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NGL RECOVERY PLANT:
TREATER OPTIMIZATION FOR WATER AND MERCAPTAN REMOVAL

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ABSTRACT

A number of process and product considerations contribute to the reliable operation of a molecular sieve natural gas treater. When the natural gas feed dehydrator to an NGL Recovery Plant was upgraded to a treater for removal of water and mercaptan sulfur, the plant soon reported a performance shortfall on the retrofitted treater. A series of escalating on-site troubleshooting and product evaluation efforts were performed that contributed to the plant's ability to completely turn around its treater performance.

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BACKGROUND

Molecular sieve adsorption is a well established processing tool in the natural gas industry. Adsorbents are extensively used for total front-end water removal in cryogenic natural gas processing and for the removal of both water and sulfur compounds in natural gas treating. Although a comprehensive understanding of the adsorption system is necessary for effective troubleshooting of both dehydrators and treaters, the added complexity of the adsorption dynamics in a natural gas treater generally demands a more rigorous troubleshooting effort than that required for dehydration units alone. The uniqueness and potential variability of each treater's feed stream also means there is no universal solution. Product selection and process parameters are often specific to each operating unit. Troubleshooting on-site ensures an accurate assessment of actual conditions.

In order to effectively evaluate the performance of an adsorption system, the process parameters need to be fully defined. This requires complete documentation of the feed and regeneration system operating conditions and comprehensive analysis of the feed composition and impurities. An adsorption system is a dynamic operation in which all of the process parameters typically have some influence on the operation of the system.

A significant variable that uniquely influences the behavior of multi-component adsorption systems like molecular sieve treaters is co-adsorption interference. For example, in a molecular sieve gas treater, co-adsorption interference by hydrocarbons or water tends to reduce mercaptan sulfur loading by inhibiting its adsorption mass transfer. Consequently, it is critical to understand the unique characteristics of the treater feed composition and the detrimental effect of heavier hydrocarbons and water on treater performance during troubleshooting efforts.

Our experience illustrates that determining the degree to which a treater's sulfur loadings are suppressed by interference from heavier hydrocarbons is rarely straightforward. Close examination of the sulfur removal characteristics of the commercial treater and on-site pilot scale testing may be required to determine the mechanism of molecular sieve capacity loss and to identify the optimal adsorbent for the treating service.

This paper discusses the methodology used to troubleshoot a poorly performing molecular sieve treater in natural gas service and explains the steps that eventually led to its successful operation. While these steps can be followed for different plants, the conclusions of each evaluation will most certainly vary as no two plants are exactly alike.

DISCUSSION

Case History

Having successfully operated its original three-vessel adsorption unit for many years as a natural gas dehydrator in which 4A-DG MOLSIV™ adsorbent was installed to protect the downstream cryogenic unit, our customer undertook a revamp to reconfigure the dehydrator (designed for water removal only) as a treater (water and mercaptan removal).

In consultation with UOP, a fourth vessel was added to provide a portion of the additional adsorption capacity needed for the expanded service of simultaneous water and mercaptan sulfur removal. The revamped four vessel system was loaded with a compound bed configuration of sulfur removal grade RK-34 and RK-35 MOLSIV adsorbents prior to being commissioned as a treater.

Reconfiguring the adsorption system to treating service also required the integration of a Selexol™ liquid solvent system to remove the desorbed sulfur from the spent regenerant stream.

However, within a few months of treater operation, the customer reported a shortfall in the mercaptan sulfur removal capacity of the adsorption system.

Commercial Treater Evaluation

To quickly assess the treater operation, UOP field engineers collected the process operating data summarized in Table I below.

Table I - Summary of Treater Operating Conditions

Adsorption	
Flowrate	245-255 MMSCFD, 3 parallel beds online
Pressure	960 psig
Temperature	90 °F
Moisture Content	50 ppmv by UOP's analyzer
Mercaptan Content	170 ppmv by outside lab analysis
Cycle Length	4.75 hrs + 4.75 hrs + 4.75 hrs

Inlet gas hydrocarbon composition by an outside lab:

CO_2	0.6015 mol%	Iso-butane	0.3349 mol%
N_2	0.8537	N-butane	0.5958
H_2S	0.6633	Iso-pentane	0.2070
Methane	88.6501	N-pentane	0.1906
Ethane	5.4898	Hexanes +	0.5576
Propane	1.8457		

Regeneration	
Flowrate	18.6 MMSCFD residue gas
Pressure	940 psig
Temperature	600 °F heater outlet
	540 °F maximum heating bed outlet
	120 °F cooling bed outlet
Cycle Length	195 minute heat step
	90 minute cooling step
Composition	97% C_1, 2% C_2, 1% N_2, <0.5% C_3+

The key process variables of treater feed rate and temperature, feed moisture and sulfur contaminant concentrations, and adsorption cycle length (Table II) were recorded so that a comparison could be made between the observed and expected water and sulfur capacity of the treater.

Table II - Treater Sequence

<table>
<tr><td>Bed A</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td><td>HEAT</td><td>COOL</td></tr>
<tr><td>Bed B</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td><td>HEAT</td><td>COOL</td><td colspan="2">ADSORB</td></tr>
<tr><td>Bed C</td><td colspan="2">ADSORB</td><td>HEAT</td><td>COOL</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td></tr>
<tr><td>Bed D</td><td>HEAT</td><td>COOL</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td><td colspan="2">ADSORB</td></tr>
</table>

The regeneration gas rate, heating temperature, cycle length, and impurity concentrations (both entering and exiting the regenerating beds) were examined to assess the regeneration effectiveness. The differential pressure across the adsorption vessels was measured as an indicator of potential mechanical deficiencies in the treater or in related equipment.

The status of the upstream feed treating equipment was discussed with the customer in an effort to identify any mechanical changes or potential problems in the feed gas train (Figure 1).

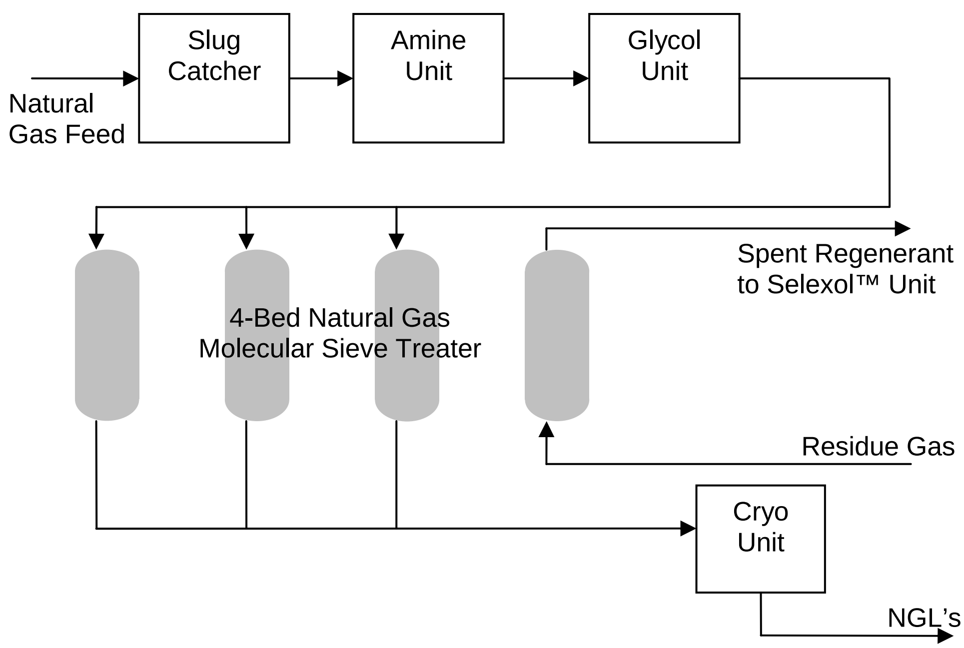

Figure 1 – Simplified Block Flow Diagram

The recent adsorbent loading and vessel inspection procedures were also reviewed with the customer in case vessel support failure or improper leveling of the adsorbent layers in these compound beds (Figure 2) might be contributing to the performance shortfall.

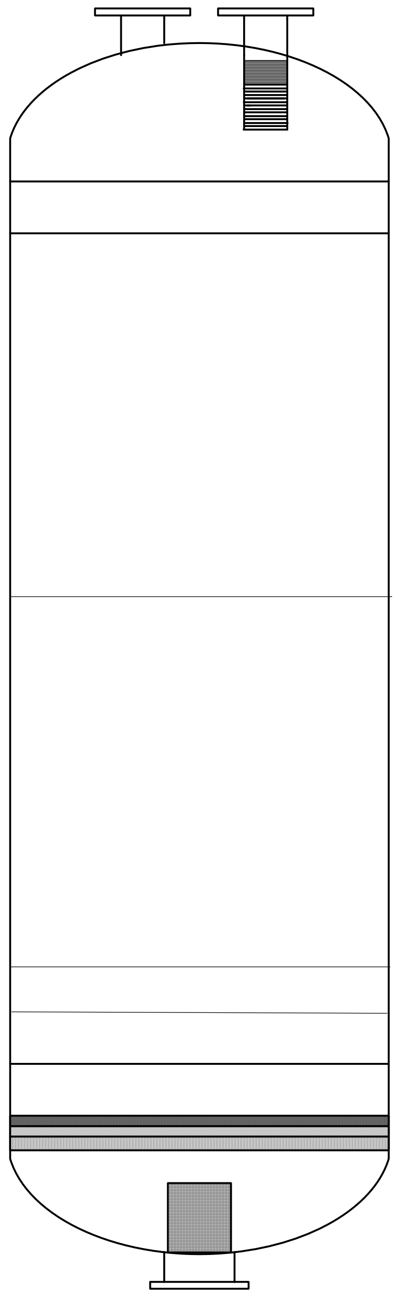

Figure 2 - Adsorbent Loading Diagram.

All of the process and mechanical factors examined have the potential to influence adsorption performance. Unfortunately, our preliminary review did not uncover the source of the treater's malperformance.

Because the treater is not equipped with online sulfur analysis, UOP field engineers assessed the treater performance by using mercaptan stain tubes to test the feed and outlets of the four vessels throughout the adsorption cycle. Shown below in Figure 3, this analysis revealed that the below predicted performance was characterized by an early and elongated mercaptan sulfur breakthrough front on all four vessels. These findings indicated that co-adsorption interference was a possible cause of the treater's mercaptan removal performance shortfall.

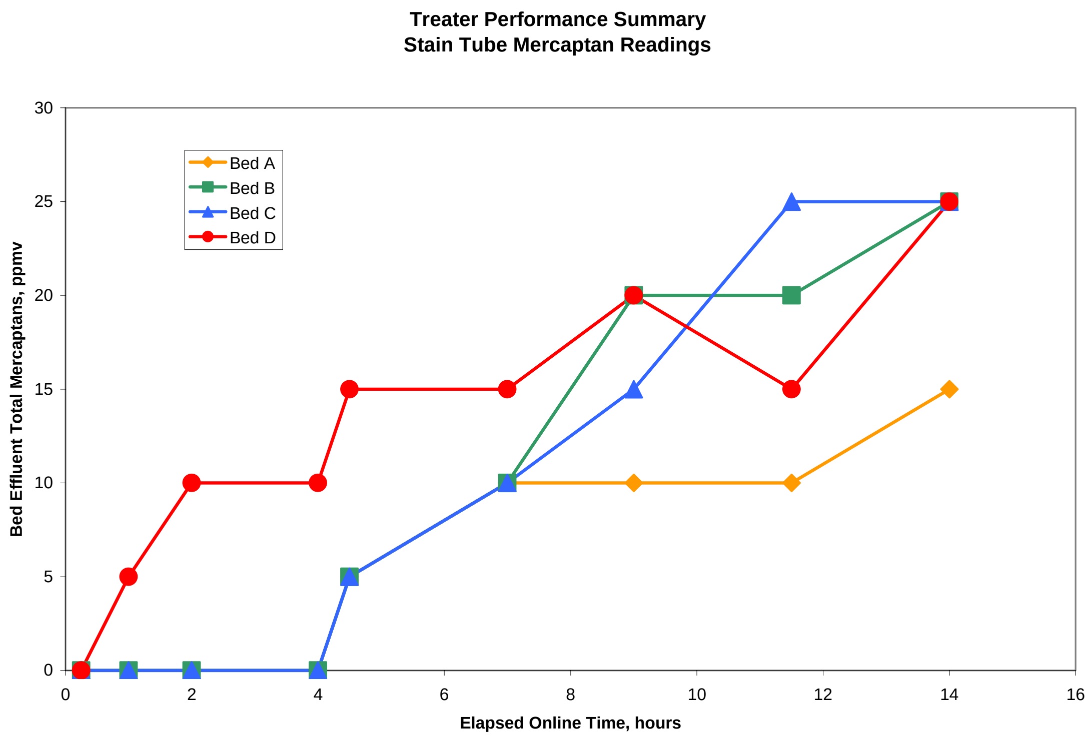

Figure 3 - Treater Performance Survey

Installed Product Accelerated Aging Test

Since no explicit mechanism of the treater's loss of capacity was identified in this preliminary on-site effort, UOP field engineers initiated a short follow-up test of the RK-34 and RK-35 adsorbents installed in this treater. Fresh samples of these adsorbents were rapidly aged by alternately exposing them to large volumes of treater feed and regeneration gas. The adsorbent samples were then sent to UOP's laboratory for analysis.

The results (Table III) of the laboratory analysis showed unusually high levels of carbon on the cycled adsorbent samples. The findings indicated that hydrocarbons in the treater feed were not effectively desorbed during regeneration and had a tendency to decompose with heat. These irreversibly adsorbed hydrocarbons and accumulated decomposition products would have created an increasing resistance to mass transfer that reduced the adsorbents' mercaptan removal performance.

Table III - Analysis of Aged Adsorbents

	RK-35	RK-34
% Carbon, measured	4.73	7.48
% Carbon, typical	<1	<2
% Carbon, fresh	<0.1	<0.1

Comparative Product Pilot Test

The next challenge was to identify the optimal adsorbent product for this customer. Knowing that hydrocarbon co-adsorption was affecting the mercaptan removal performance, adsorbents were selected and tested on-site for comparative sulfur capacity.

While there are many adsorbent options, the selection of the optimal adsorbent(s) is critical to treater performance. Adsorbents with smaller pore openings have the advantage of minimizing hydrocarbon co-adsorption and adsorbent fouling. However, this is counterbalanced by the increased mass transfer resistance of smaller pore adsorbents. Large pore adsorbents must be used for the removal of large or branched-chain mercaptans.

Two small test units (Figures 4 and 5) with local flow, pressure, and temperature indicators were brought to the site along with a portable gas chromatograph used to speciate the sulfur of the influent and effluent of the adsorbent test products. The test protocol again called for accelerated aging of the test adsorbents (Figure 4). These aged products were then (Figure 5) installed on a slipstream of the commercial treater feed for side-by-side comparisons. This test skid included a small molecular sieve pre-dryer so that the dynamic sulfur adsorption capacity of the products could be measured without interference from water. The mercaptan species in the treater feed included, on average: 35 ppmv methyl mercaptan, 70 ppmv ethyl mercaptan, 50 ppmv iso-propyl mercaptan, and 25 ppmv sec-butyl mercaptan.

Figure 4 - Product Aging Test Rig

Figure 5 - Product Comparison Test Rig

The relative sulfur capacities of the adsorbents in both single and compound bed arrangements were determined. The gas exiting each product test cartridge was sampled hourly and chromatographically analyzed for sulfur content. Figure 6 shows the effluent sulfur concentrations as a function of time onstream for RK-35/RK-34 adsorbents in combination, UI-94/RK-34 adsorbents in combination, and RK-34 adsorbent alone. As can be seen, breakthrough occurs later for the RK-34 only case than for either of the combination beds. The results indicated that superior cycled sulfur capacity would be achieved by modifying the current compound adsorbent bed with a full bed configuration of RK-34 adsorbent.

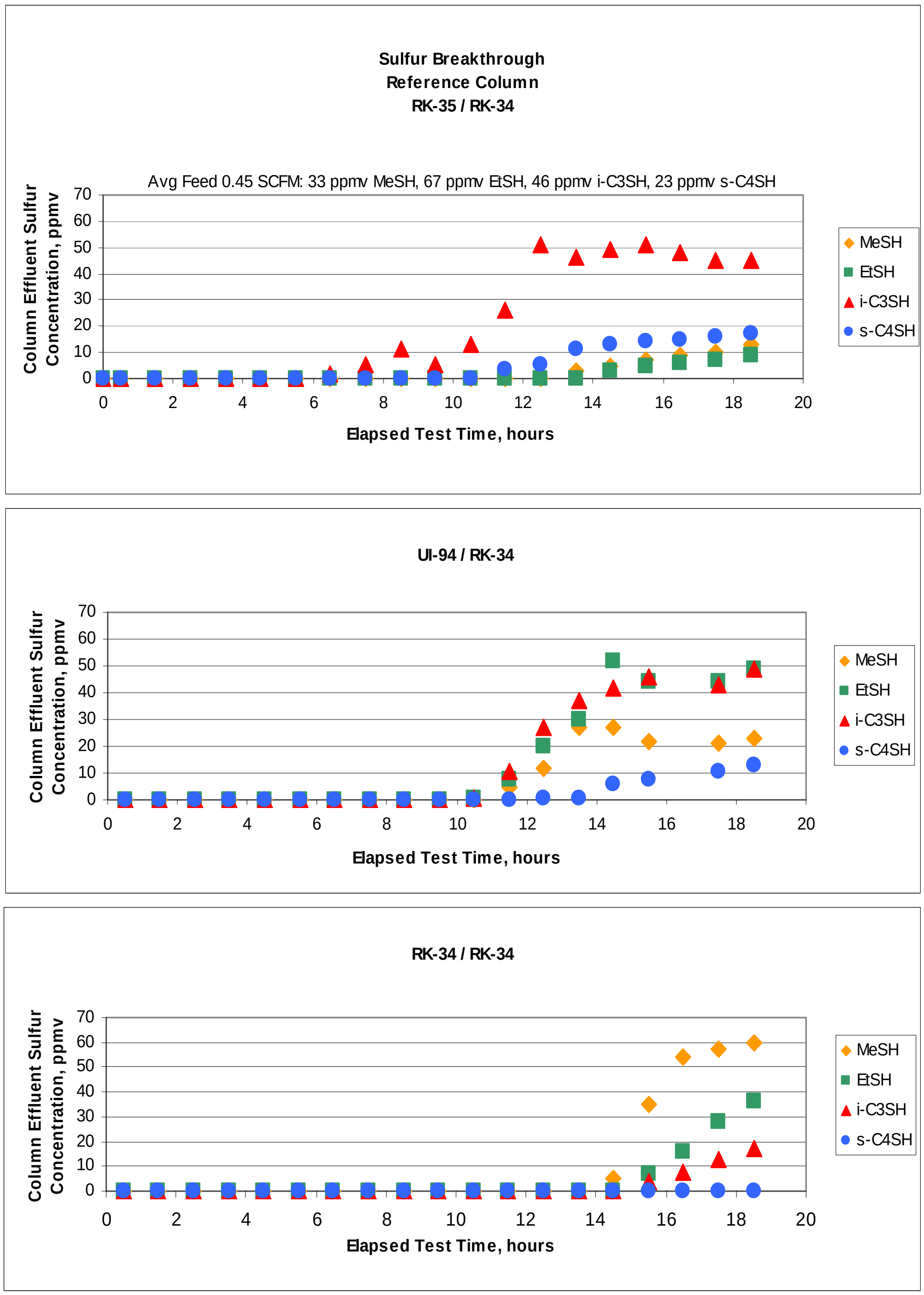

Figure 6 - Aged Adsorbent Sulfur Capacity Evaluation

During the cyclic adsorbent aging, the source of the irreversibly adsorbed hydrocarbons became evident. The process sample points showed the continuous presence of liquid hydrocarbon and glycol. Apparently, the filter-coalescer immediately upstream of the adsorption unit had been specifically designed to remove entrained glycol from the upstream TEG Unit. The unexpected presence of hydrocarbon liquids not only aggravated foaming and glycol losses in the TEG Unit, but also significantly reduced the filter coalescer's effectiveness. As a result, liquid hydrocarbon and glycol were carrying over in large quantities to the adsorption system. Plant personnel successfully resolved this problem by upgrading the filter coalescer gas/liquid separators throughout the feed gas system.

Since acceptable treater performance could not be achieved in the presence of hydrocarbon liquids, a recharge of the commercial treater with RK-34 adsorbent was recommended once the modifications of the filter coalescer were made.

Pilot Testing to Validate Product Selection

After the plant upgraded the feed gas filter/coalescer, the test protocol was repeated. Again it included accelerated aging of the adsorbents followed by side-by-side comparisons of the aged adsorbents in several configurations to study sulfur capacity. As can be seen below in Figure 7, the RK-34 adsorbent demonstrated superior mercaptan equilibrium and breakthrough capacity in this testing.

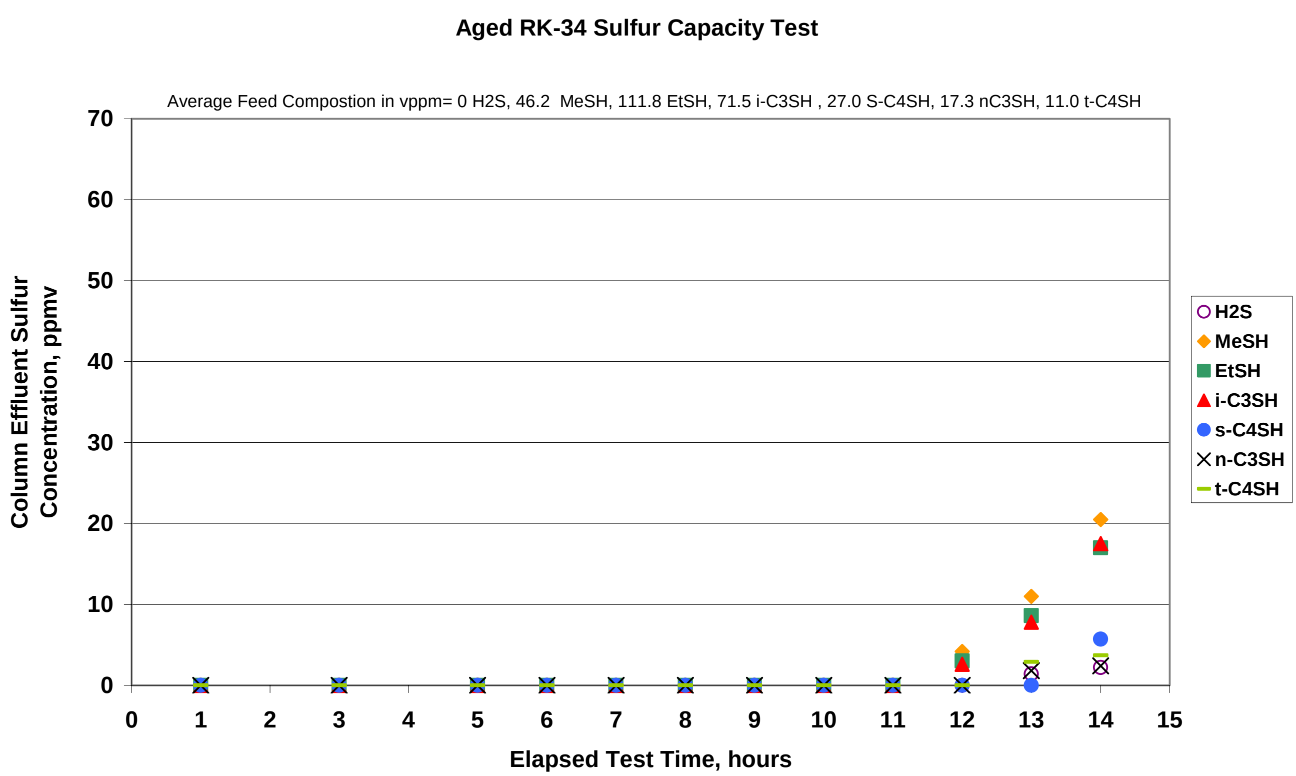

Figure 7 - Aged RK-34 Adsorbent Sulfur Capacity Test

Hydrocarbon Co-adsorption – Further Studies

To quantify the relative amount of hydrocarbon co-adsorption on molecular sieves used in natural gas treating, the adsorbents from the pilot test were further evaluated. Exposed adsorbent samples were sent to an off-site lab to determine their hydrocarbon content.

The volatile co-adsorbed hydrocarbons were measured using repetitive purges and hydrocarbon analysis of the purged gas. The adsorbents were then analyzed for residual hydrocarbon so that the total quantity of remaining co-adsorbed hydrocarbons, both non-volatile and non-desorbable, could be calculated. These methods led to the determination (Figure 8) that hydrocarbon co-adsorption was 5% lower with the RK-34 adsorbent than with the RK-38, and 17% lower when compared to RK-33 adsorbent.

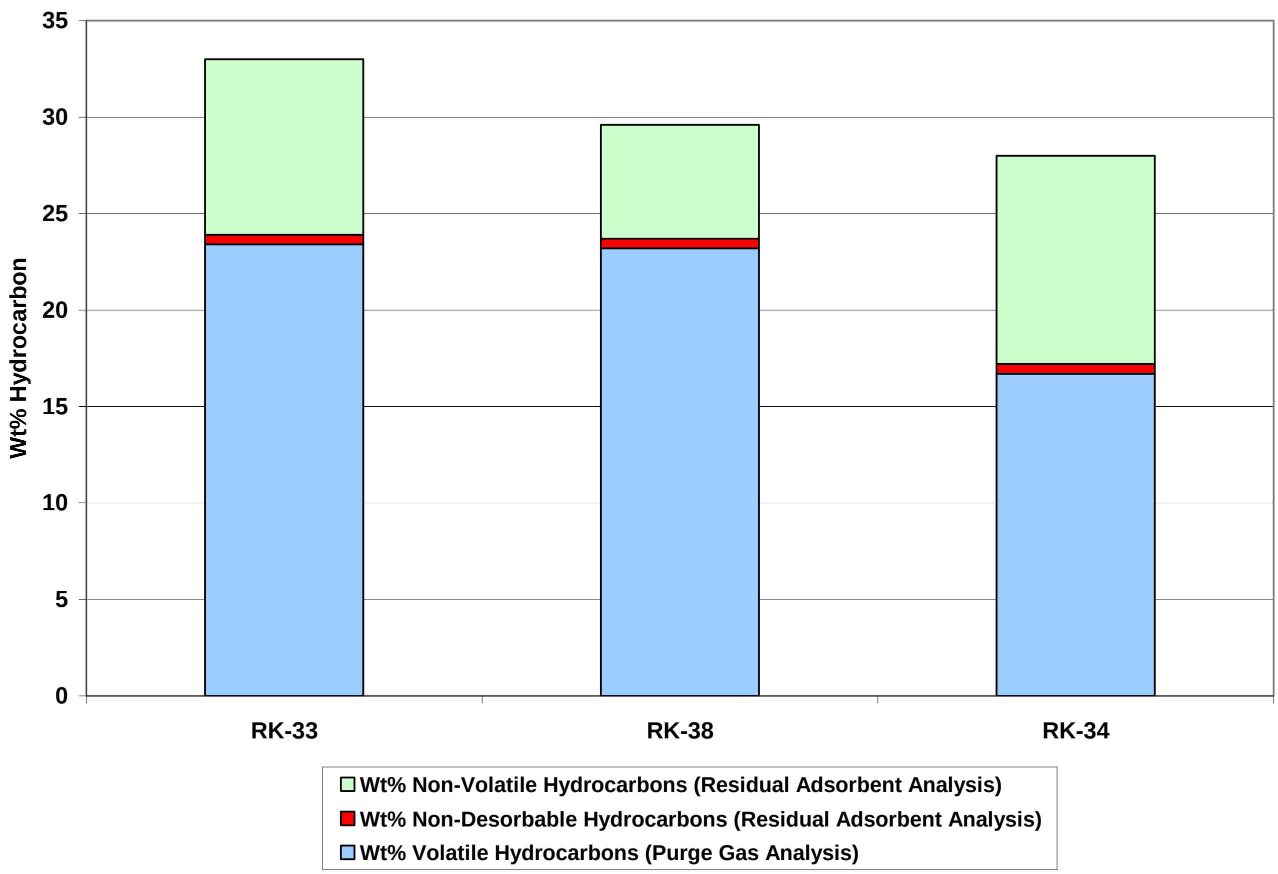

Figure 8 - Hydrocarbon Co-adsorption Data Summary

This final testing, performed with the treater feed in the absence of liquid hydrocarbon and glycol carryover, substantiated the superior mercaptan capacity and lower hydrocarbon co-adsorption characteristics of RK-34 adsorbent in this service.

CONCLUSION

Our experience illustrates that determining the degree to which a treater's sulfur loadings are suppressed by interference from heavier hydrocarbons is rarely straightforward. When there is no obvious source of performance shortfall, pilot test work can be effective in identifying the mechanism of capacity loss. In this case, hydrocarbon co-adsoption was compounded by the presence of liquid hydrocarbon carryover.

Liquid hydrocarbon carryover is a difficult to quantify and often underestimated factor in the performance of natural gas adsorption systems. The degree to which liquid carryover harms the performance of adsorption systems tends to be a function of the quantity and characteristics of the entrained liquids and of the specific adsorption application. The scope of this test work might not have advanced to pilot scale studies if the separator deficiencies had been recognized earlier in this undertaking. Yet the efforts associated with these pilot studies conclusively established liquid carryover as the overwhelming factor in the treater malperformance.

In addition, pilot testing can accurately determine the most appropriate molecular sieve products for the specific requirements of the individual treating service. In each instance, the product selection may vary.

A final on-site performance evaluation of the commercial treater validated our earlier technical recommendations, which had led to the plant's implementation of the upgraded filter coalescer and adsorbent product change. These modifications enabled the commercial treater to meet its required performance criteria. In the case of this treater, it continues to provide the desired water and mercaptan sulfur removal performance to this day.