

Media for Removing Sulfur from Natural Gas

The experience related here shows that air regeneration of activated carbon can restore its sulfur retention capacity to a high level provided the gas being treated is not subject to erratic sulfur levels.

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In the operation of a modern single train, centrifugal compressor ammonia plant, the performance of a number of catalytic reactors is critical to successful, economic operation. Much care is used in the selection, loading and operation of these reactors. In most ammonia plants operating on natural gas, selection of the sulfur removal medium is oftentimes a routine procedure requiring little investigation. This is an acceptable situation in many plants since the normal sulfur level is 5 ppm or less, and seldom over 1 to 2 ppm. However, this is not the case in operations with gas from the west Texas fields. In this region, sulfur compounds are a common problem and sometimes exist in widely fluctuating amounts. Other areas in the country will be facing similar problems as natural gas quality deteriorates. Under these conditions, the sulfur removal reactor is the most critical item of equipment since the successful operation of subsequent catalytic reactors depends upon the efficiency of this vessel.

The natural gas supply is acquired from the Panhandle Gas Field through a gathering network, and compressed to a pressure level high enough for use in the reformer. Following compression, the gas is processed in a stripping

Table 1. Feed Gas Composition

Helium	0.39
Carbon Dioxide	0.60
Nitrogen	10.43
Argon	0.03
Methane	81.55
Ethane	6.03
Propane	0.97
Butane & Higher	Trace
	100.00

H ₂ S ppm	4.7
RSH ppm	1.4
Specific Gravity	0.63

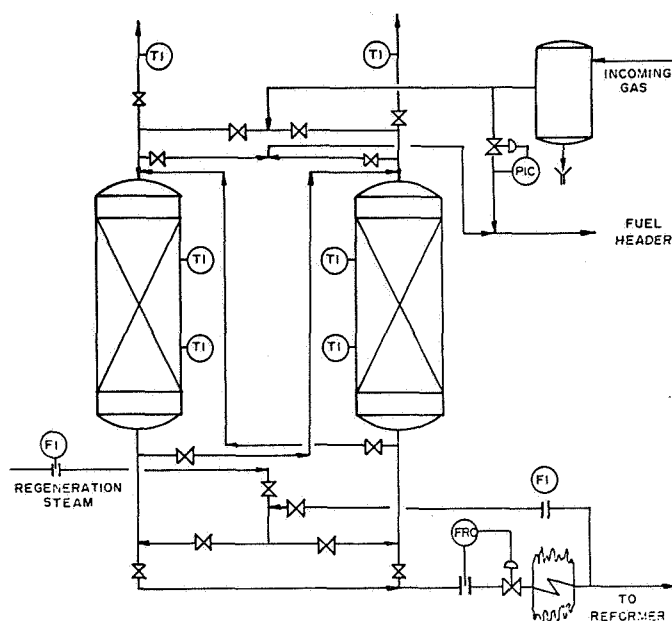


Figure 1. Desulfurizer flow scheme.

plant to remove essentially all of the gas liquids, yielding a residue gas of 950 B.t.u./std. cu. ft. higher heating value. A typical analysis of this gas is shown in Table 1. The nitrogen content of this gas is rather high. Also, the sulfur compounds are notable with H₂S concentrations at a level of about three times that of the mercaptans. No other sulfur compounds have been detected. The gas then travels through a 14 mi. pipeline to the plant battery limits where it is metered, and from there it passes through a coalescer type separator to remove all particles larger than one micron.

After the gas for fuel is diverted, the process gas then passes down through two desulfurizers either in parallel flow or in series flow as shown in Figure 1. The effluent gas is sent directly to the reformer via a flow control valve and typical heat exchange without further processing. The piping arrangement at the desulfurizers provides for 160 psig regeneration steam with flow meter, preheated natural gas line from the reformer feed, a letdown line to the low pressure fuel gas system, and vent lines. There are

two dial thermometers equally spaced along the side of the desulfurizers as well as one in the vent line. The normal space velocity in these drums is approximately 1,000 SCFH/cu. ft. of catalyst volume.

Analytical program

An on-stream sulfur titrator utilizing the bromine generation and titration principle is used. In addition, the classical wet chemistry method of Cadmium Sulfate-Iodometric Titration is used as a back-up for the analyzer. This method is quantitative for both H_2S and mercaptans. Frequent spot checks of the sulfur removal drums are made using both lead acetate paper and sodium nitroferri-cyanide test paper.

At present, the analytical program makes use of all three methods. The on-stream analyzer continuously records the sulfur content of the incoming raw natural gas, and the cadmium sulfate method is used as a back-up for the analyzer and for any other points where a quantitative measurement is needed. A quantitative analysis by cadmium sulfate is performed on the incoming natural gas at least once per day in addition to the on-stream analyzer.

The test paper is used to check various points on the sulfur removal drums every four hours. This schedule is adjusted as experience dictates. We have installed sample points at various levels on the drums in addition to the drum exit line. In this manner, we are able to follow the progression of sulfur through the bed and get advance warning of the potential loss of bed activity. Quantitative tests by the cadmium sulfate method are run periodically on the various points in test drums. This information is correlated with the raw gas analyzer in calculating the efficiency of the bed.

During the initial operation of the desulfurizers, the drums were charged with copper impregnated activated carbon, and operated in series flow. The drum first in line was taken out of service each week, regenerated, and then returned to service second in line. The carbon was regenerated with 160 psig steam at a velocity of 0.3 ft./sec. until sulfur free. During the course of this regeneration the bed temperatures would stabilize at about 500°F. The bed was cooled with sulfur free gas with a small flow of steam added. No sulfur was detected in the exit gas of the first in-line desulfurizer during this initial operating period. Analysis of the incoming gas revealed a low sulfur content of the gas of between 0.2 to 0.5 H_2S . The sulfur content of the gas to the stripping plant was 5 to 6 ppm during this same period. A possible explanation was that the iron in the new natural gas pipeline was reacting with the sulfur in the gas. After about three months of operation, the cycle life of the desulfurizers was shortened due to breakthrough of sulfur after the first drum. The cycle life continued to diminish until it was about 24 hours in length. During this period of decline, the sulfur concentration inlet to the desulfurizers increased to the 5 to 6 ppm level. The regeneration procedure was altered to include an additional steam period at low pressure. This improved the sulfur capacity

of the desulfurizers.

The sulfur content of the incoming gas became very erratic due to fluctuations in the gathering network distribution. The average sulfur content reached 12 ppm total sulfur with peaks of 24 ppm. Provisions to use 525 psig steam at 750° F to obtain higher regeneration temperatures doubled the sulfur retention ability of the carbon, but the high sulfur feed content prevented any appreciable change in the cycle. The daily regeneration of the desulfurizers, with the incipient leakage of sulfur, created problems in the operation and efficiency of the ammonia plant. The low temperature shift converter was taken out of service to avoid damage to this catalyst. Steam requirements for regeneration created inefficiencies in the steam system, and production and efficiency of the ammonia plant suffered as a result.

Investigations

The performance of the carbon indicated that the sulfur retention capacity was lower than design requirements. Instead of the 0.0845 lbs. sulfur/cu. ft. of carbon, the sulfur retention was only 0.02 lbs. sulfur/cu. ft. of carbon. A sample of the carbon was tested by the supplier and was found to have normal activity. We attributed the loss of sulfur retention capacity to the conversion of the impregnated copper oxide to the sulfide by the reactions: $CuO + H_2S = CuS + H_2O$.

Previous investigations had shown that it was questionable that steam would regenerate the impregnated metal sulfides. There also appeared to be a slight continuing decline in the sulfur retention capacity. Air regeneration was one recommendation as a means of restoring the sulfur retention capacity, but information from other plants yielded mixed reaction to this procedure. This lack of confirmation, combined with the short periods of time for regeneration, ruled out any immediate remedy of this means. Air regeneration on a token basis was attempted, but without any detectable result.

It was apparent that something had to be done. First, it was necessary to establish longer cycles, and second, to provide additional insurance for the catalytic reactors downstream. The catalyst supplier recommended that the carbon bed be replaced with a split bed. The upper portion was to be activated with impregnated carbon similar to the original material, and the lower portion of the bed with zinc oxide pellets. Zinc oxide is normally used at higher temperatures for sulfur removal, but with H_2S it would have sulfur capacity of 3% by weight at these ambient temperatures. Although the carbon bed was half size, the sulfur retention capacity of this new material should permit cycles of 3 to 4 days. The zinc oxide would prevent any sulfur breakthrough of the carbon passing on to any succeeding catalyst. The predicted life of the zinc oxide for the sulfur level in the raw gas feed was about three months. We fabricated an experimental drum 8 in. in diameter by 35 in. tall with a catalyst volume of approximately 1 cu. ft., and connected it to the main incoming gas line. Flow through the drum was measured with a rotameter. This vessel was charged with zinc oxide

and test runs were made on several charges at various flow rates. The results of these tests, while they did not verify the predicted life of the zinc oxide, did indicate the ability of the material to remove sulfur for a satisfactory period in this particular service.

At this same time, investigation was made into other means of sulfur removal. Regenerative scrubbing systems such as amine, hot potassium carbonate, DGA, etc., were ruled out due to time and investment costs, as was hot zinc oxide. Caustic scrubbing system was eliminated due to the carbon dioxide content of the gas and the resulting caustic consumption which would have created waste disposal problems. Molecular sieves were studied, but experiments with these were postponed pending results obtained with other materials.

Iron sponge was investigated to ensure that all means for sulfur removal had been considered. We had no experience with iron sponge and little knowledge of it, but the more we learned about this material made it more and more attractive for our purposes, so we set up a program to investigate it further. A drum identical in size to the one used with zinc oxide was constructed, and means provided water to be injected and removed. The vessel was loaded with 15 lbs. of commercial grade iron sponge. Boiler feed water was used for water injection to the vessel. Many gas flow and water injection rates were tried. The results of these tests supported the work in this field reported by Zapffe and others (1,2). Due to our lack of previous experience with this material, no changes in the process were made at this time pending the results of the experimental work. The carbon-zinc oxide split bed was installed in both desulfurizers.

Intermediate operating experience

The carbon-zinc oxide desulfurizers were put in service and the initial results were very good. The sulfur retention capacity equaled or exceeded the design capacity. Three day cycles were observed initially. Because of the zinc oxide in the lower portion, the regeneration procedure was altered to avoid contact of this material with wet or saturated steam. Hot sulfur free natural gas was used for the initial warm-up period until a temperature of 350 °F had been reached. This gas flow was at a space velocity of 300 std. cu. ft./hr. total cu. ft. of catalyst and was recovered in the fuel gas system. When the desired temperature was reached, regeneration was completed using steam in the manner previously described.

After three cycles, an upset of the gas supply quality occurred. The sulfur content increased rapidly to about 12 ppm, each of H₂S and RSH. After this, the deterioration of the sulfur retention capacity of the carbon became apparent. The regeneration procedure was reviewed and air regeneration was attempted following guidelines suggested by Grant (3,4). The procedure was to warm up with gas as previously described, and bring the bed temperatures up and stabilize at approximately 400° F with steam. The air was then slowly introduced with the steam and gradually increased until 3,000 ppm oxygen level was attained. A temperature limit of 420° F was

Table 2. Regeneration Summary.

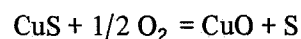
Method	Medium	Velocity ft./sec.	Pressure, psi	Temperature °F	Check	lbs. sulfur ft. ³ °C
1	160 lb. steam	0.313	80	500	s	0.0048
2	160 lb. steam	0.313	80	500	S	
	160 lb. steam	0.324	40	500	HC	0.0092
3.	525 lb. steam	0.268	80	600	S,HC	0.0200
4.*	Methane	0.062	450	350	—	—
	160 lb. steam	0.313	80	500	S,HC	>0.0752 (N ₂) 0.0419(U ₂)
5*	Methane	0.062	450	350	—	—
	160 lb. steam	0.313	80	400	—	—
	160 lb. steam & air	0.280	80	420	Δt, O ₂	
	525 lb. steam	0.268	80	600	S,HC	0.076 (Initial) 0.046 (Final)

*Carbon-Zinc oxide split bed

Note: HC represents tests for hydrocarbon.

S represents Tests for sulfur.

maintained to avoid any possible ignition of the carbon. As a temperature increase of about 30 to 35° F was noted, it was necessary to lower the steam temperature as the air flow was increased. The 3,000 ppm oxygen level was lower than the recommended 5,000 ppm, but equipment limitations did not permit this higher concentration. The air flow was maintained until the temperatures began to approach the steam temperature. After the air flow was stopped, the steam temperature was increased to complete the evolution of the sulfur and hydrocarbons present. During the initial heat up phase, efforts were made not to exceed 400° F. This was due to the recommendation that the compound structure might be altered so as to interfere with the oxidation of the sulfide if this temperature were exceeded prior to air injection. The reaction for the air regeneration is:



During the air regeneration, sufficient oxygen was injected to oxidize the metal impregnants.

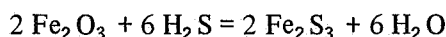
The sulfur retention capacity of the carbon was improved by this method to approximately the same value as the new material. This level of performance was not retained and the sulfur retention capacity slowly decreased to about ½ of the design value of about 0.046 lbs. sulfur/cu. ft. of carbon. Table 2, which summarizes the various regeneration methods, shows the regenerative medium used, the regeneration conditions of velocity, pressure and temperature, the test or check used as a criterion for completion or control for that particular step, and the average sulfur retention capacity in lbs. of sulfur/cu. ft. of carbon for that regenerative method. Meanwhile, the experimental work of the iron sponge

material appeared to be encouraging. Guided by our experience and observations, the decision was made to install iron sponge as the sulfur removal medium.

Present operation

Iron sponge has been used for many years in the natural gas industry for sweetening sour, raw gas, and has been widely used in municipal utility systems for removing sulfur from sewage gas. It has seen limited use in gas processing due to its batchwise operation.

Iron sponge is wood shavings impregnated with a special dehydrated form of iron oxide coating on wood. Several grades, as related to iron oxide content, are available as 6.5 lbs., 9 lbs., 15 lbs., and 20 lbs. of active iron oxide per bushel of shavings. The material normally is available in two bushel sacks. Normal design is for bed size to permit bed depths of 10 ft. which creates sufficient pressure drop to give good distribution. Bed diameter should be sufficient to limit the sulfur deposition to a maximum of 15 grains/sq. ft./min. Residence time should be about 60 seconds in an oxygen free system. Our reactor is considerably wider than this design criteria with a resultant residence time of about 120 seconds. This is considered fairly slow and the distribution may suffer as a result. The iron oxide reacts with the sulfides in the following manner:



Systems that are to be periodically regenerated with air are normally charged with 9 lb. iron sponge. Since we were interested in greater sulfur retention, the 15 lb. iron sponge grade was recommended. The theoretical sulfur retention capacity is 0.56 lbs. of sulfur/lb. of iron oxide or about 8.4 lbs. of sulfur/cu. ft. of sponge.

The iron sponge must be kept fairly moist, normally about 40% by weight, to keep the iron in a hydrated form. This moisture requirement necessitates saturating the gas with water. The pH of the sponge is usually 8 or higher, which can be maintained by the addition of caustic of soda ash.

One of the desulfurizers was taken out of service and regenerated with steam only. After cooling, the bed was flooded with water to thoroughly cool the carbon and zinc oxide. This also served to reduce the possibility of sulfur compounds adhering to the wall and creating a hazard for the workmen. The carbon and zinc oxide were removed. The drum was modified as shown in Figure 2. A spray nozzle was installed in the inlet piping for spraying boiler feed water to saturate the gas. Additional sample points were installed at regular intervals in the wall of the drum to monitor the sulfur "front" through the bed. A drain line was installed to a collection pot. After the modifications were complete, the drum was charged with the same volume of iron sponge as it had been with activated carbon. During the charging, the sponge was thoroughly watered with a hose. After the charging was completed, the drum was put in service.

The sponge iron drum was placed in the first in-line position followed by the remaining carbon-zinc oxide

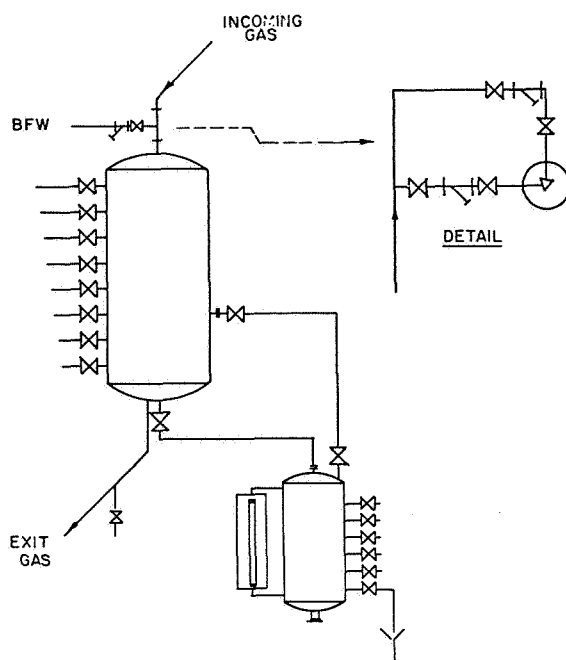


Figure 2. Revised iron sponge desulfurizer.

desulfurizer. As boiler feed water is injected in the gas stream immediately before the inlet nozzle, the amount of injected water is measured and recorded. The water is injected at a rate slightly greater than that required to saturate the gas. The excess water accumulates at the bottom of the drum and drains to the collection pot which is blown down on a regular basis. The accumulation of water is then noted. The difference in the water injected and the water collected is closely checked. This volume has normally agreed with the theoretical amount of water required to saturate. The pH of the water is checked periodically and caustic added to the injection water as required. The wall sample points of the drum, as well as the exit, are monitored as previously described. These has not been any detectable sulfur in the effluent gas since the sponge iron was placed in service in June 1969, but about 12% of the sponge bed has been consumed since that time. This is in excess of design requirements, but the effect of bed shape, velocity fluctuations, and other factors will have to be evaluated. Due to the configuration of this material, concern about the potential pressure drop was understandable. In actual operation the pressure drop has been about 3.5 psi, or about twice that for the carbon.

The most attractive feature of the iron sponge in this particular service has been its economical advantage. A replacement charge of iron sponge and the labor to install it costs a total of \$4,500. The annual operating cost for power, water and chemicals is \$600. The cost of carbon and the labor to change it amounts to a total of \$46,000, and the annual operating cost for steam, gas, and power at four day cycles is \$7,550. Allowing for a two year life of the carbon, the annual expense for this material would be \$30,550. Assuming a six month life, or about ¼ the theoretical life, for the iron sponge, the annual expense is \$9,600. The savings would be \$20,950 per year using the iron sponge instead of the carbon.

In conclusion

Our experience in using west Texas gas for the synthesis of ammonia has been challenging, and we have learned much about the problems of sulfur removal as a result. Keep in mind that the conclusions that follow are the result of exposure to this particular problem and that changes in equipment limitations, quality criteria, and economic considerations could result in different solutions to another problem, no matter how similar.

1. Metal impregnated, activated carbon will do an excellent job of removing sulfur compounds when the sulfur content is low, but is subject to loss of capacity as the length of service accumulates.

2. Our brief experience showed that air regeneration of such carbon can restore the sulfur retention capacity of this material to a high level. This is based on the premise that the gas being treated is not subject to erratic sulfur levels.

3. Comparative studies of regeneration means and procedures indicate that not enough study or evaluation of these programs have been made. In the course of our investigations in small laboratory size reactors utilizing high steam flows, it was determined that regeneration at full steam flow can restore the carbon to approximately new condition. This practice is not possible in plant scale equipment due to the excessive steam volumes required,

fluidizing velocity limitations, and equipment restrictions. There should be room for improvement in this area.

4. Iron sponge as a solution to our problem is a valuable material in sulfur removal at lower concentrations. By use of this material, we have been able to maintain a sulfur free feed gas, with a minimum of operator attention. Although this material can be difficult to discharge, the advantages easily offset this problem.

Literature cited

1. Zapffe, F., *Oil and Gas J.*, 60 (September 10, 1962).
2. *Oil and Gas J.*, 61, 103 (August 19, 1963).
3. Grant, R. J., private communication to the author.
4. , "The Adsorption of Hydrogen Sulfide by Copper and Copper-Iron Impregnated Carbons," Report No. 4-1141-3, Pittsburgh Chemical Co.