Experimental Study of Removing Trace H_2S Using Solvent Coated Adsorbent for PSA

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Application of compressed natural gas (CNG) as the fuel of motor vehicles will continue to grow. A key requirement for this application is the removal of trace content of H_2S from the fuel. A pressure swing operation was proposed to take the task. The key technique therein is to modify the ordinal adsorbents with a film of solvent. The dual modes of absorption by solvent and adsorption by the interior adsorbent provide a higher H_2S capacity than each mode alone and render the sorbent regeneration possible at ambient temperature. Experiments are performed on a two-column process to study the effect of operation condition on process performance. Consecutive cycling of the operation proves that the pressure swing technique can be used to remove the trace content of H_2S in practice, which represents a major breakthrough in natural gas purification technology. © 2006 American Institute of Chemical Engineers *AIChE J,* 52: 2066–2071, 2006
Keywords: natural gas, hydrogen sulfide, removal, pressure swing operation

Introduction

Removal of hydrogen sulfide from gas mixtures is an important industrial operation since a lot of organic and inorganic sulfuric compounds is usually contained in the fossil fuels (coal, petroleum, natural gas) and, hence, contained in their processing products. Hydrogen sulfide is the major contaminant of natural gas, especially after preliminary sweetening treatment. The content of H_2S in natural gas must be decreased to less than 6 mg/m^3 before feeding CNG (compressed natural gas) vehicles. However, the practical content is quite often higher than 100 mg/m^3 in some places. Apparently, removal of the trace H_2S contamination is an important and compulsive task of some NGV fuel stations. To protect the environment and save petroleum, the number of NGVs will continue to grow. Therefore, the purification task of natural gas becomes more important.

Conventional methods of removing H_2S from a gas mixture[1-4] are not suitable for the specified task because the content of H_2S is little, for which the adsorption technique is efficient.[2-7] However, the adsorbent saturated with H_2S cannot be regenerated at the ambient temperature.[8] Therefore, instead of PSA (pressure swing adsorption), TSA (thermal swing adsorption) must be adopted. However, TSA is not preferable because heating and heat-exchanging facilities must be included in the purification process, which leads to an increase in the fuel cost and quite often is unacceptable due to the limited space of the fuel station.

Instead of conventional solid adsorbents, a new kind of sorbent that covered with a liquid film was applied for a pressure swing operation to remove the trace H_2S contamination in the present study. Porous solids coated with a layer of liquid are usually used in chromatography.[9] The liquid layer functions as the separation agent and is named as the stationary phase, and the solid grains are named as the carrier. However,

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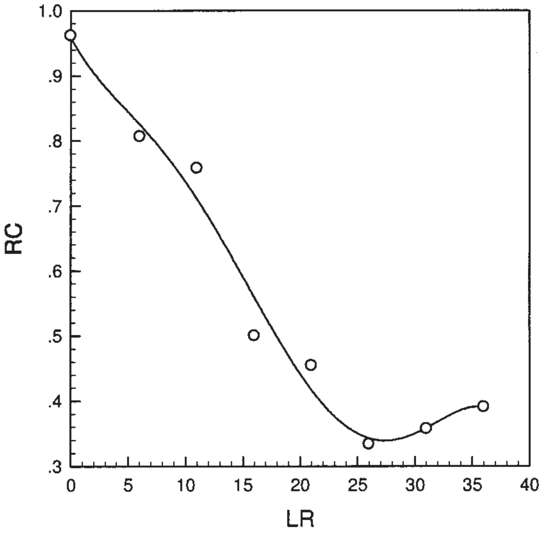

Figure 1. Effect of TEA-loading ratio on regeneration cost.

such packing material has never been applied for a PSA process previously. Chromatography usually operates in a batch manner and, therefore, is not preferable for large-scale production. PSA is a continuously operated process and, hence, is preferred. The liquid layer on the solid surface affords the sorbent better selectivity and may allow it to be regenerated easily. It was experimentally shown that such sorbent could be regenerated at ambient temperature, and the dual modes of absorption by the solvent and adsorption by the adsorbent provided a higher sorption capacity for H_2S than the solvent or adsorbent alone.[10,11] Performance of pressure swing operation relying on this kind of sorbent was experimentally studied presently. Operational condition of a two-column process was first determined, and the multi-cycle operation under the condition was performed at ambient temperature.

Experimental Procedures

The sorbent

The adsorbent used is mesoporous silica gel of particle size 0.28-0.45 mm provided by Qingdao Ocean Chemicals, China. Specifications of the product provided by the supplier include: bulk density 420 g/L; BET surface area 335 m^2/g; pore volume 0.85 ml/g; average pore size 8-10 nm. The physically adsorbed water in the silica gel was removed before experiments with heating in vacuum at 120°C. Solvent quantity in the sorbent is expressed in the loading ratio (LR), which is the percentage weight ratio of solvent to the adsorbent.

The solvent selected to coat the adsorbent must satisfy some requirements. First, it possesses the selective solubility of H_2S. Second, the solubility of H_2S is sensitive to the bulk gas pressure. Third, it possesses a high boiling point and is chemically stable. NMP (N-Methyl-2-Pyrrolidone) and TEA (triethanolamine) meet the condition. NMP is widely used as a solvent of removing H_2S in the absorption technology. The normal boiling point of NMP is 202°C. The solubility of H_2S in NMP is rather sensitive to its partial pressure. TEA has an even higher normal boiling point (360°C) and stronger basic property; therefore, it is more stable and shows larger H_2S capacity and is used in the present study. The sorption capacity of the sorbent for H_2S depends on the loading ratio of TEA.[11] Larger LR results in relatively high H_2S capacity, but the quantity of purified gas used for the regeneration of saturated sorbent is also high. Therefore, the ratio of sweeping gas over the purified gas is defined as the regeneration cost:

$$RC = \frac{t_r F_r}{t_a F_a}$$

where t_r is the time for thorough regeneration, F_r is the flowrate of sweeping gas, t_a is the breakthrough time, and F_a is the flowrate of feeding gas. The effect of loading ratio, LR, on RC is shown in Figure 1. Apparently, RC = 26 yields the least RC and, therefore, was adopted in the present study. Other operation conditions may also affect the regeneration cost, and the value of RC is used as an index of process performance for the selection of operation conditions.

The adsorption isotherm of H_2S on the selected sorbent at 298 K is shown in Figure 2 for the tested partial pressure range of H_2S. Compared to the isotherms on amine-modified silicas,[12] the range of H_2S partial pressure is the same, but the sorption capacity of the present sorbent is nearly 100 times less. It might be originated in the weaker basicity of TEA and the less specific surface area. However, the weaker basicity of the sorbent surface and the less sorption capacity allow the sorbent regeneration at the ambient temperature.

The testing process

The experimental process shown in Figure 3 consists of two columns, which are made of stainless steel of inner diameter 10 mm and length 250 mm. In each column, 11 g silica gel loaded 2.86 g TEA (LR = 26%) is packed in a section of length 230 mm. There are two passages for the feeding stream: one for pure methane (the purity is above 99.9%), and the other for the mixture of methane and H_2S with H_2S concentration 1340 ppm. The content of H_2S at the column entrance was maintained at 170 ppm by adjusting the flow rate in the two

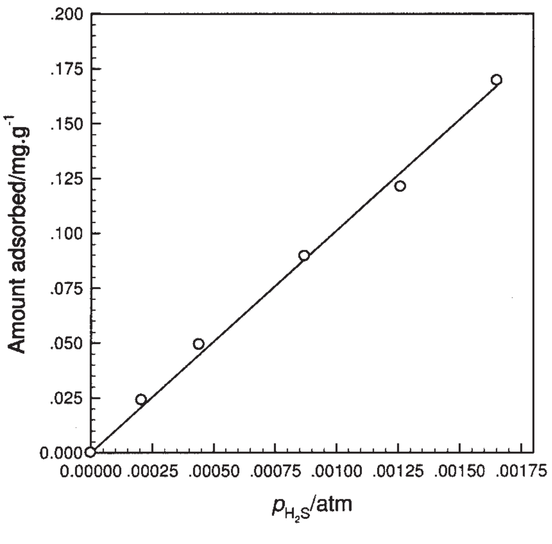

Figure 2. Adsorption isotherm of H_2S on the TEA-modified silica gel at 298 K (LR = 26%).

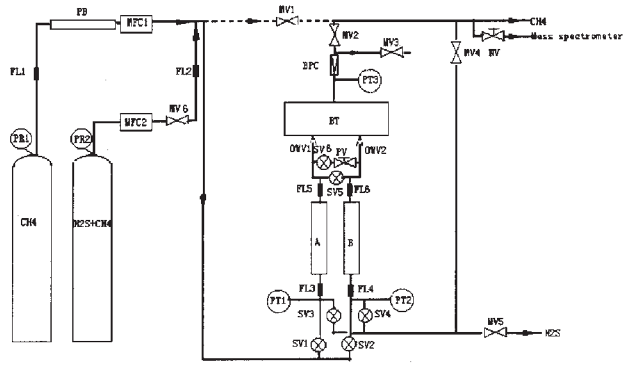

Figure 3. Experimental process with two columns.

PR: Pressure regulator; PT: Pressure transducer; FL: Filter; MFC: Mass flow rate controller; PB: Dryer bed; BT: Buffer tank for pure methane; OWV: One way valve; PV: Purging valve; MV: Manual valves; NV: Metering valve; SV: Solenoid valve; BPC: Backpressure controller.

passages. The volume of the buffer tank prepared for pure methane was 0.05 liter, and the feeding rate was kept at 400 cm^3/min. The consecutive steps included in an operational cycle were:

Re-pressurization (RP): Solenoid valve SV_1 opens, and a feeding stream flows into the column.

Adsorption (A): One-way valve OWV_1 opens when the column pressure becomes higher than the pressure of the buffer tank (BT) and adsorption starts. The valve SV_1 closes at the end of the adsorption step.

Pressure equalization (PE): Valve SV_5 opens at the time SV_1 closes, and the step of pressure equalization initiates at the exit ends of both columns.

Blowing down (BD): SV_3 opens and SV_5 closes at the end of the PE step. The column pressure decreases to the atmospheric.

Purge (PG): Valve SV_6 opens when BD ends, and part of purified gas from another column enters and counter-currently purges the column. The purging rate can be adjusted with changing the opening of valve PV.

Re-pressurization starts again after the purge step.

A computer program controlled the action of the solenoid valves and the mass-flow controllers via the LabCards. Composition of the gas stream was in-situ analyzed with a mass spectrograph. The process tests were performed at 290 K, and the effect of room temperature on the operation is later discussed.

The operation pressure

Operation pressure is the highest pressure of a pressure swing operation at which H_2S is taken up by the sorbent. An appropriate operation pressure must be determined for a given separation task and chosen sorbent. Breakthrough curves were collected at different pressures, and the result is shown in Figure 4, where c_0 and c are the concentration of H_2S in the feed and the exit stream, respectively. It is shown that higher pressure leads to longer breakthrough time, that is, larger capacity for H_2S. However, it also results in a smaller separation coefficient and higher energy cost. The effect of operation pressure on the regeneration cost, RC, is shown in Figure 5. Apparently, a moderate pressure, 0.43 MPa, is appropriate.

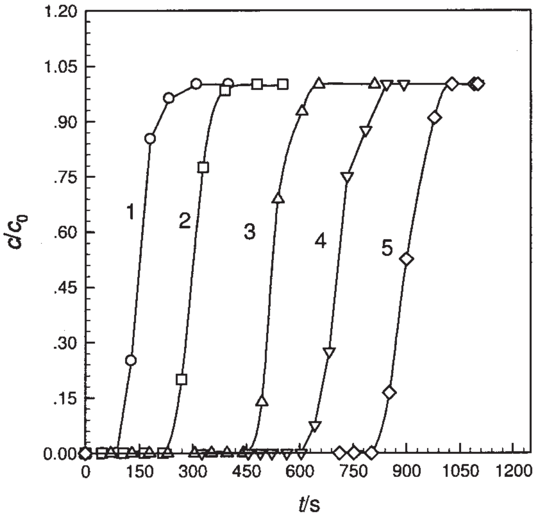

Figure 4. Effect of pressure on breakthrough times.

1: 0.1 MPa; 2: 0.22 MPa; 3: 0.43 MPa; 4: 0.63 MPa; 5: 0.83 MPa. T = 290.5 K; Feeding rate = 400 cm^3/min; C_0 = 170 ppm.

The purging ratio

How much product is used to purge the sorbent bed is an important operation condition. A larger amount is favorable for improving product purity, but product recovery will reduce. The quantity of purging gas is quantified by the purging ratio, defined as[13]:

$$\frac{P}{F} = \frac{Methane \cdot quantity \cdot in \cdot purging \cdot stream}{Methane \cdot quantity \cdot in \cdot feed \cdot stream} = \frac{Q_{PG}y_P}{Q_F y_F}$$

where Q is the flow rate and y is the molar fraction of methane. The subscripts PG, P, and F denote the streams of purging, product, and feed, respectively. The effect of P/F on performance is shown in Figure 6. While recovery unimodally de-

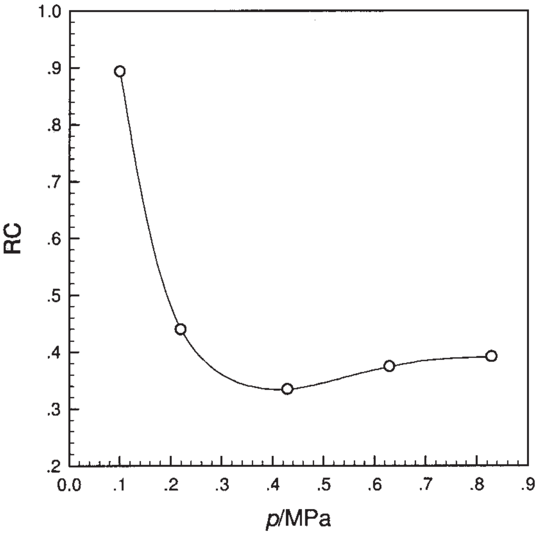

Figure 5. Effect of operation pressure on regeneration cost.

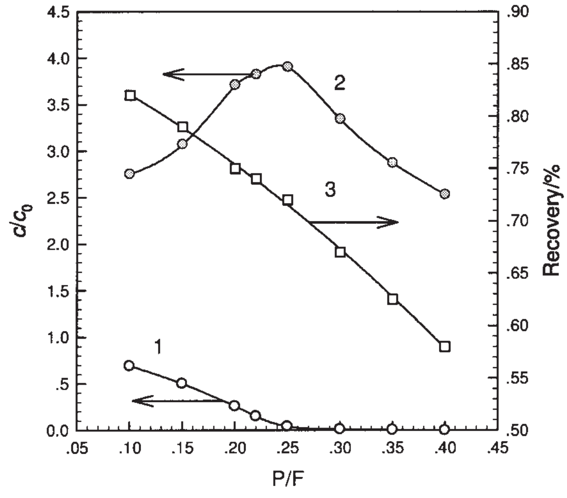

Figure 6. Effect of P/F on process performance.

1: H_2S content in product; 2: H_2S content in exhaust; 3: recovery. P = 0.43 MPa; $t_A = t_{PG} = 350$ s.

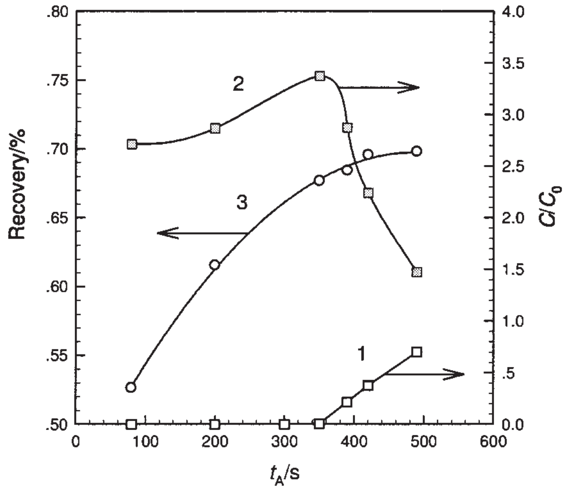

Figure 7. Effect of adsorption time on process performance.

1: H_2S content in product; 2: H_2S content in exhaust; 3: recovery. (P/F = 0.3, $t_{PE} = 2$ s, $t_A = t_{PG}$).

creases with the increasing P/F, the content of H_2S in the product does not change when P/F > 0.25. The content of H_2S in the exhaust stream reaches its maximal value at P/F = 0.25. It means that smaller P/F cannot totally get the sorbed H_2S off the sorbent, and larger P/F results in dilution of H_2S in the exhaust gas. Therefore, 0.25 is the critical value of P/F for the experimental condition. To guarantee the purity of the purified gas, P/F = 0.30 was selected in experiments and the content of H_2S in the product stream dropped to below 1 ppm.

Time allocation in an operation cycle

Adsorption Time (t_A). The time allocated for the adsorption step must be shorter than the breakthrough time at a chosen operation pressure; therefore, the adsorption time, t_A, should be less than 420 s, the breakthrough time for pressure 0.43 MPa. The length of the adsorption time affects the location of the front edge of the concentration profile in the sorbent bed and, therefore, affects the product purity. On the other hand, longer adsorption time leads to higher product recovery. The effect of adsorption time is shown in Figure 7. Although recovery increases with adsorption time, a saturation trend is shown on curve 3. Product purity will not be affected if $t_A < 350$ s; however, longer adsorption time will result in higher content of H_2S in the product. There is an optimal adsorption time (350 s) that allows the H_2S concentration in the exhausted gas to reach maximum, which corresponds to the maximal use of the sorbent bed. Therefore, 350 s was selected as the adsorption time.

Blow Down Time (t_{BD}). The column pressure drops down to the atmospheric in the blow down step. The length of blow down time may affect the extent of regeneration of the sorbent. Therefore, three different times, 0, 10, and 20 s, were tested for blow down and the effect is shown in Figure 8. For the times tested, the content of H_2S in the product and the exhaust varied for only 0.01, and the recovery varied for only 1%. Therefore, although the effect exists, it is not considerable, and the blow down time, t_{BD}, was set to zero in order to reduce the duration of an operation cycle. It means the purging step initiates as soon as the column pressure releases to atmospheric.

Purging Time (t_{PG}). Different purging time means different rate of purging stream for a chosen purging ratio. Two purging times were tested at conditions of: $t_A = 350$ s and $t_{PE} = 2$ s. The effect is shown in Figure 9. It is seen that longer purging time yields higher product purity, higher recovery, and higher H_2S content in the exhaust; therefore, it is preferable for the system. However, purging time cannot be longer than the adsorption time for the two-column process. Therefore, t_{PG} was set equal to 350 s. It is seen in Figure 9 that H_2S content in the exhaust gas reaches maximum at a lower value of P/F when the purging time is shorter; however, the maximal concentration is considerably lower than that reached by a longer purging time. The effect of purging time indeed reflects the effect of the purging rate, which must be compatible with the rate of desorption and diffusion.

Pressure Equalization Time (t_{PE}). The step of pressure equalization aims to increase the recovery of both product and

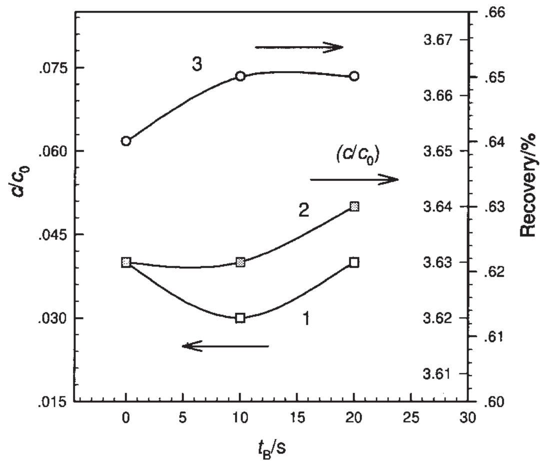

Figure 8. Effect of blow down time on process performance.

1: H_2S content in product; 2: H_2S content in exhaust; 3: recovery.

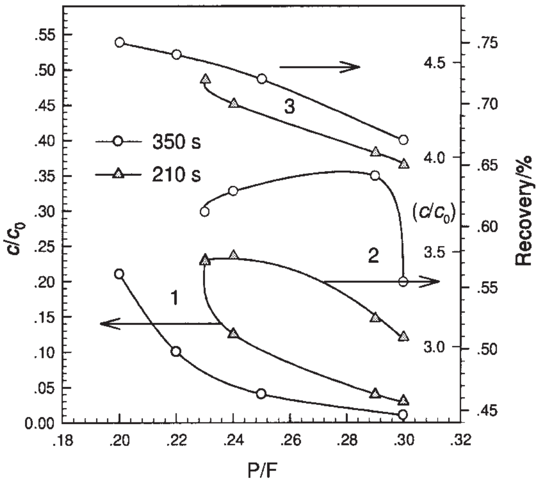

Figure 9. Effect of purging time on process performance.

1: H_2S content in product; 2: H_2S content in exhaust; 3: recovery.

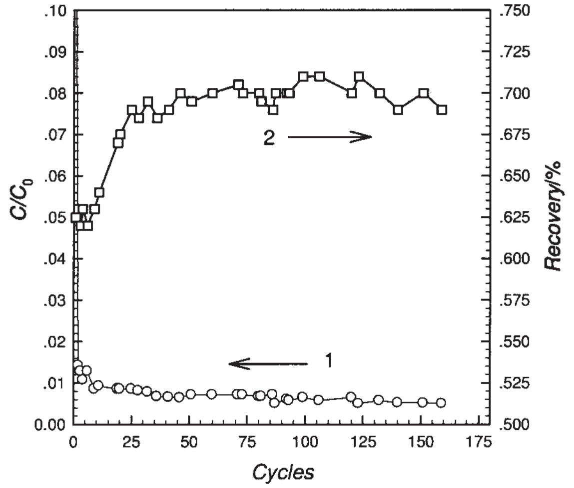

Figure 10. Process performance on continuous operation.

1: H_2S content in product; 2: recovery.

mechanical energy. However, too long a time for this step will cause desorption of H_2S, and too short a time will cause disturbance of the sorbent bed; therefore, an appropriate time allocated for pressure equalization is quite important. Different lengths of time, 2, 5, 10, and 20 s, were used as the pressure equalization time in experiments. The shortest time resulted in high recovery and high concentration of H_2S in exhaust, therefore, the pressure equalization time was set equal to 2 s.

Summary of Time Allocation. The period of an operation cycle lasted for 704 s, in which 350 s was allocated for re-pressurization and adsorption, 350 s for blowing down and purging, and 2 s for pressure equalization (twice a cycle).

Test on continuous operation

To test the operability of the pressure swing sorption process at ambient temperature, continuous operation was carried out for 160 cycles under the previously determined condition. Variation in product purity and recovery is shown in Figure 10. It is shown that product purity dropped to about 1 ppm after 5 cycles, and the recovery reached stable in about 30 cycles. Since there are only two columns operating in the process, the product purity and the H_2S concentration in the exhaust gas vary remarkably with time in a cycle, as shown in Figure 11. The content of H_2S in the product and the exhaust stream varies inversely. However, both concentrations will approach constant if more columns are included in the process.

Test on effect of environment temperature

It is known that environment temperature affects the performance of a PSA process.[14] This effect might be of special concern due to the coverage of solid adsorbent with a film of liquid solvent. For example, whether the process can or cannot operate for different places or different seasons. Therefore, variation of the sorption capacity with temperature and the regeneration performance at different temperatures were tested. Breakthrough curves were collected on a single column at temperatures of 253, 273, 290, 298, and 313 K. The sorbent and column packing were kept the same as mentioned in the previous section. The content of H_2S in the feeding stream was 190 ppm and the feeding rate was 280 Ncm^3/min. The column was purged with pure methane after being saturated, and the regeneration curves at different temperatures were obtained. The flow rate of the purging stream was kept at 100 Ncm^3/min. It was shown that higher temperature yielded shorter adsorption time and shorter purging time; therefore, shorter period of an operation cycle. Lower temperature yielded the opposite consequence, but pressure swing operation was still feasible.

Conclusion

It is demonstrated that a pressure swing sorption (PSS) process operated at ambient temperature can be used to remove the trace H_2S contamination due to the use of a solvent-coated adsorbent. Such adsorbent can be regenerated by pressure reduction and back-purge with the purified gas. The critical purging ratio in the present experiments is 0.25. A smaller

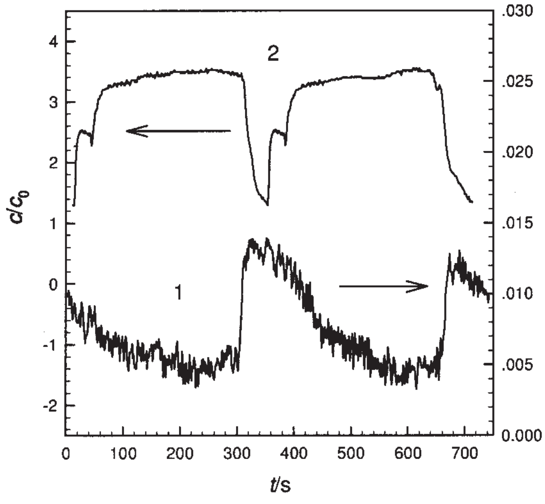

Figure 11. Recorded H_2S content in product (curve 1) and exhaust (curve 2) during a cycle.

purging ratio is possible if the mass transfer kinetics could be improved. Therefore, the new technique can replace the conventional thermal swing adsorption (TSA) mode of purification, which requires high temperature regeneration. This represents a major breakthrough in natural gas purification technology.

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