

## **Sorbents For Natural Gas Desulfurization**

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Natural gas is the fuel of choice for fuel cell applications due to its extensive existing supply infrastructure. However, the sulfur level in the natural gas needs to be reduced to less than 0.1 ppm for use in the fuel cells. TDA has developed SulfaTrap™ series of sorbents to effectively remove sulfur by adsorption from natural gas streams and has been carrying out field demonstrations with fuel cell developers for the past two years. In this paper we have compare the performance of the TDA's SulfaTrap sorbents with commercially available adsorbents.

### **Introduction**

Power generation using fuel cells is the most efficient and pollution free technology. It is becoming an economic alternative to the power supply through central grid. The fuel cells have the flexibility to operate on a variety of gaseous fuels such as natural gas, LPG, hydrogen or on liquid fuels like methanol, gasoline, diesel or logistic fuels. Pipeline natural gas is often the fuel of choice for fuel cell applications because of its abundance and well-developed infrastructure. Natural gas contains sulfur odorants such as thiols (mercaptans) and sulfides, which are added to ensure safety and to detect gas leaks. These sulfur compounds poison the fuel cell electrodes and catalysts, degrading the fuel cell voltage output. Sulfur compounds also poison the catalysts used in the fuel processor, which converts the hydrocarbon fuel into the hydrogen needed by the fuel cells. Therefore, sulfur level in the fuel needs to be reduced to sub ppm levels (typically less than 0.1 ppm) to protect the catalysts and electrodes used in the fuel cell and fuel processor (1,2,3).

Traditionally, hydrodesulfurization (HDS) is used to remove organosulfur compounds in refineries. HDS process is too complex and the cost of using HDS to remove sulfur compounds to sub ppm levels is far too large for fuel cell systems. Due to the major cost advantages, most developers of the small-scale fuel cell systems have opted to remove sulfur from the feed gases using ambient temperature expendable adsorbents. Several materials have been tested for desulfurization of both liquid and gaseous fuels, including a range of commercially available sorbents (i.e., zeolites, activated carbon, activated alumina). However, an important drawback of ambient temperature adsorbents is the fact that their sulfur uptake capacity is generally low (i.e., <1g of tetrahydrothiophene per liter of sorbent), requiring large quantities of sorbent. Hence there is a need for high capacity ambient temperature sorbents. High capacities will also ensure a long operating life, which would increase the interval between the periodic removal of the sorbent beds (ideally, the life of the sulfur guard bed should be equal or greater than the life of the fuel cell stack).

TDA has developed “SulfaTrap” a high capacity sorbent for desulfurization of natural gas and LPG. SulfaTrap removes the sulfur bearing odorants to sub ppm levels. The sorbent is now being used in the field demonstrations of various fuel cell developers in-line with their fuel cells. Natural gas contains few ppm to few hundred ppm of moisture and sometimes the moisture level could go as high as 4000 ppm. This could have an effect on the adsorption and selectivity of the sulfur species. Depending on the sorbent and the nature of the sulfur species water either competes for adsorption sites or induces side reactions. Zeolites and activated alumina are used in commercial drying applications; they are hydrophilic and adsorb water strongly. In this paper we have compared the performance of TDA’s SulfaTrap series of sorbents with commercial sorbents under both low and high moisture conditions.

### **Experimental Details**

The sorbents are tested as particles (80-100 mesh) in automated test units. To carry out a short yet meaningful accelerated test, 0.25 cc of sorbent is loaded in a fritted quartz reactor and the natural gas containing known concentration of odorants is diluted using sulfur-free natural gas to get a gas-hourly-space velocity (GHSV) of 60,000 h<sup>-1</sup>. Natural gas used in the tests has 50 ppmv H<sub>2</sub>O. The tubing and fittings used were all coated with Teflon or Silicosteel<sup>TM</sup> (Restek Corporation) to prevent sulfur adsorption in the lines. The gas from the exit of the reactor is analyzed for the sulfur compounds using a GC equipped with a RTX-1 capillary column and a flame photo ionization detector (FPD). The detection limit of the FPD is 0.05 ppmv. From the effluent sulfur concentration the sulfur adsorption capacity is calculated at breakthrough.

### **Results and discussion**

We identified a representative baseline conditions with typical sulfur-bearing odorants and carried out accelerated tests to evaluate their performance and compare it to that of the new materials developed at TDA. For quick comparison, accelerated tests were carried out at high gas hourly space velocities (GHSV), 60,000 h<sup>-1</sup> (corresponding to very short gas solid contact times). The performance of each sorbent was evaluated at an identical baseline condition; the sulfur-laden natural gas stream contained 12.3 ppmv dimethyl sulfide (DMS), 8.9 ppmv tert-butyl mercaptan (TBM), 8.9 ppmv tetrahydrothiophene (THT). These higher than pipeline gas sulfur concentrations and short contact times allowed observation of the breakthrough profiles of these odorants in relatively short times. Figure 1 shows the DMS breakthrough profiles for various sorbent samples. A special emphasis is given to the DMS because DMS was the most difficult sulfur compound to remove from the natural gas i.e., DMS breakthrough occurs before that of TBM or THT.

Among the samples tested, the DMS breakthrough occurred first with the Norit carbon sample at 30 min followed by the Grace Davison zeolite-X at 72 min (indicating that the zeolite-X has approximately 2.5 times higher DMS capacity than the Norit carbon). The TDA SulfaTrap<sup>TM</sup> (referred to as SulfaTrap<sup>TM</sup> – R3) showed better performance than the commercial sorbents. The DMS breakthrough occurred at 720 min corresponding to a sulfur adsorption capacity of 3.12% wt. Table 1 shows the breakthrough adsorption capacities for all samples shown in Figure 1. The pre-breakthrough sulfur adsorption capacity is defined as the lb of total sulfur adsorbed per lb of sorbent when the breakthrough of the first sulfur compound was observed.

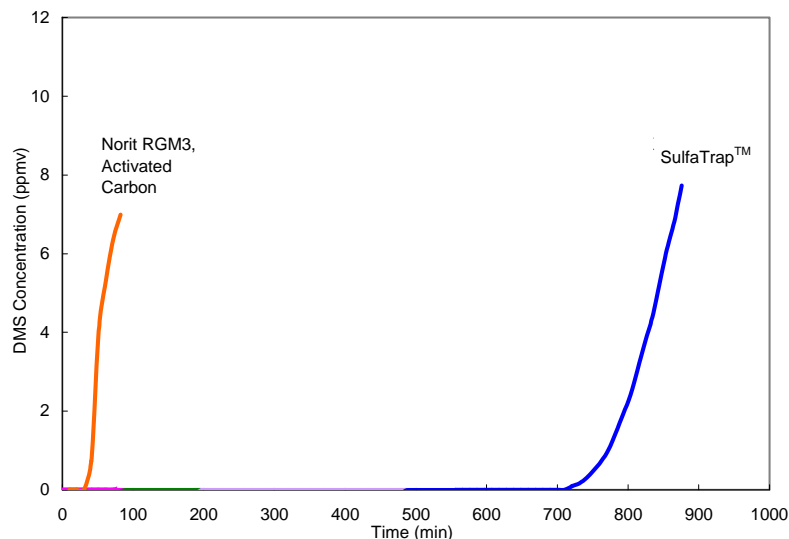


Figure 1. Comparison of TDA’s SulfaTrap™ sorbent with other adsorbents. All samples were tested at  $60,000 \text{ h}^{-1}$  in a natural gas mixture containing 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at  $T= 20^{\circ}\text{C}$ ,  $P= 5 \text{ psig}$ .

Table 1. Pre-breakthrough capacities calculated for the samples shown in Figure 1.

Sample	Pre-Breakthrough Capacity (% wt. S)
TDA’s SulfaTrap™ Sorbent	3.12%
Grace X Zeolite	0.36%
Norit RGM3 Activated Carbon	0.18%

The breakthrough profiles of all sulfur species for TDA’s SulfaTrap™ - R3 sorbent are presented in Figure 2. In agreement with the prior literature, DMS breakthrough occurred first at 720 minutes, followed by the breakthrough of TBM at 1080 minutes. The breakthrough of THT was never observed during 1400 minutes of testing. These results suggest that the affinity of the sorbent is weakest for the DMS and strongest for the THT. The saturation sulfur capacity of the sorbent was calculated as 3.88% wt. (the saturation capacity is the total sulfur loading of the sorbent measured when the DMS concentration at exit of the bed was equal to its inlet value).

In addition to the small-scale tests, we also tested the performance of a few samples in large-scale (engineering-scale tests that can be easy to scale-up). In these tests, we used 25 cc of sample and a calibrated gas mixture containing synthetic natural gas, with 50 ppmv water and 50 ppmv DMS. The DMS breakthrough profiles are shown in Figure 3 for two of the samples and the test results are reported in Table 2. The first test was done on activated carbon (Norit RGM3 Activated Carbon), which is the current industry standard. The second test was done with our SulfaTrap™ sorbent. Our sorbent greatly outperformed the activated carbon, with 3.2% wt. breakthrough capacity. Note that the sulfur adsorption capacity measured in the large-scale tests and small-scale accelerated tests were in good agreement (3.2% wt. capacity vs. 3.12% wt., for TDA SulfaTrap™-R3, and 0.18% vs. 0.13% for Norit RGM3).

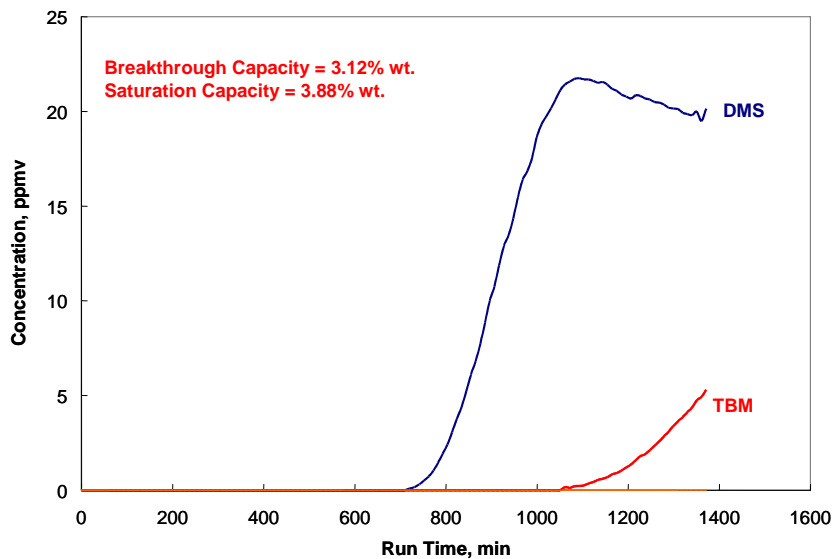


Figure 2. Breakthrough profiles of sulfur components from TDA's SulfaTrap™ – R3 sorbent. Natural gas with 12.3 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT at 60,000 h<sup>-1</sup>, T= 20°C, P= 5 psig.

Table 2. The sulfur adsorption capacities in large-scale tests.

Sample	Breakthrough Capacity (% wt. S)
Norit RGM3 Activated Carbon	0.13%
TDA's SulfaTrap™ sorbent	3.20%

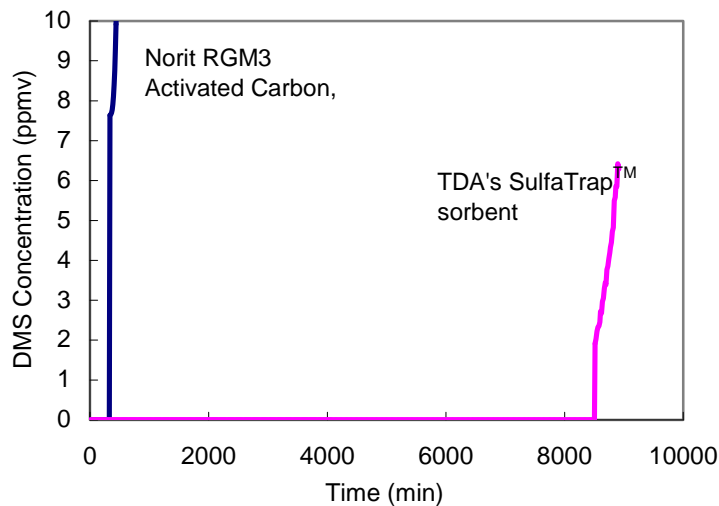


Figure 3. Comparison of breakthrough profiles for two samples tested in the large-scale apparatus. Both samples were tested in a natural gas mixture with 50 ppmv water and 50 ppmv DMS. The GHSV= 1,500 h<sup>-1</sup>, T=20°C, P= 50 psig.

## Effect of Moisture

The presence of water reduced the sulfur adsorption capacity of all sorbents. The capacity of the zeolite-X is reduced the most by approximately 83%, showing zeolite-X's high affinity for the water vapor. The water most likely adsorbs on the surface of the sites, competing with the sulfur. It is worth noting that Yang and his coworkers saw a similar reduction for copper exchanged Y zeolite, which lost 75% of its breakthrough capacity in the presence of 300 ppmw H<sub>2</sub>O (4). Activated carbon had minimal drop in capacity in the presence of water, but its dry capacity was an order of magnitude lower capacity than TDA's SulfaTrap<sup>TM</sup>-R3. As shown in Table 3, the capacity of the SulfaTrap<sup>TM</sup>-R3 sample is also reduced in the presence of 50 ppmv water vapor. However, the competition with water vapor was less of a problem (only 24% drop compared to 83% for commercial zeolite) for the SulfaTrap<sup>TM</sup>-R3 sorbent, and its dry capacity was approximately 800% better than that of zeolite X, and 1600% better than activated carbon.

Table 3. Effect of moisture on various sorbents.

Sample	Dry Capacity	Wet Capacity	Percent Capacity Loss
TDA's SulfaTrap <sup>TM</sup> -R3 Sorbent	3.1%	2.4%	24%
Grace X Zeolite	0.36%	0.06%	84%
Norit RGM3 Activated Carbon	0.18%	0.17%	2.3%

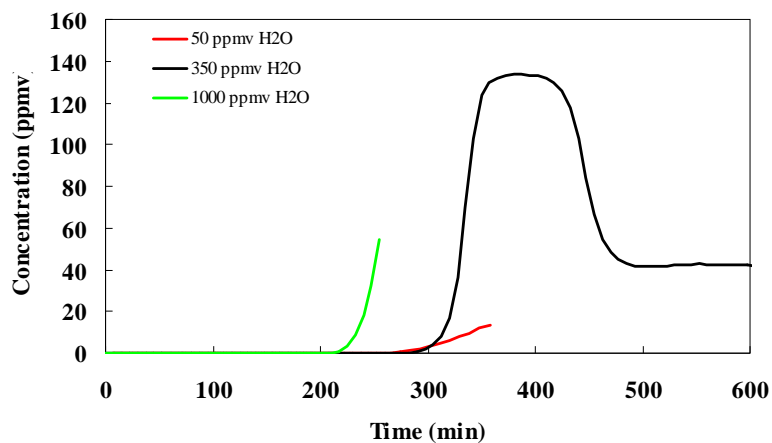


Figure 4. The effect of moisture level on DMS adsorption in TDA's SulfaTrap<sup>TM</sup>-R3 Sorbent. T= 22°C, P= 5 psig, Natural gas with 46 ppmv DMS at 60,000 h<sup>-1</sup>.

We analyzed the effect of increased levels of moisture on SulfaTrap<sup>TM</sup>-R3. From Figure 4 we see that as the moisture content in the natural gas stream increases from 50 to 350 ppmv the DMS breakthrough point does not change but the shape of the breakthrough curve does change. The DMS wave front is sharp and the breakthrough curve goes over the inlet DMS concentration of 46 ppmv. This "roll over" is widely seen in the breakthrough curves of multicomponent feed mixtures and is a result of competitive adsorption of water and DMS. Water adsorption wave front sweeps through the bed and it desorbs some of the adsorbed DMS giving rise to the roll over. As we increase the moisture level further to 1000 ppmv the DMS breakthrough capacity drops by 30%. The breakthrough capacities are reported in Table 4. This shows that moisture

levels up to 350 ppmv has only minimal impact on the performance of SulfaTrap™-R3 for DMS removal.

Table 4. The Effect of moisture level on DMS and mercaptan adsorption on TDA's SulfaTrap™-R3 Sorbent.

Feed Gas mix	Adsorbate	H <sub>2</sub> O (ppmv)	Breakthrough Sulfur loading (wt%)
DMS (~46 ppmv) in Natural gas	Dimethyl Sulfide (DMS)	50	1.75
		350	1.64
		1046	1.27

At very high moisture levels of 4000 ppm, SulfaTrap™ – R2 (another SulfaTrap™ Series sorbent) performs better than SulfaTrap™ – R3. In fact sulfur removal capacity of SulfaTrap™-R2 does not change due to moisture levels. Fuel cell manufacturers often prefer a sorbent which is more robust and does not have appreciable changes in sulfur capacity with fluctuations in moisture level which could some times reach as high as 4000 ppmv H<sub>2</sub>O. Figure 5 shows the breakthrough of DMS in the presence of 4000 ppmv H<sub>2</sub>O on SulfaTrap™ – R2 and R3 for comparison.

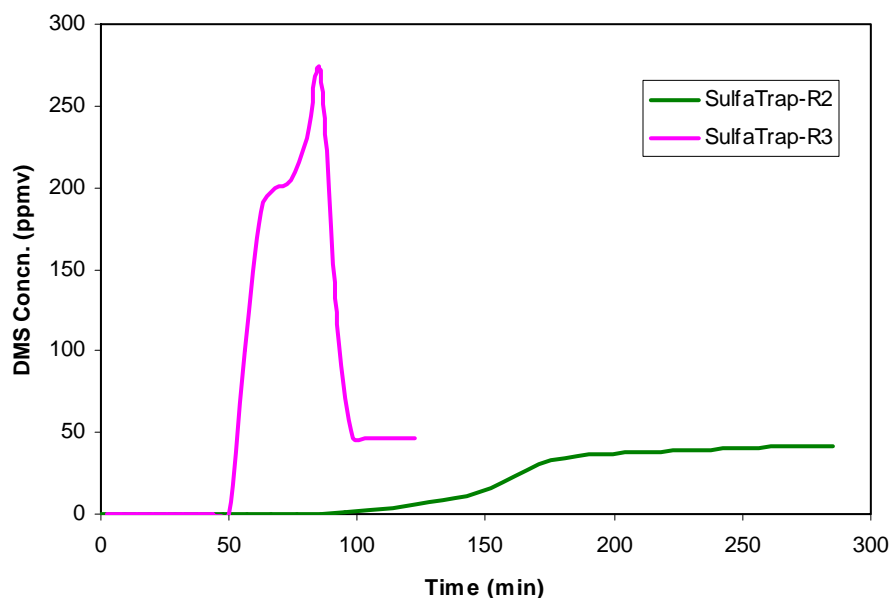


Figure 5. Effect of 4000 ppmv H<sub>2</sub>O on the breakthrough of DMS on various sorbents. Inlet DMS = 50 ppmv. GHSV = 60,000 h<sup>-1</sup>.

### Effect of Temperature

Depending on the geographic location and the season, the desulfurization system used in residential units has to work over a wide range of temperatures. In the bench-scale tests, we evaluated the performance of the SulfaTrap™ sorbent at three different temperatures. To carry out the 0/5°C test, the reactor was placed in a chiller to maintain a low and stable temperature. For the 40/45°C test, the reactor was heated using heat tapes.

Figure 6 and Figure 7 shows the DMS breakthrough profiles in a dry and wet natural gas mixture respectively at the three temperatures.

Table 5 and Table 6 lists the pre-breakthrough sulfur adsorption capacity at each temperature for dry and wet natural gas mixtures. It is observed that as the temperature increases, the sorbent capacity decreases (at 40/45°C, the sulfur capacity of the sorbent is reduced by 35-40% in comparison to that can be achieved at 19/22°C). Such temperature dependence suggests that the removal of the sulfur compounds is purely based on physical interactions. It is important to note that the SulfaTrap™ sorbent is fully regenerable, and once the sorbent reaches its capacity all the sulfur-bearing odorants can be driven off from the surface with a mild temperature swing by heating the bed to 300°C. Previously, we demonstrated that the sorbent could maintain its sulfur adsorption capacity through many adsorption/regeneration cycles [5] by simple heating. Thus, the observed decrease in the capacity at higher temperatures was expected.

Table 5. Sulfur adsorption capacity as a function of temperature.

Testing Temperature	Run Time (min)	Capacity
5°C	830	3.59%
19°C	720	3.12%
40°C	237	1.02%

Table 6. Sulfur adsorption capacity as a function of temperature for wet natural gas.

Testing Temperature	Run Time (min)	Capacity
0°C	359	2.35%
22°C	289	1.75%
45°C	152	1.00%

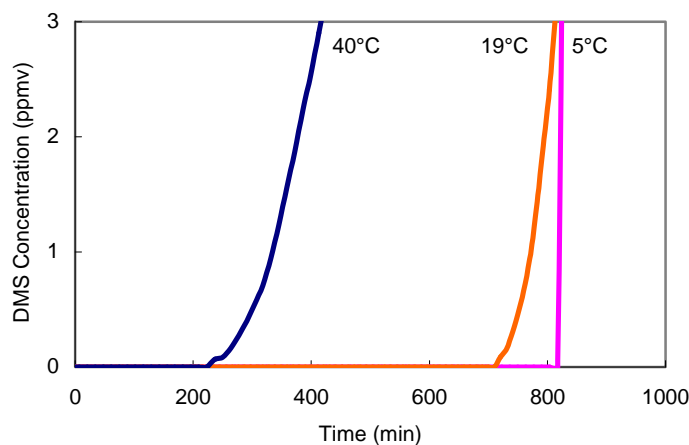


Figure 6. Effect of temperature on sorbent performance. TDA's SulfaTrap™ sorbent tested in dry natural gas mixture with 12.9 ppmv DMS, 8.9 ppmv TBM and 8.9 ppmv THT, P= 2 psig.

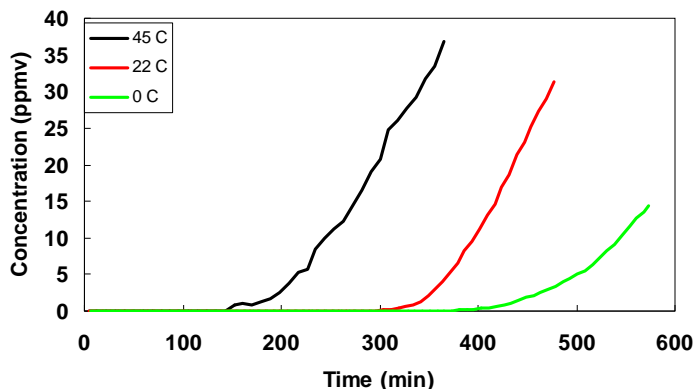


Figure 7. Effect of temperature on sorbent performance for DMS removal in the presence of moisture 50 ppm. GHSV = 60,000 h<sup>-1</sup>

### Conclusions

This study shows TDA's SulfaTrap<sup>TM</sup> has higher capacity for natural gas desulfurization than commercial zeolites and carbon samples and also that water competes with odorants for adsorption sites and negatively impacts the performance of all desulfurization sorbents. Commercial zeolites lose most of their capacity in the presence of water while TDA's SulfaTrap<sup>TM</sup>-R3 still has high sulfur capacity. At very high moisture levels TDA's SulfaTrap<sup>TM</sup>-R2 showed very good capacity. There is competition between water and DMS for the adsorption sites in SulfaTrap<sup>TM</sup> - R3 and for the case of SulfaTrap<sup>TM</sup> - R2 we observed that there is no competition between water and DMS for adsorption sites. The order of selectivity for odorants on SulfaTrap<sup>TM</sup> is THT > TBM > DMS.

### ACKNOWLEDGMENTS

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