8 PSA process are illustrated by SMR off-gas fractionation for the production of hydrogen and carbon dioxide. Capital and power savings of this process as well as other advantages compared with the previous technology are discussed.

INTRODUCTION

Carbon dioxide and hydrogen are major commodity chemicals both in the United States and around the world. Large hydrogen consumers include petroleum refineries, methanol producers, other chemical manufacturers, and metal industries. In the past, refineries were generally net hydrogen producers while most of the remaining hydrogen requirements were served by the merchant market. Recent demands for reformulated gasolines and low sulfur diesel fuels to meet increasingly stringent environmental regulations combined with poorer quality crude oils as feed have increased the hydrogen requirements of many refineries, turning them into net hydrogen consumers. These trends have produced an expanding market for merchant hydrogen.

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Gaseous carbon dioxide is a building block in the manufacture of agricultural chemicals. It is also injected into oil wells for enhanced oil recovery (EOR). In liquid or solid form it finds wide use in the beverage and food industries.

The majority of on-purpose hydrogen production (as opposed to off-gas purification) involves the reaction of natural gas and steam at high temperature and pressure over a catalyst in the steam methane reforming process (SMR). The principal reaction products are hydrogen, carbon dioxide, and carbon monoxide. The reactor effluent is saturated and also contains unreacted methane as well as any nitrogen that entered with the natural gas. Carbon monoxide is further reacted with water over a shift catalyst to produce more hydrogen and carbon dioxide. The resulting effluent, after cooling, typically contains about 75% hydrogen and about 20% carbon dioxide with traces of carbon monoxide, methane, nitrogen, and water.

Pressure swing adsorption (PSA) processes have become the purification process of choice for high purity hydrogen production from SMR off-gas. These processes (*1*) use multiple vessels filled with an adsorbent(s) that is selective for all the impurities in the feed stream over hydrogen. Because of this selectivity, the impurity level, which is typically about 25% in the feed to the PSA, can be reduced to a few parts per million (ppm) in the hydrogen product. A typical cycle includes a feed (adsorption) step, one or more pressure reduction steps, a purge step, and one or more repressurization steps. Multiple beds are required to allow several regeneration steps to be carried out simultaneously with the feed step. The waste stream, which contains all of the incoming impurities as well as some hydrogen, is recycled as low grade fuel for the burners that fire the steam methane reformer. Feed pressure will often be equal to the pressure of the natural gas, while the hydrogen product will be slightly less and the waste or fuel stream will be in the range 5 to 15 psig. The feed temperature will depend on the temperature of the available cooling water (probably about 80 to 100°F).

The PSA process described above allows the recovery of only one relatively pure component. In the past, when carbon dioxide was also recovered as a pure product, either a physical or chemical absorption process was used. Examples of this type of process include monoethanolamine (MEA) and hot potassium carbonate (Benfield, Catacarb). These absorption processes have high capital costs and high maintenance requirements because of the relatively high operating temperatures combined with the corrosive nature of the solvents. Additionally, significant energy is required for regeneration of the solvents. Therefore, a separate process scheme for CO_2 recovery combined with a H_2 PSA system for H_2 were needed when both H_2 and CO_2 production was required.

Lately, there has been some theoretical discussion in the literature (*2–4*) concerning the recovery of two products from a multicomponent gas mixture via adsorption only. However, the first commercial process was announced by Air Products in mid-1980s (*6*). The GEMINI-9 process, introduced in 1986 as an economically attractive alternative to the above-described absorption–adsorption system, was demonstrated at an on-site plant at Butler, Pennsylvania (*5*, *7*).

GEMINI-9 PROCESS

As the name implies, the GEMINI-9 process contains 9 beds. Six of these beds (A beds) are packed with Na-X zeolite which selectively removes carbon dioxide from the feed gas. The remaining three beds (B beds) are packed with a combination of Na-X and Ca-A zeolites which selectively remove the remaining traces of carbon dioxide as well as the feed carbon monoxide, methane, and nitrogen. A flow schematic of the process is shown in Fig. 1, and the process cycle is outlined in Fig. 2. A detailed process description is given elsewhere (*5–7*).

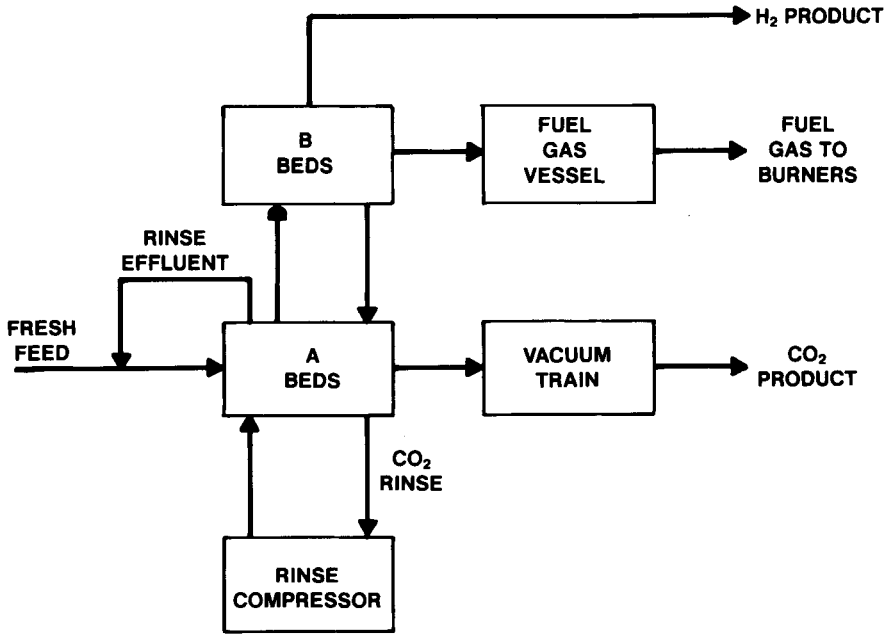

FIG. 1. Flow schematic for the GEMINI-9 process.

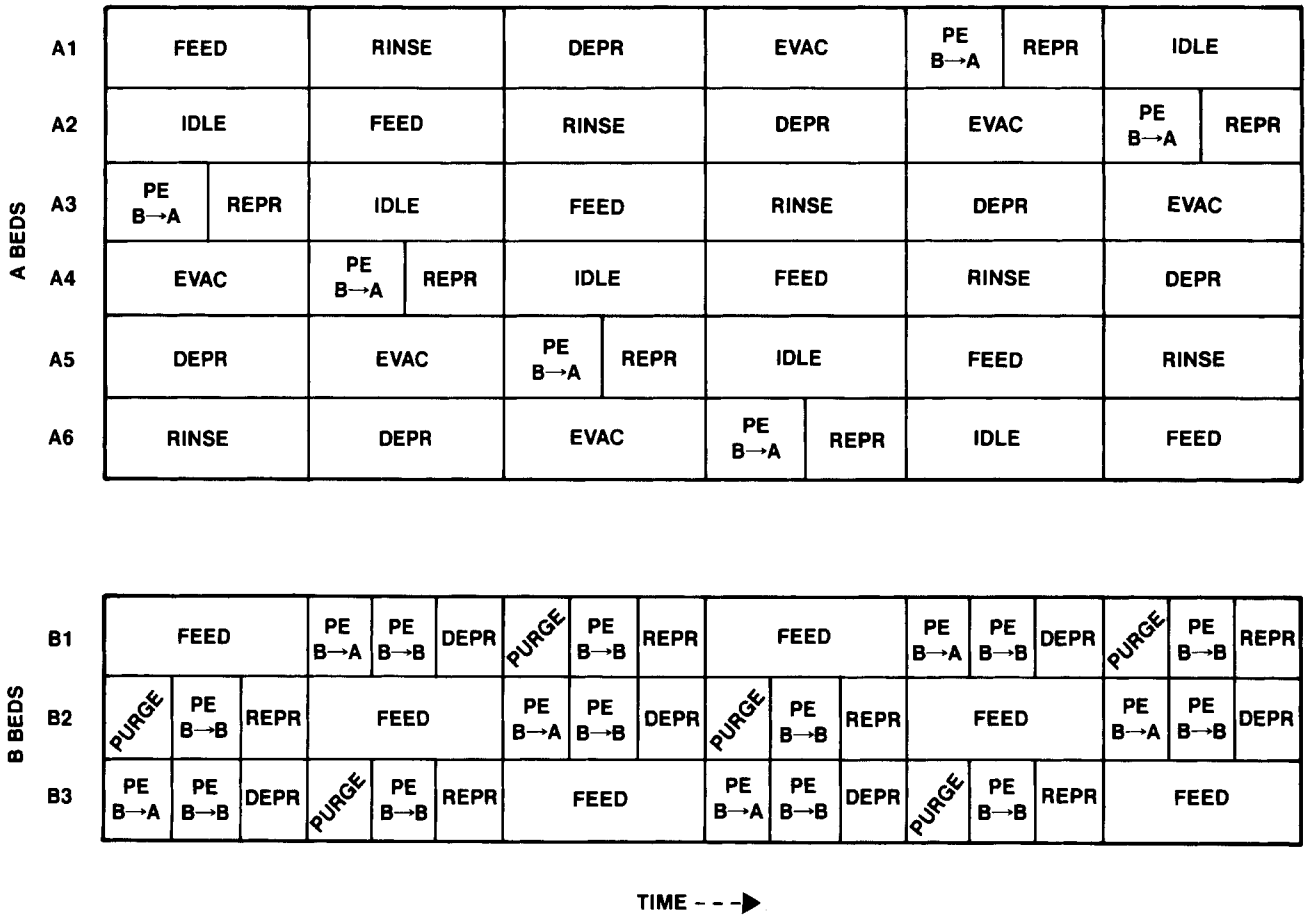

FIG. 2. Process cycle steps for the GEMINI-9 process.

OPERATING DIAGRAM

Operation of the A beds in the GEMINI-9 process can be depicted with the help of the equilibrium isotherms in Fig. 3. At the end of the feed step the A beds are at point 1 on the feed isotherm. In the next step, the beds are rinsed with high pressure, high-purity CO_2. At the end of this step the A beds are at point 2 on the pure carbon dioxide isotherm. The A beds are then depressurized to point 3, and the depressurized gas is recompressed and used as the rinse gas for the high pressure rinse step. The A beds are then evacuated to point 4, and carbon dioxide desorbed between points 3 and 4 constitutes carbon dioxide product. Since the adsorbent is saturated with pure carbon dioxide at the end of the high pressure rinse (point 2 on Fig. 3) and the depressurization (point 3 on Fig. 3) steps, carbon dioxide product obtained during the evacuation step (between points 3 and 4 on Fig. 3) is of very high purity. However, this is achieved at the cost of compressing the depressurized gas, obtained between points 2 and 3 on Fig. 3, and recycling this as the high pressure rinse gas between points 1 and 2 on Fig. 3.

Mathematical modeling of the depressurization step (*8*) revealed that gas phase concentration of the more strongly adsorbed species increases as the pressure in an adsorbent bed is decreased. This is qualitatively shown in Fig. 4. This leads to the elimination of the expensive high pressure rinse step from the GEMINI-9 process. As shown on the operating diagram in

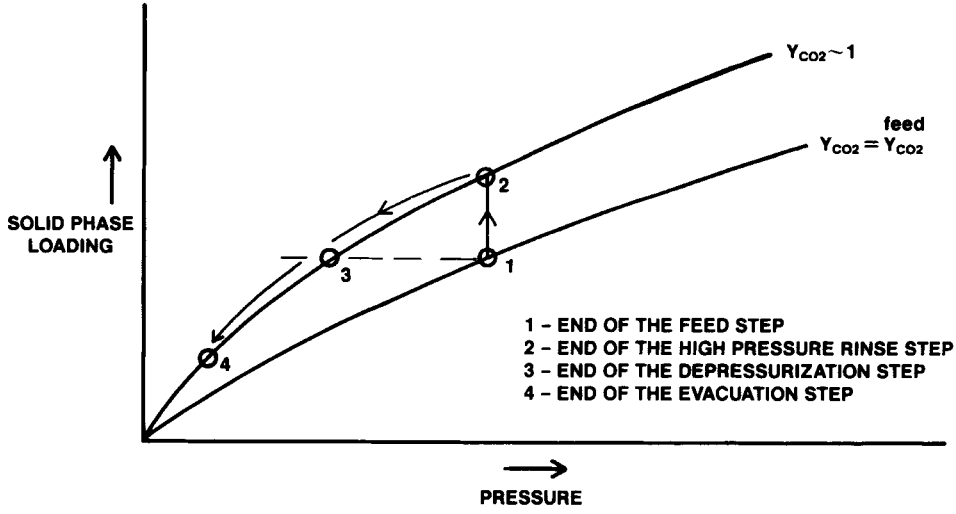

FIG. 3. Operating diagram for the GEMINI-9 A beds.

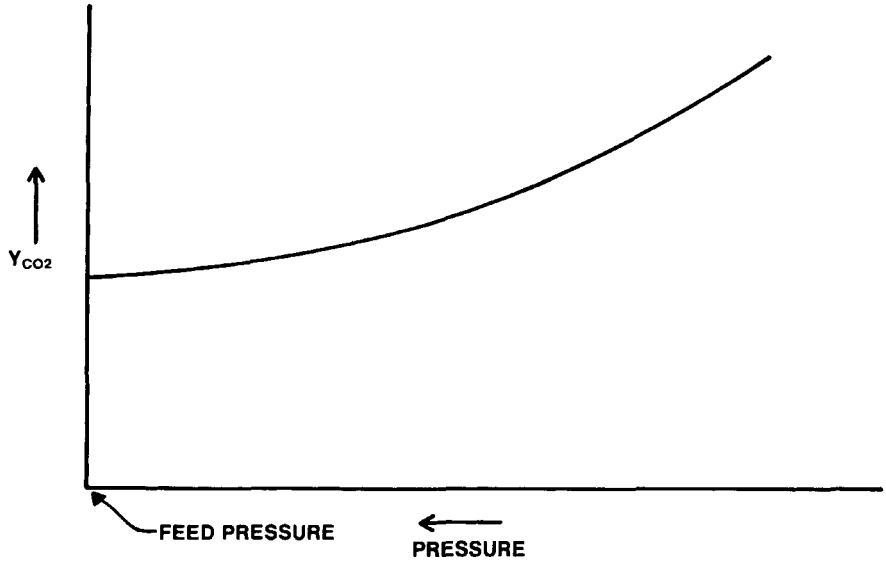

FIG. 4. Depressurization effluent from an adsorbent bed.

Fig. 5, if the A beds saturated with feed gas at point 1 are directly depressurized to point 2, the gas phase concentration of carbon dioxide increases to high levels. This bed is then evacuated to point 3, and the gas desorbed between points 2 and 3 constitutes carbon dioxide product. Due to high selectivity of carbon dioxide over hydrogen, the purity of the evacuated gas is high enough for most practical applications. The concentration level of carbon dioxide in the evacuated gas can be further increased, if desired, by choosing a higher selectivity adsorbent, higher feed pressure, or higher concentration of carbon dioxide in feed gas (*8*). To enhance carbon dioxide recovery, the depressurized gas, obtained between points 1 and 2 on Fig. 5, is compressed and recycled to the feed.

Since the bed at the start of the depressurization step is saturated with feed gas rather than with pure carbon dioxide as in the GEMINI-9 process, the quantity of recycle gas which has to be compressed in this cycle is much smaller than the quantity of high pressure rinse gas which had to be compressed in the GEMINI-9 cycle. This results in net savings and the new state-of-the-art GEMINI-8 process.

GEMINI-8 PROCESS

This process contains four A and four B beds. A flow schematic of the process is shown in Fig. 6, and a process description based on the cycle chart in Table 1 is given below.

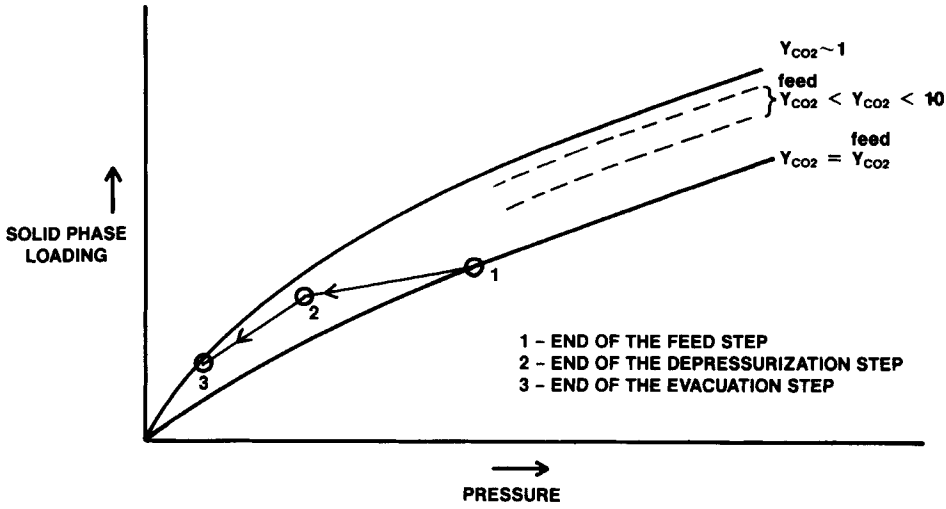

FIG. 5. Operating diagram for the GEMINI-8 A beds.

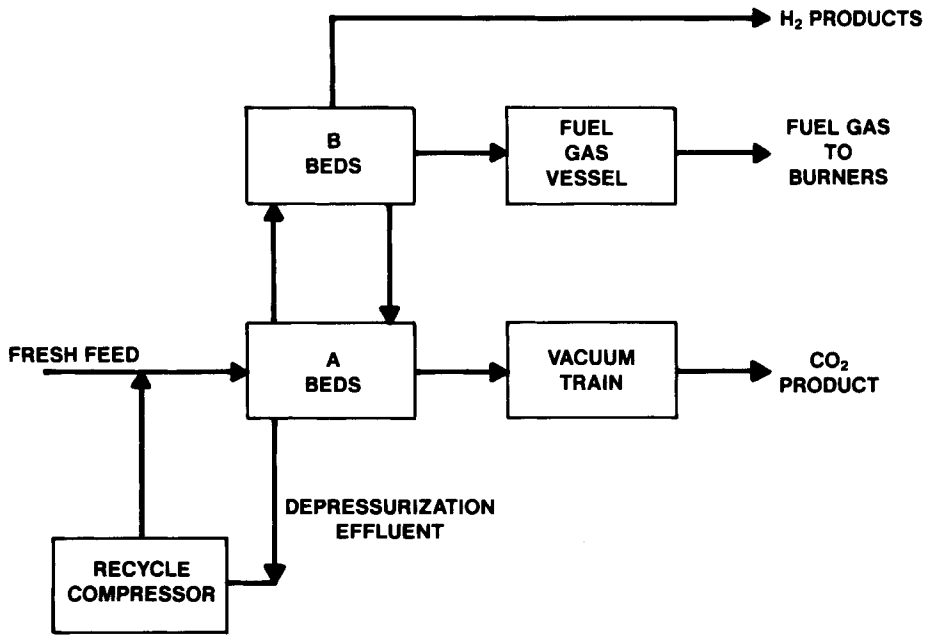

FIG. 6. Flow schematic for the GEMINI-8 process.

TABLE 1
Process Cycle Steps[a]

Time period	Bed							
	A1	A2	A3	A4	B1	B2	B3	B4
1	A	PE1	EV	DP	A	PU	I	PE1
2	A	I	EV	DP	A	PE2	PU	PE2
3	A	RP	EV	DP	A	RP	PU	DP
4	A	RP	EV	DP	A	RP	PU	I
5	DP	A	PE1	EV	PE1	A	PU	I
6	DP	A	I	EV	PE2	A	PE2	PU
7	DP	A	RP	EV	DP	A	RP	PU
8	DP	A	RP	EV	I	A	RP	PU
9	EV	DP	A	PE1	I	PE1	A	PU
10	EV	DP	A	I	PU	PE2	A	PE2
11	EV	DP	A	RP	PU	DP	A	RP
12	EV	DP	A	RP	PU	I	A	RP
13	PE1	EV	DP	A	PU	I	PE1	A
14	I	EV	DP	A	PE2	PU	PE2	A
15	RP	EV	DP	A	RP	PU	DP	A
16	RP	EV	DP	A	RP	PU	I	A

[a]A = Adsorption.
DP = Depressurization.
EV = Evacuation.
PE1 = First pressure equalization.
PE2 = Second pressure equalization.
PU = Purge.
RP = Repressurization or final pressurization.
I = Idle.

A Beds

Feed (Adsorption) Step

The feed gas to the A bed is the reformer effluent after it has been catalytically shifted for minimum carbon monoxide and maximum hydrogen and carbon dioxide. This feed typically contains about 75% hydrogen and 20% carbon dioxide with trace amounts of the other components. However, this composition may vary somewhat depending on the operating conditions of the reformer. The feed pressure is generally equal to the natural gas feed pressure to the reformer. The required product hydrogen pressure is usually relatively high so the GEMINI-8 cycle is run at the reformer pressure to minimize product compression costs. Feed temperature will be set by the temperature of the available cooling water. During the feed step, the effluent from an A bed continues to a B bed which is

also in the feed step. This step is continued until carbon dioxide is just beginning to break through to the B bed and then concluded to minimize carbon dioxide loss in the waste stream from the B bed. At the end of the feed step the void gas composition in the A bed is essentially the feed composition. The adsorbed phase is primarily carbon dioxide.

Depressurization

The bed is then depressurized cocurrently from the feed pressure to atmospheric pressure. The effluent from this step is compressed and recycled as feed to another A bed. Recycling of the depressurized gas is responsible for the high recovery of both H_2 and CO_2 products from this process.

Evacuation

This is the step that produces high purity carbon dioxide (97+%) product. The bed is connected to the suction of the vacuum blowers to reduce the bed pressure below atmospheric. The vaccum system is a series of rotary lobe type gas blowers. The primary impurities in carbon dioxide product are hydrogen and water and traces of carbon monoxide, methane, and nitrogen.

Pressure Equalization and Repressurization

The evacuated A bed is connected to a B bed that has just completed an adsorption step. This pressure equilization reduces the void gas (containing a substantial fraction of hydrogen) that is lost during the subsequent B bed depressurization and improves the hydrogen recovery of the process. Finally, both an A and B bed are repressurized to feed pressure with some of the hydrogen effluent from the B bed on a feed step.

B Beds

Feed (Adsorption) Step

The effluent from the A bed during the feed step described above passes directly to a B bed in series. A typical feed composition might be 94% hydrogen, 2% carbon dioxide, 3% methane, 0.5% carbon monoxide, and 0.5% nitrogen. The exact composition will depend on the operating conditions of the reformer which set the feed conditions to the A bed. The impurities are selectively adsorbed and the effluent from the B bed is the high purity hydrogen product. With this cycle, impurity levels are low as 5 to 10 ppm can be achieved at economical levels of production. As mentioned before, the feed step ends when carbon dioxide begins to break

through from the A to the B bed. The hydrogen purity is controlled by the amount of hydrogen purge, as will be explained later.

B Bed to A Bed Equalization

At the end of the feed step the B bed is connected to an A bed that has just completed an evacuation step for pressure equilization. In this way some of the void gas in the B bed is saved, preventing loss of some of the void hydrogen during the subsequent depressurization step.

B Bed to B Bed Equalization

Following the B to A equalization, the same B bed is connected to another B bed that has just completed the purge step and is at about 5 to 15 psig. Again void gas is saved in this step, further improving hydrogen recovery.

Depressurization

Finally, the B bed is depressurized countercurrently to the purge pressure. A fraction of the carbon monoxide, methane, and nitrogen impurities from the feed as well as some carbon dioxide are rejected in this step.

Purge

Next the B bed is purged countercurrently with some of the hydrogen effluent from the B bed on the feed step. The remaining impurities from the feed are rejected in this step, and the mass transfer zones are sharpened and moved to the inlet end of the bed. The purge effluent from this step and the desorption gas from the previous step are collected in a surge vessel and recycled to the reformer furnace as fuel for the burners. This vessel has an operating pressure of 2 to 7 psig and provides the fuel gas at constant pressure to the burners. The quantity of purge per cycle determines the hydrogen product purity. Since more purge gas is required to obtain higher product purities, hydrogen recovery declines as hydrogen product purity is increased. Almost invariably, the hydrogen product specification for carbon monoxide is less than 5 ppm because it is a poison for many of the catalytic processes where hydrogen is used. Methane and nitrogen, on the other hand, are inerts in many processes and relatively high levels are acceptable. The order of impurity breakthrough in this cycle is nitrogen followed by methane followed by carbon monoxide. Therefore, in cases where methane and nitrogen are acceptable in hydrogen product, hydrogen purge can be relaxed, increasing hydrogen recovery.

B Bed to B Bed Equalization and Repressurization

The final steps are equalization with another B bed and repressurization with a portion of the hydrogen effluent from a B bed on the feed step. During the countercurrent repressurization step, the repressurizing hydrogen acts as additional purge gas, further moving the mass transfer zones to the feed end of the B bed.

PROCESS DEVELOPMENT UNIT

The new GEMINI-8 cycle was tested in our labs in a process development unit (PDU). This unit contains a feed mixing station, a four-bed process section, associated analytical equipment, and the automation gear for process control, data acquisition, and data reduction. It was operated to demonstrate process feasibility, obtain process data for commercial designs, and determine the effect of process variables on process optimization.

The mixing station allowed flexibility in varying the feed conditions. The valve and piping layout were planned to minimize the void volume in relation to the adsorber beds. Although the PDU has only four beds, each bed follows the same steps as the equivalent bed in the cycle. Sufficient analytical equipment was provided to follow the concentration profiles of the products and of the intermediate internal streams.

Cycle sequence control and data acquisition and reduction were handled by the central process computer. "Real time" data were available during the runs to monitor the progress of each test. Tests were conducted using this unit to obtain design data for the GEMINI-8 process. The same PDU had been used previously to obtain GEMINI-9 design data (*7*). The measured product carbon dioxide purity with the GEMINI-8 cycle was 97+% compared to 99+% with the GEMINI-9 cycle. This purity is satisfactory for most gas phase applications and is suitable as a feed to a carbon dioxide liquifier.

PERFORMANCE COMPARISON

A summary of cycle performance for both the GEMINI-8 and GEMINI-9 processes is given in Table 2. Experimental results showed that the volume of desorbed gas in the GEMINI-8 cycle was 25 to 50% less than in the GEMINI-9 cycle. This translates to less power for the recycle compressor as well as a smaller compressor size.

An additional savings was found when the relationship between desorbed gas volume and composition was examined for the A bed. The first part of the desorbed gas is close to the feed gas composition. As desorption continues, the desorbed gas composition approaches that of pure carbon dioxide (Fig. 4). This means that the last fraction of the desorbed gas is

TABLE 2
Performance Comparison

	GEMINI-8	GEMINI-9
H_2 purity (mol %)	99.999	99.999
H_2 recovery (%)	86	87
CO_2 purity (mol %)	97.0+	99.0+
CO_2 recovery (%)	86	91
Relative compressor size	0.43	1.00
Relative compressor power	0.57	1.00
Relative vacuum blower power	0.86	1.00
Number of adsorbent beds	8	9
Number of switch valves	50	68

close enough to the evacuation gas composition so that it can be recovered as additional product. The power per unit of carbon dioxide product is reduced because more product is obtained per unit of vacuum power and the desorbed gas that is taken as product does not have to be recompressed for recycle to the feed. Also, the desorbed gas fraction with the highest carbon dioxide concentration is at the lowest pressure. Therefore, by not recycling this fraction of gas, a large amount of the recompression power is saved.

The number of A beds was reduced from 6 to 4 because of the elimination of one cycle step, and this resulted in improved communication with the B beds (Fig. 7). The number of B beds was increased from 3 to 4 to improve the cycle step matching between the A beds and the B beds. The elimination of one net bed resulted in a capital saving as compared with the GEMINI-9 process. As a result of the bed elimination and cycle step simplification, piping for the valve skid was less complicated (Fig. 7). The GEMINI-8 process requires 18 less switch valves than does the GEMINI-9 process, giving additional capital savings.

Another benefit of GEMINI-8 configuration is that it allows the elimination of a product surge tank which is required in GEMINI-9 to balance the hydrogen product flow over the course of the cycle.

DEMONSTRATION PLANT

A commercial on-site GEMINI-9 unit was designed with data from the PDU and installed at Butler, Pennsylvania, in late 1986. The PSA replaced a MEA/cryogenic hydrogen purification system which had been part of the original plant design in 1967. Startup time was minimal (about 1 week) because of the extensive test program that was completed in the lab prior to the beginning of the plant operations. Scaleup was in virtually one-to-

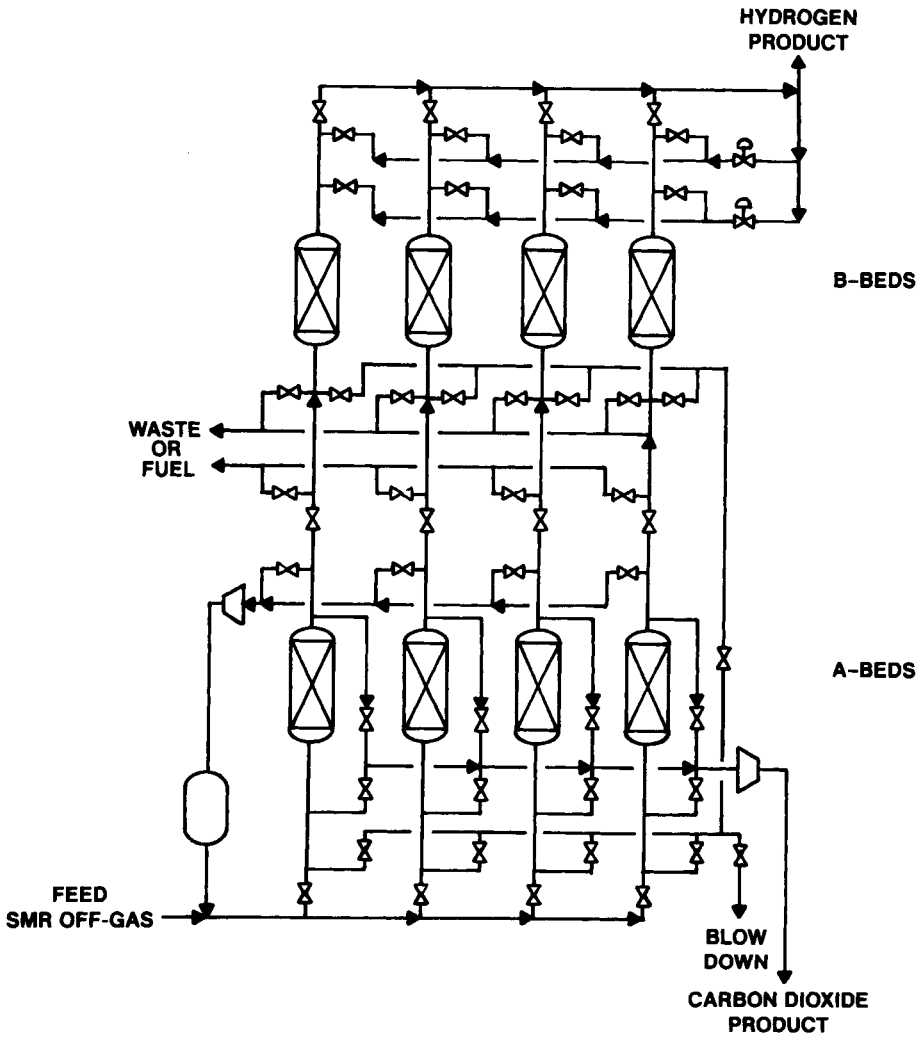

FIG. 7. Process schematic for the GEMINI-8 process.

one agreement for all aspects of the plant performance for the GEMINI-9 cycle. The principal customer for the hydrogen is Armco Specialty Steels Division (for heat treating of metal alloys), and Air Products also sells some hydrogen in the merchant market. The demand is quite variable, and the plant has demonstrated the ability to lower production efficiently as demand fluctuates. The GEMINI-8 cycle was also demonstrated in the

same plant. Scaleup was again in virtually one-to-one agreement with PDU data.

The plant is controlled by a programmable logic controller (PLC). The PLC is used to control plant turndown, shutdown, alarms, and process control and monitoring. The GEMINI cycles can operate over a wide range of feed conditions with turndown capability of 30% of design flow rate. The production rate is set by the total cycle time. The feed time is set by carbon dioxide breakthrough from the A beds. As this cycle time is adjusted, each step time is adjusted proportionately to maintain a balanced cycle. Methane concentration in hydrogen product is monitored continuously, and the purge gas quantity is adjusted to maintain the desired product purity.

CONCLUSIONS

A new process (*9*) has been developed to obtain two pure products from SMR off-gas. Experimental data confirm significant reductions in power requirement, equipment, and capital cost compared to the previous GEMINI-9 cycle that was developed for this application. The advantages of high hydrogen recovery and flexible operating conditions, which were features of the GEMINI-9 cycle, are retained in the new GEMINI-8 process.

All-in-all, the GEMINI-8 cycle results in lower power and lower capital than the GEMINI-9 cycle, at the insignificant cost of CO_2 product purity.

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REFERENCES

1. H. Stewart and J. Heck, Paper Presented at the 64th National AIChE Meeting, 1969.
2. P. Cen and R. T. Yang, *Sep. Sci. Technol., 20*(9&10), 725–747 (1985).
3. P. Cen, W. Chen, and R. T. Yang, *Ind. Eng. Chem., Process Des. Dev., 24,* 1201–1208 (1985).
4. S. J. Doong and R. T. Yang, *AIChE J., 32*(3) (1986).
5. W. C. Kratz, D. L. Rarig, and J. M. Pietrantonio, *Adsorption and Ion Exchange: Fundamentals and Applications* [*AIChE Symp. Ser., 84*(264)], 1988.
6. S. Sircar, "Separation of Multicomponent Gas Mixtures," U.S. Patent 4,171,206, (1979).
7. S. Sircar and W. C. Kratz, *Sep. Sci. Technol., 23*(14&15), 2397–2415 (1988).
8. R. Kumar, *Ind. Eng. Chem., Res., 28,* 1677 (1989).
9. R. Kumar, W. C. Kratz, D. L. Rarig, D. E. Guro, and W. P. Schmidt; U.S. Patent 4,914,218 (1990).

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