USE OF MOLECULAR SIEVES FOR AMMONIA PLANT FEED DESULFURIZATION

Based on performance over a 2 yr. period in a commercial plant, ability of sieves to consistently provide practically sulfur-free feeds can help operations in numerous ways.

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Steam reforming plants using natural gas for the preparation of ammonia synthesis gas can profitably increase their operating efficiency by using molecular sieves to remove sulfur compounds from the natural gas feedstock.

By removing the sulfur, catalyst efficiency is improved with the result that the overall methane leakage rate is minimized. This in turn results in lower utility costs due to lower temperature operation in the reforming section and a lower inerts purge rate in the ammonia recovery section. Other economic benefits are realized but since cost of the natural gas feedstock typically amounts to 30-60% of the total manufacturing cost, depending on plant capacity and natural gas cost, these savings alone can be quite worthwhile.

Data presented here on how molecular sieves are used to achieve feed gas desulfurization are based on successful commercial operating experience over a 2 yr. period. Comparative performance data for desulfurization with impregnated activated carbon are also presented.

Methane reforming highlights

More than 85% of the ammonia manufactured in the United States and Canada is obtained via the steam reforming of natural gas. With natural gas feedstock representing such a high portion of manufacturing cost, minimum methane leakage through optimum utilization of the steam reforming and shift catalysts reduces the feedstock requirements, fuel requirements, catalyst replacement costs, and ammonia production loss.

Highest catalytic activity is achieved by operating with a sulfur-free feed since the nickel-loaded reforming catalyst and the zinc loaded low-temperature shift catalyst are both poisoned by sulfur. Sulfur compounds entering the reformer cause a reversible poisoning of the steam reforming catalyst. If the operating temperature is increased to maintain a fixed methane leakage rate, the sulfur compounds tend to strip from the catalyst bed until an equilibrium condition is achieved, and pass on into the shift converter section of the plant.

Increased fuel consumption and shorter tube life result at the higher operating temperature. Poisoning of the expensive, low temperature shift catalyst is irreversible. As sulfur compounds enter the low temperature shift converter, efficiency of the catalyst to generate hydrogen decreases, increasing the load on the downstream methanation unit and raising the overall methane leakage. Replacement of the catalyst is eventually required to achieve low overall methane leakage.

How molecular sieves are used

Molecular sieves have a strong adsorption selectivity for such sulfur compounds as hydrogen sulfide, mercaptans, sulfides, and polysulfides in the presence of a light hydrocarbon mixture such as natural gas. Typical commercial applications include the desulfurization of reformer recycle hydrogen and isomerization feed to protect sulfur-sensitive catalysts in petroleum refining. Molecular sieves are employed by the natural gas industry for the removal of water, carbon dioxide, and sulfur compounds in natural gasoline plants, helium plants, and natural gas liquefaction plants. They are most frequently utilized by the process industries whenever an extremely low effluent contaminant level is required.

A typical dual bed natural gas desulfurization system utilizing molecular sieves is shown in Figure 1. While one bed is desulfurizing, the other bed is regenerated with hot fuel gas. A molecular sieve desulfurizer offers a number of economical and practical operating advantages. The sulfur compounds desorbed during regeneration are diluted by the purge gas and pass into the plant fuel system. This avoids the potential pollution problem caused by venting odorous sulfur compounds in concentrated form to the atmosphere. The plant energy balance is not disturbed since steam is not required for regeneration of the adsorbent beds.
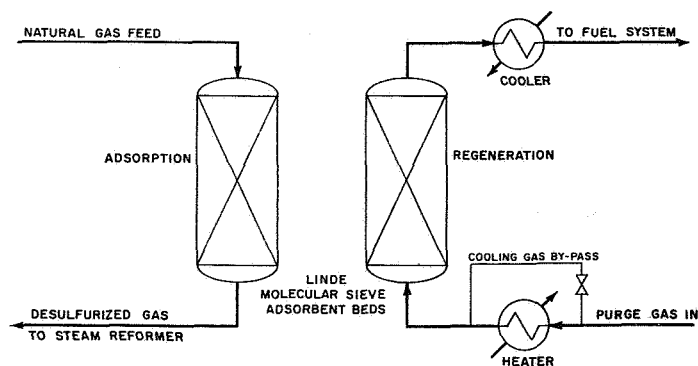

Figure 1. Feed gas desulfurization with Linde molecular sieves.

Equipment corrosion problems do not exist because steam regeneration is not used and because molecular sieves do not contain any kind of corrosive halide or metal activator. The sieve is used in a large enough particle size so there is no bed

movement or loss of bed packing at moderate gas velocities. Molecular sieves are inorganic and have no detectable vapor pressure even at temperatures in excess of the design temperature for the adsorption vessel and auxiliary equipment.

Commercial experience of units

Several molecular sieve natural gas feed desulfurizers have been in service in ammonia plants for the past few years. The performance data for one of these installations, a typical medium size modern ammonia plant, will be presented. The plant has all the major process units, i.e. natural gas desulfurization, primary and secondary reforming, high temperature and low temperature shift conversion, carbon dioxide removal, methanation, ammonia synthesis, and ammonia recovery. The plant went on-stream in May, 1966. Sieves have been used in the desulfurization section since start-up.

The dual-bed desulfurizer as shown in Figure 2 was designed to remove hydrogen sulfide, mercaptans, sulfides and residual sulfides (total sulfur measurements reported in this paper do not include carbonyl sulfide) to less than 0.5 ppm by volume total sulfur in the natural gas feed to the primary reformer. Each bed purifies for 48 hr. before being regenerated.
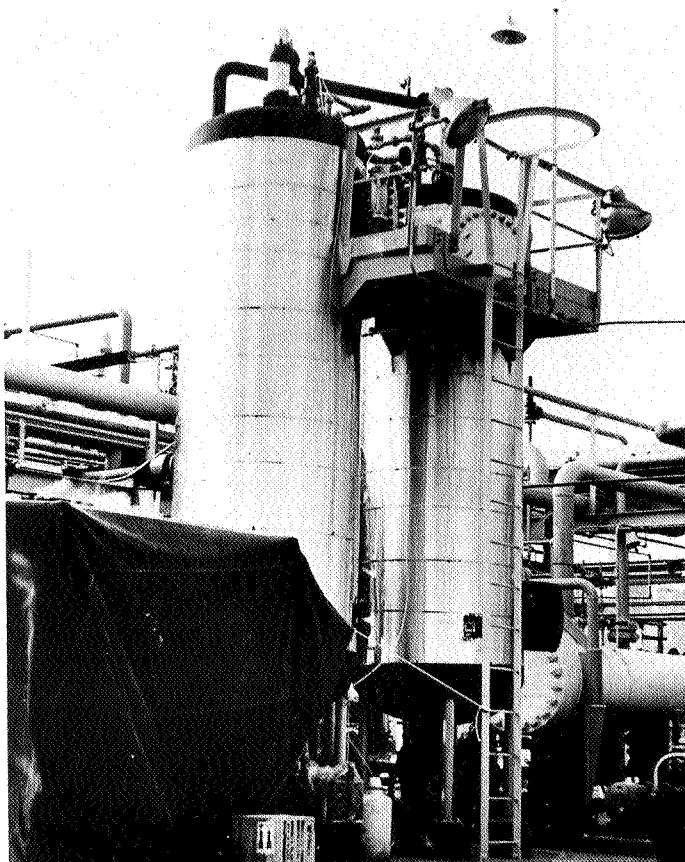

Figure 2. Molecular sieve used for ammonia plant feed gas desulfurization.

The feed gas composition in terms of hydrocarbon content and sulfur content fluctuates somewhat, depending on its source. Typical feed composition is shown in Table 1. The sieve desulfurizer system has consistently provided feed gas to the primary reformer containing less than 0.3 ppm by volume peak total sulfur concentration, since start-up 2 yrs. ago. Such plant upsets as feed rate and composition fluctuations, inadequate regeneration due to underheating, extended on-

Table 1
Typical natural gas feed composition

mol%*	7 Mo. after startup	23 Mo. after startup
Methane	95.3	93.8
Ethane	3.4	4.5
Propane	0.89	1.1
iso-Butane	0.12	1.13
Normal butane	0.15	0.20
Pentanes	0.07	0.13
Hexanes	0.07	0.04
ppm (vol.)		
Hydrogen sulfide	0.4-0.8	—
Mercaptans	0.5-0.9	—
Sulfides	1.1-1.9	—
Residual sulfides	0.9-1.5	—
Total sulfur	3.5-4.8	4.0-5.0

*Results obtained by chromatograph.
**Results obtained by Barton electrolytic titrator.

stream adsorption times, and pressure surges have occurred during this period. Also at this particular plant, compressor oil has been carried into the sieve desulfurizer from the upstream reciprocating compressors.

Despite these fluctuations and process upsets, the desulfurizer has provided trouble-free operation with the exception of an occasional malfunction in the regeneration gas electrical superheater. The outstanding performance of molecular sieve is shown in Figure 3 and Table 2. During the 2 yr. on-stream period, the total average sulfur content of the raw natural gas feed was reduced from approximately 4.5 ppm to less than 0.06 ppm by the sieve treaters.

At start-up, the performance of the molecular sieve desulfurizer was not analyzed. However, a pilot-plant run with fresh sieve under scaled-down commercial operating conditions was subsequently made. The measured performance in the pilot plant coincided with that of the commercial unit after 7 mo. operation, as shown in Figure 3.

Table 2
Commercial molecular sieve desulfurizer performance

Sulfur concentration ppm(vol)	At Startup	7 Mo. after Startup	23 Mo. after startup
Natural gas fedstock Feed to primary reformer	4.0-5.0	3.5-4.8	4.5
At 24 hr.	0.06	0.05	0.10
At 48 hr.	0.21	0.25	0.30

Sieves vs. activated carbon

Comparative performance data for Linde molecular sieve versus a commercial grade of impregnated activated carbon were also obtained at the ammonia plant site in a dual bed mobile pilot unit. The operating temperature, pressure, and mass flow rate were identical to those of the commercial sieve feed gas desulfurizer. The sulfur concentration in the effluent gas from the adsorbent beds was monitored with Barton titrators. Extensive instrumentation was employed to assure safe, smooth operation, as well as to provide meaningful results.

The normalized desulfurization performance of the sieve versus an equal volume of impregnated carbon is shown in Figure 4. The sieve removes a noticeably larger fraction of
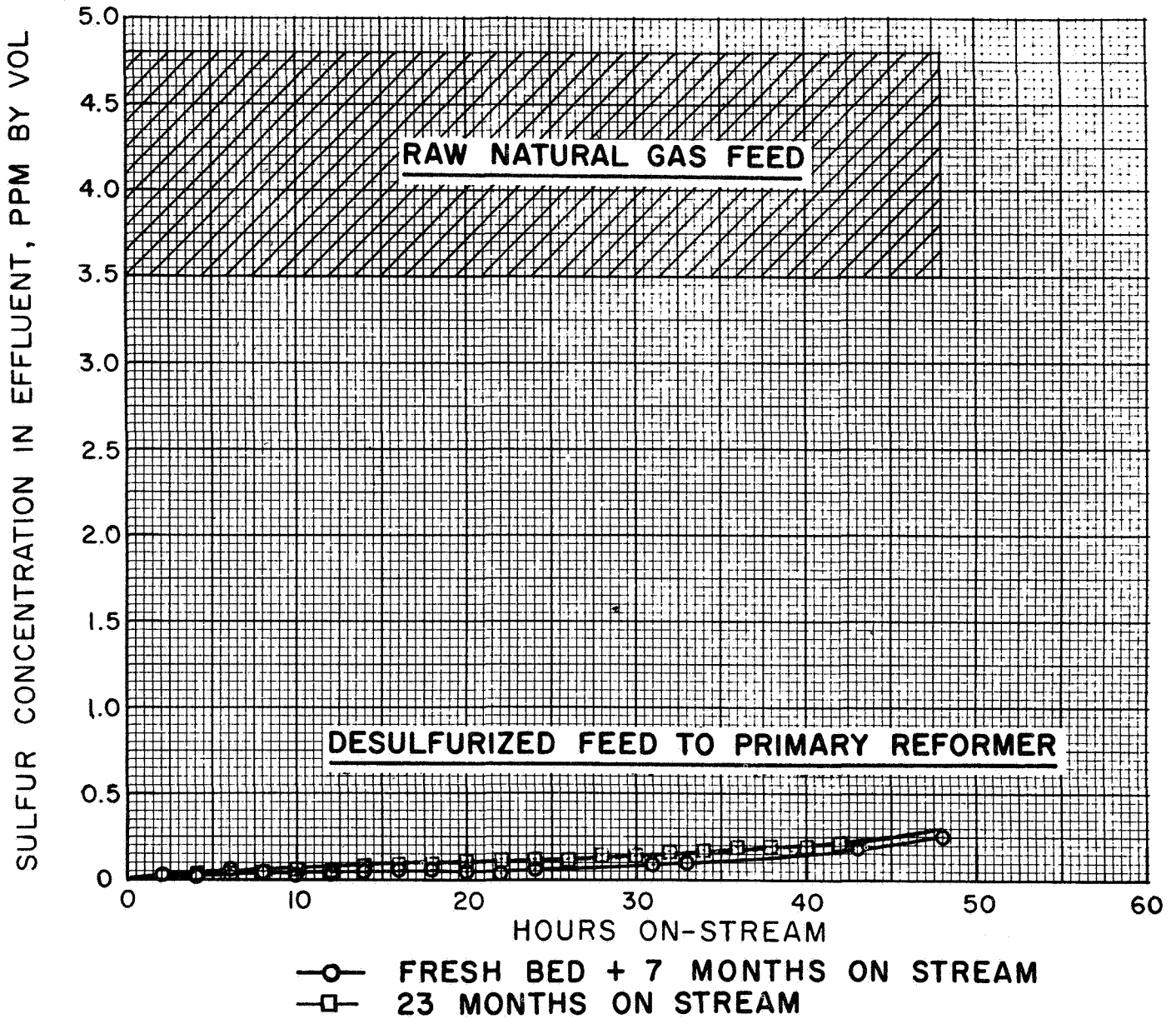
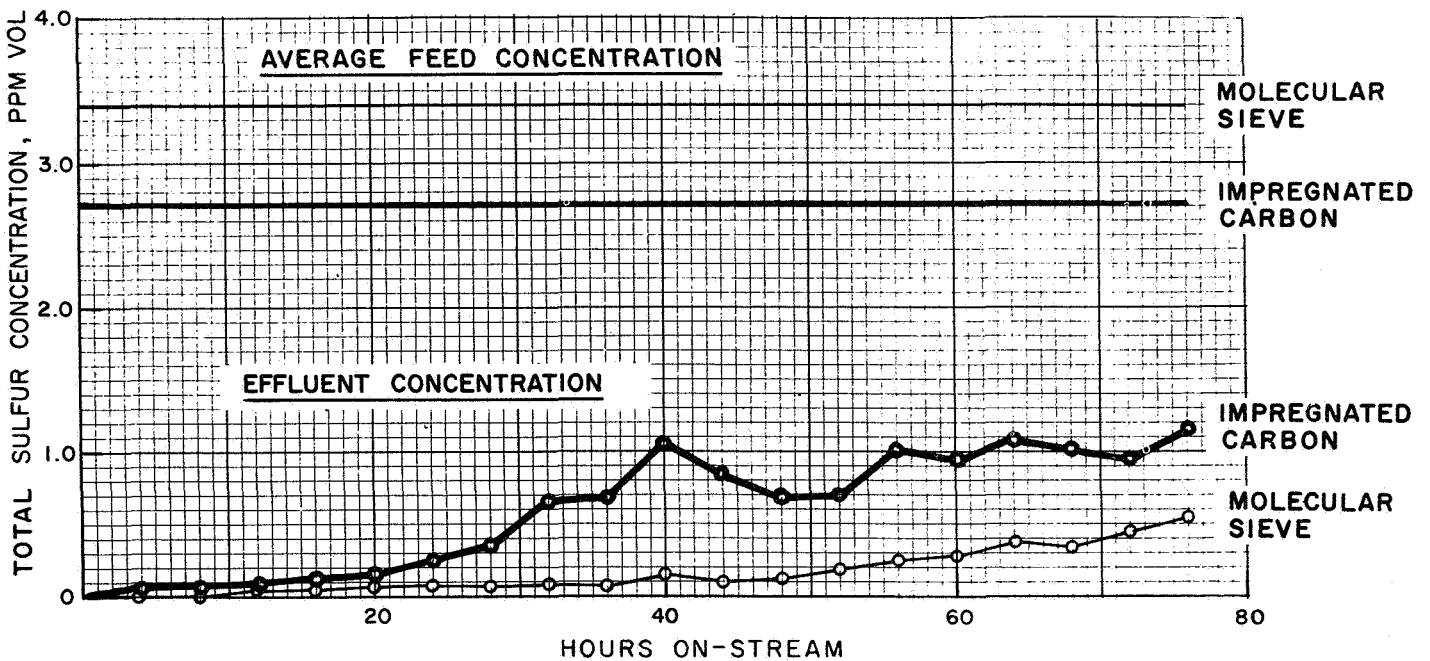Figure 3. Molecular sieve desulfurizer: Commercial performance over 2-yr. period.

Figure 4. Compartive performance of molecular sieve and impregnated carbon.

the total sulfur from the feed gas than does the impregnated carbon. As can be seen in Figure 5, which is a replot of the sulfur breakthrough data, the carbon bed of equivalent volume will pass over seven times more sulfur into the ammonia plant during a typical 48 hr. on-stream adsorption period.
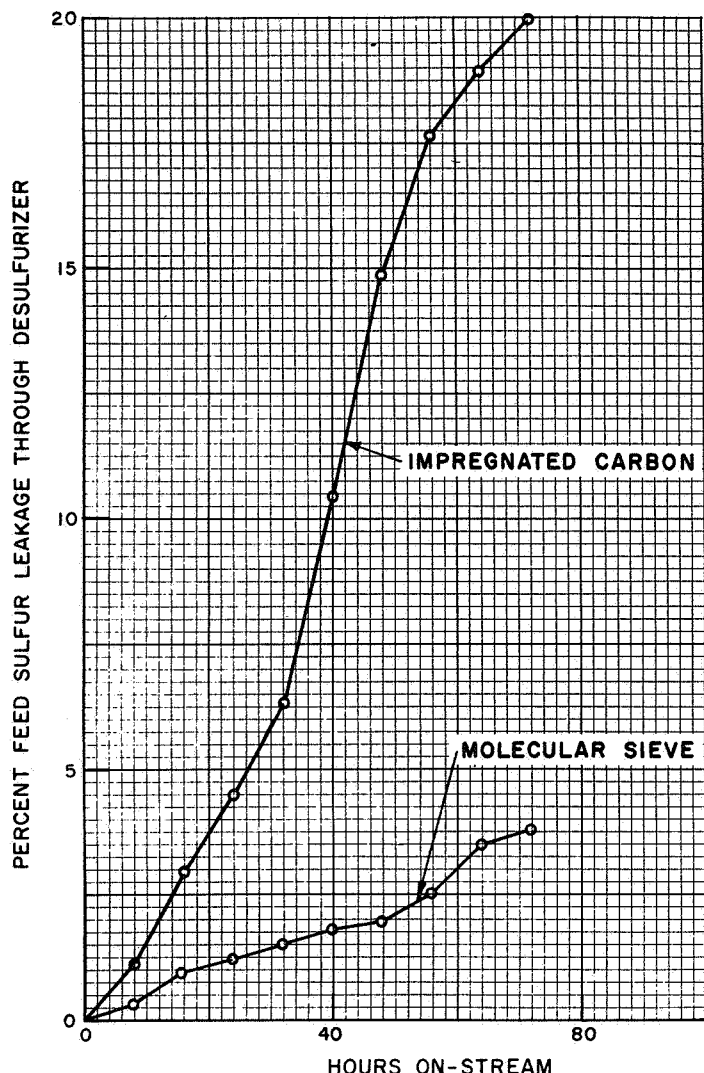

Figure 5. Molecular sieves out-perform impregnated carbon in steam reformer feed gas desulfurization.

The superior desulfurization performance of the molecular sieve results in a significantly longer low temperature shift catalyst life, plus a lower fuel requirement and longer steam reformer furnace tube life because of the lower possible reforming temperature. The data replotted in Figure 6 provides a basis for comparing the relative amounts of gas which each adsorbent can process for any given tolerable sulfur level in the desulfurized gas. For example, with a maximum effluent sulfur level of 0.2 ppm the molecular sieve can process 2.4 times as much feed gas per unit volume of adsorbent as can the impregnated carbon, i.e., the sieve stays on-stream for 53 hr. compared to 22 hr. for the equal volume of impregnated carbon receiving feed gas at the same flow rate. The relative treating capacity of the two adsorbents for effluent sulfur levels of 0.1, 0.2, 0.5, and 1.0 ppm, respectively, are summarized in Table 3. The relative performance of the two adsorbents in terms of *sulfur leakage* through each bed (from Figure 5) for a 24 hr. and a 48 hr. on-stream time is also summarized in Table 3.

Operations at lower pressures

The results for operating the sieve and impregnated carbon beds at a slightly lower operating pressure (the only change in operating conditions) are presented in Figure 7. The relative desulfurization capacities and respective sulfur leakage for the two adsorbents are also summarized in Table 3. Overall relative performance at the lower operating pressure was comparable to that already reported.

In addition to total sulfur analysis, a breakdown of the sulfur compounds into hydrogen sulfide, mercaptans, sulfides, and polysulfides in the process streams was obtained during the test period. A Barton electrolytic titrator was used. The measured sulfur contents of the natural gas feedstock are summarized in Table 4. A brief discussion of the analytical methods used and their reliability is given in the next section.

A breakdown of the sulfur compounds in the treated gas was made during the lower pressure operation. As shown in Table 5, the sieve is highly selective for the removal of hydrogen sulfide, mercaptans, and sulfides. The impregnated carbon is specific for only mercaptans. The molecular sieve also removes a higher fraction of the residual sulfides present in the feed.

The design of the commercial sieve ammonia plant feed gas desulfurizer was based on the removal of hydrogen sulfide, mercaptans, organic sulfides, and organic polysulfides. Al-

Table 3
Overall desulfurization performance of molecular sieve versus impregnated carbon.

	Impregnated carbon	Molecular sieve	Impregnated carbon	Molecular sieve
Reference	Fig. 4-6	Fig. 4-6	Fig. 7	Fig. 7
Feed sulfur, ppm (vol)	2.7	3.4	3.4	3.4
Relative amount of gas processed per unit volume of adsorbent (molecular sieve/impregnated carbon)				
0.1 ppm S in effluent	1.0	2.9	1.0	2.9
0.2 ppm S in effluent	1.0	2.4	1.0	3.3
0.5 ppm S in effluent	1.0	2.5	1.0	3.7
1.0 ppm S in effluent	1.0	2.3	1.0	2.0
Percent feed sulfur leakage through desulfurizer				
After 24 hr. on-stream	4.5	1.3	6.2	0.5
After 48 hr. on-stream	14.8	2.0	16.7	3.8

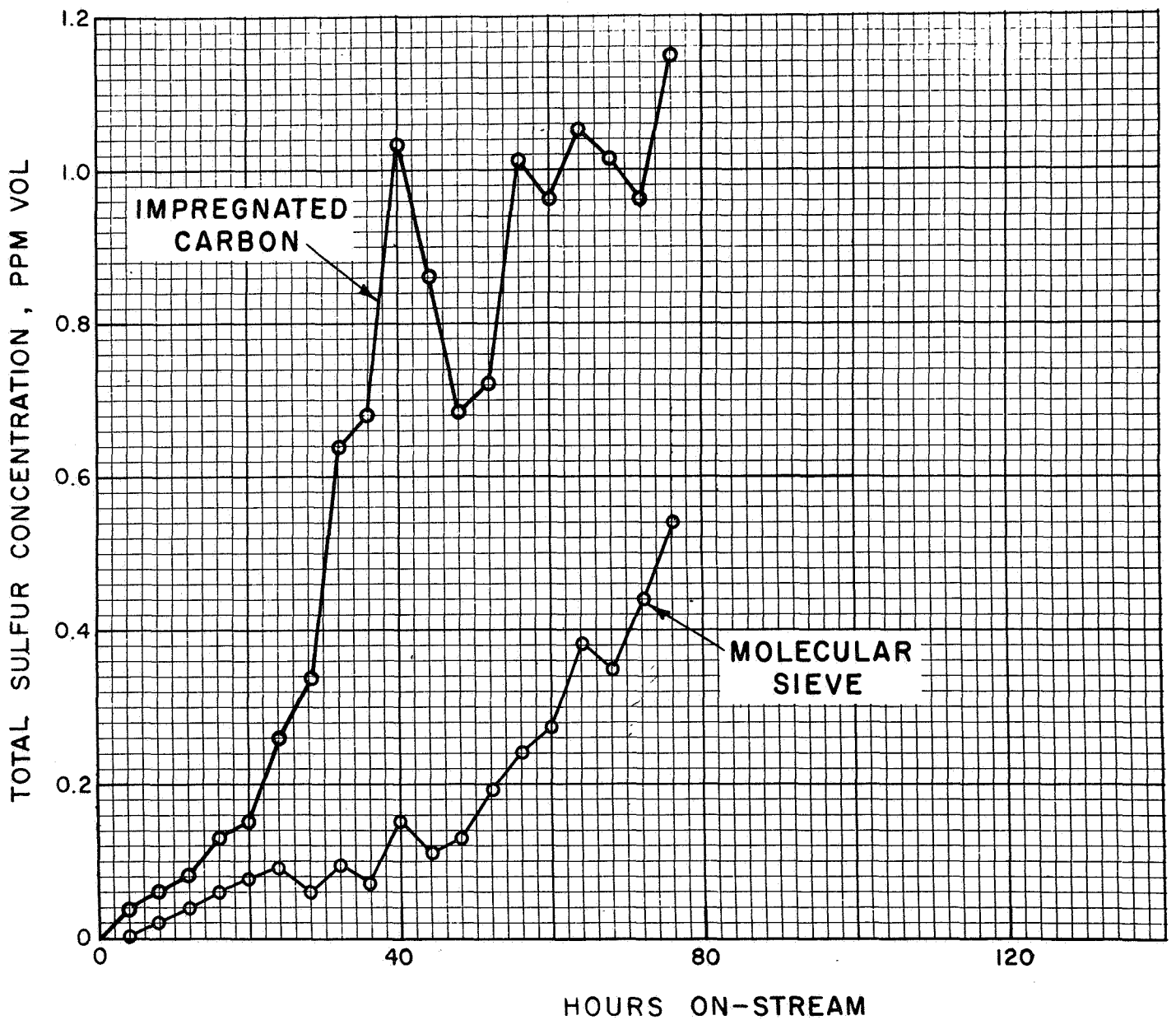AVERAGE FEED CONCENTRATION
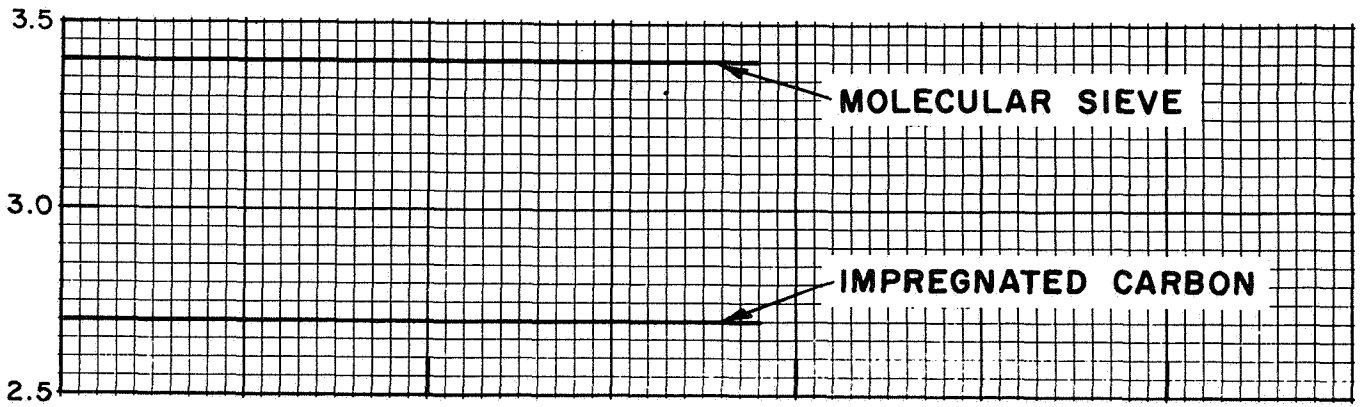
EFFLUENT CONCENTRATION

Figure 6. Comparative performance of molecular sieve versus impregnated carbon.

AVERAGE FEED CONCENTRATION

MOLECULAR SIEVE AND
IMPREGNATED CARBON

4.0

3.0

EFFLUENT CONCENTRATION

SULFUR CONCENTRATION, PPM VOL

1.2

1.0

IMPREGNATED
CARBON

0.8

0.6

0.4

MOLECULAR
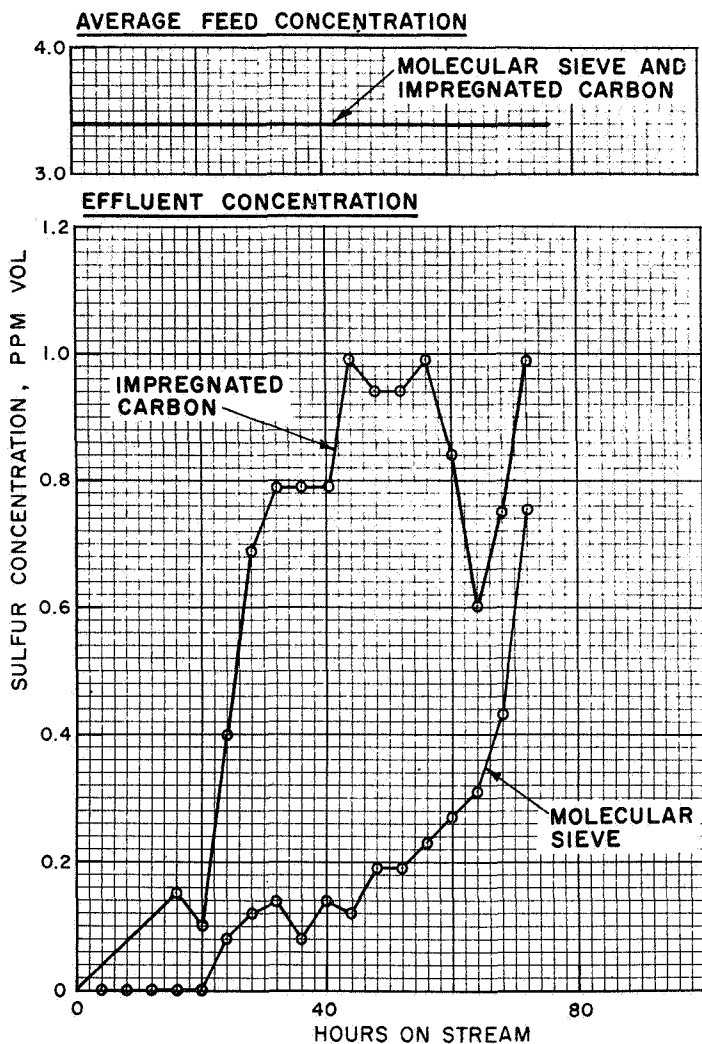SIEVE

0.2

0

0   40   80

HOURS ON STREAM

Figure 7. Compartive performance at lower operating pressure of molecular sieve versus impregnated carbon.

though not detected earlier, carbonyl sulfide has been recently found present in the feed gas. An additional field test program beyond the scope of this paper has provided a basis for adapting the sieve desulfurizer to also accomplish carbonyl sulfide removal.

Analysis of sulfur compounds

To serve as a basis for possible shortening of desulfurizer cycle time in times of high feed sulfur levels, accurate continuous monitoring of sulfur compounds in the raw natural gas feed and reformer feed streams is desirable. Reducing the time for the treating step will then reduce the amount of sulfur passing into the reformer and shift converter. It is generally known that when the sulfur loading on the low temperature shift converter catalysts reaches 0.20 to 0.25 wt.%., the activity level drops to below 50% of its initial level.

A continuous total sulfur analyzer provides a good method for monitoring sulfur concentration. There are several commercially available instruments which operate on the principle of generating a reactive agent by passing an electrical current through a suitable electrolytic solution. The solution can be hydrobromic acid or a potassium bromide-sulfuric acid solution.

The gas sample is continuously bubbled through the acid solution and the sulfur compounds react in the cell solution with electrolytically generated bromine. The end point of this reaction is automatically maintained at a constant value by means of sensing electrodes, which match the bromine generation to the rate of sulfur pick-up. The bromine generating current, which varies directly with the concentration of sulfur compounds present, is recorded.

Besides determining total sulfur, these instruments are capable of identifying sulfur groups, (e.g. hydrogen sulfide, mercaptans, sulfides and residual sulfur) by incorporating a train of bubbler solutions. It is important to point out that the total sulfur determined without using à bubbler train is usually different from that obtained by a train and summing the sulfur

Table 4
Sulfur compounds in the feed gas.

	Sulfur level, ppm by volume					Total system
	Using filter system					Total
	H$_2$S	RSH	RSR	Residual	Total	Total
Impregnated carbon*	0.4	0.5	1.6	1.0	3.5	2.7
Molecular sieve*	0.8	0.9	1.7	0.9	4.3	3.4
Impregnated carbon†	0.8	0.9	1.7	0.9	4.3	3.4
Molecular sieve†	{0.6	0.8	1.9	1.5	4.8	3.7
	{0.4	0.9	1.1	1.4	3.8	3.0

*Reference Figures 4-6
†Reference Figure 7

Table 5
Specificity of molecular sieve versus impregnated carbon in sulfur removal.

	Sulfur level, ppm by volume					Total system
	Using filter system					Total
	H$_2$S	RSH	RSR	Residual	Total	Total
Impregnated carbon*						
Feed	0.8	0.9	1.7	0.9	4.3	3.4
Effluent—18 hr. from start	0.5	0.1	0.6	0.4	1.6	1.0
Molecular sieve*						
Feed	0.6	0.8	1.9	1.5	4.8	3.7
Effluent—16 hr. from start	0	0	0	0.4	0.4	0.3

*Reference Figure 7

in each sulfur group. Since mercaptans or organic sulfides do not require the same amount of bromine for reaction as sulfur combined as hydrogen sulfide, the discrepency is expected.

Use of a bubbler train is the more accurate method. These instruments are temperature sensitive. It is generally advisable to place the instrument in a semi-enclosed enclosure to avoid wide temperature variations, since the instruments tend to be temperature sensitive. During this work, Barton Model 286 electrolytic titrators were employed.

Standardization method used

The titrators were standardized in the laboratory against a temperature programmed chromatograph coupled with a microcoulometric cell. This is perhaps the most advanced and powerful tool for identifying sulfur compounds and measuring their concentrations. The basic principle involves the separation of individual sulfur compounds by a carefully selected chromatographic column by passage through a combustion tube. The sulfur compounds present form sulfur dioxide which is then titrated automatically with coulemetrically generated iodine. The Barton was found to be a reliable instrument for monitoring plant operation.

With these titrators, it is important to establish that the internal filter system is working efficiently if reliable analyses are to be obtained. The sulfur level in the sample gas is obtained by difference between electrolytic titration readings for the sample gas and a blank. The blank reading is established with sample gas treated in the filter system section within the instrument to remove any sulfur compounds.

If the filter system is not properly maintained, it will not do a good job of removing sulfur from the sample gas. This results in a higher-than-true blank reading, which in turn leads to a lower-than-true sulfur analysis. With an inefficient filter system, the feed gas to the primary reformer can contain more sulfur than read on the titrator by the plant operator. The substitution of Linde molecular sieve adsorbent into the filter system will achieve complete sulfur removal for the blank sample and provide reliable sulfur determinations.

The Barton does not have the capability for detecting carbonyl sulfide. A Dohrmann microcoulometer was used in the field tests to determine carbonyl sulfide in the natural gas feed.

Conclusions

Based on the performance over a 2 yr. period of an ammonia plant feed gas desulfurizing, molecular sieve can consistently provide an effluent sulfur level of <0.3 ppm. The sieve system is not sensitive to such typical plant upsets as pressure surges and occasional underheating of the adsorbent beds during regeneration. The strong selectivity of molecular sieve for hydrogen sulfide, mercaptans, and sulfides makes the system relatively insensitive to moderate fluctuations in the type of sulfur compounds present in the feed gas.

Field pilot plant tests show that molecular sieve can treat 2-4 times as much gas per unit volume of adsorbent as can impregnated carbon. With equivalent adsorbent bed volumes, sieves will remove 98% of feed sulfur versus 85% for impregnated carbon, at typical plant operating conditions. Molecular sieve has greater adsorption selectivity for the removal of hydrogen sulfide, mercaptans, sulfides, and polysulfides from natural gas compared to impregnated carbon.

Acknowledgment

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Discussion

Q. In comparing the impregnated carbon and the molecular sieve, what is the relative cost per unit volume? We've talked about comparing them under the same space velocities.
LEE: I think the price of the impregnated carbon varies, depending on the individual contract between the supplier and the ammonia plant operating personnel.
Q. Just a rough number would be satisfactory.

LEE: Molecular sieve is slightly more expensive than impregnated carbon on a volume by volume basis. The previous speakers have borne out quite clearly that the initial cost of the adsorbent or the catalyst is not the criteria to evaluate the economic return of an ammonia plant operation.
Q. Number two, what effect does water or moisture in the feed gas have on the molecular sieve.?

LEE: Molecular sieve does dehydrate and desulfurize simultaneously. In fact, molecular sieve systems are used in natural gas driers to remove water to less than one part per billion.

Q. In our case we don't want to remove the water, and if it is there, does it do harm?

LEE: No, it does not harm the moecular sieve system.

Q. Number three, what effect does the higher hydrocarbons in liquid form have on—you mentioned the oil from compressors. But this is a little different.

LEE: The molecular sieve system is capable of handling heavier hydrocarbons. I mentioned there are several other applications for desulfurization of higher hydrocarbon feedstocks using molecular sieves.

Q. Number four, does it remove chlorides?

LEE: Well, let me answer the question in this way. Since molecular sieve has strong selectivity for polar molecules, it can remove halides. It depends basically upon what type of halides present and what type of molecular sieve is used.

Q. I think one of the reasons that the molecular sieve is capable of handling the hydrocarbons is the fact that it does not adsorb the hydrocarbons, is that not correct? It doesn't have much capacity for the hydrocarbons.

LEE: This is correct to a certain degree. Molecular sieves adsorb sulfur compounds more selectively than hydrocarbons such as propane, butane and pentane. These hydrocarbons will leave the molecular sieve adsorber system ahead of the sulfur contaminants during the adsorption step.

Q. Well, comparing a Mole Sieve then with a carbon adsorption system which is—would have a much higher capacity for the hydrocarbons, is there not the danger of having heavier hydrocarbons leaking through a mole sieve and causing coking problems in the heating system, particularly in the transfer line going to the primary reformer?

LEE: No. There is no danger of heavy hydrocarbons leaking through the molecular sieve system, if we are refering to heavier trace hydrocarbons in the C_8+ range. They will be retained on the molecular sieve during the adsorption step, and pass into the fuel system with other sulfur compounds during the regeneration step.

Q. Sometimes you have natural gas supply coming from three or more pipelines, different composition of gas and different composition of sulfur and amounts—how does that effect the operation of your sieve?

LEE: This again is one of the real strong advantages of using a molecular sieve system. Molecular sieve system can cushion these feed fluctuations quite well because of the strong selectivity of molecular sieve for sulfur compounds. I would like to mention that one of the commercial plants which was designed to handle 40 ppm of sulfur in the feed, but no significant problems were observed when the feed sulfur compound went up to over 100 ppm occasionally.

If the feed composition is known to have wide fluctuations, the molecular sieve desulfurizer can be designed ahead of time to cope with these continuously varying conditions.

Q. What temperature is required to achieve regeneration of the sieve and how long does it take?

LEE: In regenerating molecular sieves, the temperature is selected to suit the limitations and requirements of each ammonia plant. Generally, it takes eight hours or longer. The temperature level is not too much different from the normal operating conditions for carbon drums, say, about 450°F and upwards. It depends on the composition of the natural gas—the sulfur compounds and the hydrocarbons present.

Q. It's my understanding that molecular sieve will adsorb water more strongly than any other compound and thus displace anything that might be present on the bed. In other words, if you had a natural gas that had a fairly high water, you would need to have a bed maybe two or three times the size you would expect to have because of the sulfur. Is this true?

COLLINS: The typical feed being desulfurized is pipeline natural gas containing 4 to 7 lb. H_2O/MMSCF. On this basis, the fraction of bed that's required to accomplish dehydration is small.

If we can back up for a second, I would like to comment on the use of molecular sieves for hydrocarbon removal. Molecular sieve is an adsorbent with good selectivity for high molecular weight hydrocarbons as well as for sulfur compounds. Although the sulfur compounds are more selectively adsorbed over butane or even pentane, the heavier hydrocarbons are removed along with the sulfur. They end up going to the fuel system in the regeneration purge gas.

Q. You touched on the subject of carbonyl sulfide removal. I'd be interested in whatever you can tell us on that subject. A second question, also relating to the question asked earlier on water content of the gas, would a drastic change in the water content of the natural gas from say seven pounds to 20 or 30 pounds, as might happen, would that tend to displace sulfur materials from the bed?

A third question, does carbon dioxide behave in a manner similar to water?

COLLINS: If the amount of water in the feed gas is known, the system is initially sized to handle this quantity of water without passing any sulfur. As a ball park estimate, in going from a system containing 4 to 7 lb. H_2O/MMSCF to one containing 20 to 30 lb. H_2O/MMSCF, something in the range of 20 per cent more molecular sieve must be added to hander the higher feed water content.

If the system is sized to handle a gas containing about 7 lb. H_2O/MMSCF, the molecular sieve can handle a brief surge in feed water content from an upset condition. However, if the surge lasts a while, the effluent sulfur content may begin to rise slowly. The sulfur is not displaced from the molecular sieve bed in a slug and does not pass as a slug into the downstream system.

Sulfur compounds are more strongly adsorbed on Molecular sieve than carbon dioxide. The difference in the molecular sieve bed size to desulfurize a feed containing two per cent versus one containing 10 to 20 per cent carbon dioxide is small.