DESIGNING CUSTOMIZED DESULFURIZATION SYSTEMS FOR THE TREATMENT OF NGL STREAMS

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Abstract

The purpose of this paper is to define and evaluate the key sequential steps required in transmitting, sampling and speciating sulfur laden NGL streams, in order to recommend and install absorbents capable of passing pipeline copper strip tests. An evaluation of the sulfur adsorption characteristics of specific sample containers will be given along with sample container material recommendations. A description of speciation instrument options will be followed by a description of the method for choosing and testing absorbents from an appropriate range to remove the sulfur species present in the speciated NGL.

A case study will be discussed demonstrating sulfur absorbent selection after a sour liquid is sampled, speciated and treated using an absorbent in a plant slipstream treater in the field.

The effect of sulfur species, concentration, temperature and pressure on the candidate absorbent will be discussed.

Introduction

Purification processes for natural gas, refining and petrochemical feed stocks are of primary importance to the modern chemical and fuel industries. Various contaminants are commonly found in NGL streams and their presence can result in a failure to meet pipeline and copper strip specifications. The growing trend towards applying more severe emission/environmental standards and the economics of refining and petrochemical process optimization, require that NGL streams be purified to ever more stringent standards.

A primary contaminant found in most virgin NGL streams is sulfur, present as H_2S, elemental sulfur and often in various organic forms. These sulfur compounds are known poisons for the majority of refinery processes, even when present at low ppb levels [often below the level of detection for many facilities] and are significant contributors to atmospheric pollution. Plant and pipeline operators may experience design, operational and maintenance issues when sulfur levels exceed set catalytic, environmental or transmission specifications.

Desulfurization of fuels is a self-evident requirement to control acid gas emissions and meet legislation standards. The continuing trend toward lower emission fuels is evident with recent changes in legislation mandating low sulfur gasoline and diesel in many parts of the world; price differentials are evident between low and high sulfur fuel oils.

The base technology of non-regenerable fixed bed desulfurization has not changed significantly over the years, continuing to rely on classical chemical and physical reactions. However, the activity of desulfurization processes has continuously developed in response to the increasing demands of downstream processes and emission legislation. The use of fixed bed systems for purifying NGL streams is both practical and cost effective.

NGL streams can vary significantly in terms of their hydrocarbon and sulfur content. Matching the appropriate absorbent to purify a specific NGL is key in designing any fixed bed system. Sequential steps should be taken to ensure an appropriate match is made between candidate absorbent and specific NGL. The steps include sampling the NGL in question, transportation from plant site to laboratory,

speciating its hydrocarbon and sulfur content, screening an appropriate absorbent to test under realistic conditions either in-lab or at-site.

The Duke Energy Field Services Patrick Draw facility is a fractionation plant processing NGL components for sale to refining and petrochemical customers in Wyoming. In 2002 Duke approached Johnson Matthey Catalysts to supply a fixed bed absorbent in order to meet a total sulfur specification in an NGL stream. After full NGL characterization, absorbent screening commenced utilizing a fully instrumented slipstream test reactor located at the depropanizer bottoms section of the process plant. After taking the sequential steps described, an appropriate absorbent was identified and successfully tested in the slipstream test reactor. This case study is designed to illustrate the steps required when designing a customized desulfurization system for the treatment of an NGL stream.

NGL Sulfur Specifications

In many areas of the world the transportation of lower molecular weight hydrocarbon fractions such as NGL is dependent upon a pipeline specification being achieved. Such specifications are tending towards lower sulfur levels, with new ceilings being imposed by governments and associated legislative agencies on both upstream operators and downstream refineries. Reactive sulfur [H_2S] are soon to be replaced by total sulfur specifications, meaning the traditional technology gap for treating "non-reactive" sulfurs must be bridged prior to the implementation of these tighter specifications. One of the most commonly used methods of product specification testing is the copper strip test for lower molecular weight liquid hydrocarbons [ASTM D-1838-84 and D-130-83]. The test is ubiquitous amongst operators since it is cheap, simple to perform and generates instant results. However, there is a degree of subjectivity associated with the test in terms of requiring the correct lighting, angle of strip inspection etc. The test has been designed to limit the corrosion of pipeline materials by H_2S, hydrolyzed COS, elemental sulfur and polysulfides

Often after passing a copper strip, liquids transported down a pipeline, or by rail car, will fail subsequent strip tests after either blending or hydrolysis or some combination of both. Elemental sulfur lay down in storage containers caused by the presence of iron on their inner surfaces is also a known source of copper strip failure after previous strip passes.

Existing solid absorbents [both regenerative and non-regenerative] used on gas and fractionation plants are capable of removing H_2S to levels below which a transportable liquid will pass a copper strip test. Currently though there is a lack of appropriate products to remove certain less reactive species present in levels, often equal to and exceeding those of H_2S. In future the tighter specifications outlined above will require a greater absorption efficiency in the removal of less reactive S species often found to co-exist with H_2S in NGL streams.

Non-regenerable mixed metal oxide absorbents

Using non-regenerable fixed bed absorbents to desulfurize NGL streams is a cost effective means to provide ultra purification. The low capital expenditure associated with using solids is seen in terms of their ease in commissioning, operation and maintenance. NGL sulfur absorbents are most effective in applications where no more than 400 lbs per day of sulfur is introduced to the bed inlet. In order for absorbents to be effective, they should contain within their structure a sufficiently high degree of porosity with an appropriate pore size distribution allowing an internal pore penetration of sulfur molecules within the NGL.

H2S removal using zinc oxide has long been the refinery industry choice when using solid non-regenerable absorbents. Zinc oxide normally operates within a temperature range of 300-700 $^{\circ}$F.

Increasingly, gas plant operators prefer to treat hydrocarbons at low temperatures to reduce the cost of heating the feed stream. At temperatures below 250 ^{o}F, H2S absorption capacity for un-promoted zinc oxides falls to levels of 5-10 % wt/wt S and higher surface area, promoted mixed metal oxides are required if reasonable capacities are to be achieved in service. Oxides of metals such as copper, manganese, lead, silver and iron are used in combination when less reactive organo-sulfur species require absorption and/or operational temperatures are below 250 ^{o}F.

Mixed metal oxide absorbents [Fig.1] are utilized in low temperature NGL desulfurization applications and are often formulated to obtain high surface area active phases.

[Fig.1] Mixed metal oxide absorbents for the low temperature desulfurization of NGL

The materials generally have lower packing densities and enhanced macroporosity to reduce diffusion limitations across the metallic lattice. Careful selection of metal oxides from within a range of absorbents is required when considering the removal of specific sulfur molecules from specific NGL streams. Inappropriate selection can result in metals absorbing non-target sulfur molecules leading to competitive absorption and therefore suppressing the design maximum pick-up capacity. Key steps are necessary when matching an NGL with a specific sulfur removal requirement to an absorbent with a specific removal capability.

Plant site key steps in the selection of a customized desulfurization system

Several important factors need to be considered when selecting an appropriate absorbent[s] for a particular NGL sulfur purification duty. The temperature and pressure of the NGL stream to be treated will impact on absorbent selection as will the nature of the NGL itself.

Obtaining as much information as possible about the NGL to be treated is critical in making the best choice of absorbent. Viable candidate absorbents should be compatible with the NGL in question and will preferably have been successfully used on similar streams under similar conditions.

NGL characterization will determine not only which absorbent should be tested, but also the level of sulfur removal capacity to expect. The final design of absorbent bed is greatly influenced from the outset by ensuring key sequential steps are successfully followed when sampling the NGL at site [Fig.2]
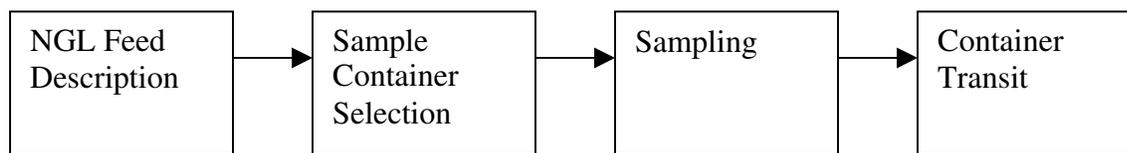
[Fig.2] Plant site NGL sampling

NGL feed description

A basic description of the NGL to be treated is often available from the operator. Typically the hydrocarbon content within a stream will be known with an approximate concentration level for each fraction. Feed density or specific gravity will also be known as will in some cases, the type and level of sulfur species present. It is important for the absorbent supplier to account for as much of this information as possible when beginning the process of designing and supplying a customized desulfurization system. Of particular importance in designing the most effective desulfurization system is the copper strip test rating of the NGL in question. This is often readily known by the plant operator.

Sample container selection

The selection of an appropriate sample container is integral to the process of obtaining, transporting and accurately analyzing the sample in question. Containers must be capable of storing NGL for up to 10 days from the point of sampling to the point of analysis and be sufficiently durable to withstand air, sea, road and rail transportation. A container must be physically and chemically inert towards the NGL it carries, sulfur absorption from the NGL onto the inner surface of the container is avoided by selecting a container that is completely passive toward the sulfur species in the NGL. The process by which a container absorbs sulfur is known as sulfur passivation and thermally and chemically treated [lined] containers are available to limit or eliminate the possibility of this phenomenon occuring. [Fig.3]

[Fig.3] Chemically treated [lined] cylinders

Sample container selection – laboratory studies

A controlled laboratory study was performed on the reactivity of several common sulfur species [known to exist in NGL streams] with the lining of various metal sample cylinders commonly used to

transport similar NGLs. ***Passivity*** shown by iron, aluminium and other related transition metals involves the loss of a cylinder's chemically inert nature in a corrosive environment. Adsorption of sulfur species onto the inner lining of containers made from the metals in question follows, resulting in a compromise in cylinder integrity with erroneous sulfur levels being reported.

The scope of the study was to determine to what degree each sulfur species reacted with different types of metal cylinder over a period of time. The following types of cylinder were used in the study:

Carbon steel
Aluminium
Teflon-lined aluminium
Stainless steel

Each cylinder was filled to a pressure of 1000 psig with an NBS traceable standard gas containing approximately 10 parts per million / volume of the sulfur compounds in Fig.4

Sulfur species	Concentration / ppmV
Hydrogen sulphide	10.1
Carbonyl sulphide	10.2
Methyl mercaptan	10.1
Ethyl mercaptan	10.4
2-Propyl mercaptan	10.9
Dimethyl sulphide	10.2
Dimethyl disulfide	10.4

[Fig.4] Sulfur compounds versus concentration

After introducing the sulfur components listed above to each cylinder, analysis was performed to determine the amount of passivation displayed towards each sulfur compound with time. Sulfur analysis was performed using a sulfur chemiluminescence detector [SCD] at intervals of 1 hour, 2 hours, 24 hours and 72 hours after initial cylinder gas filling. SCD Calibration was carried out using two primary NBTS sulfur standards. [Figs.5 to 8] show the extent to which the different sulfur components adsorb from the gas phase onto the inner lining of each cylinder.

Stainless Steel
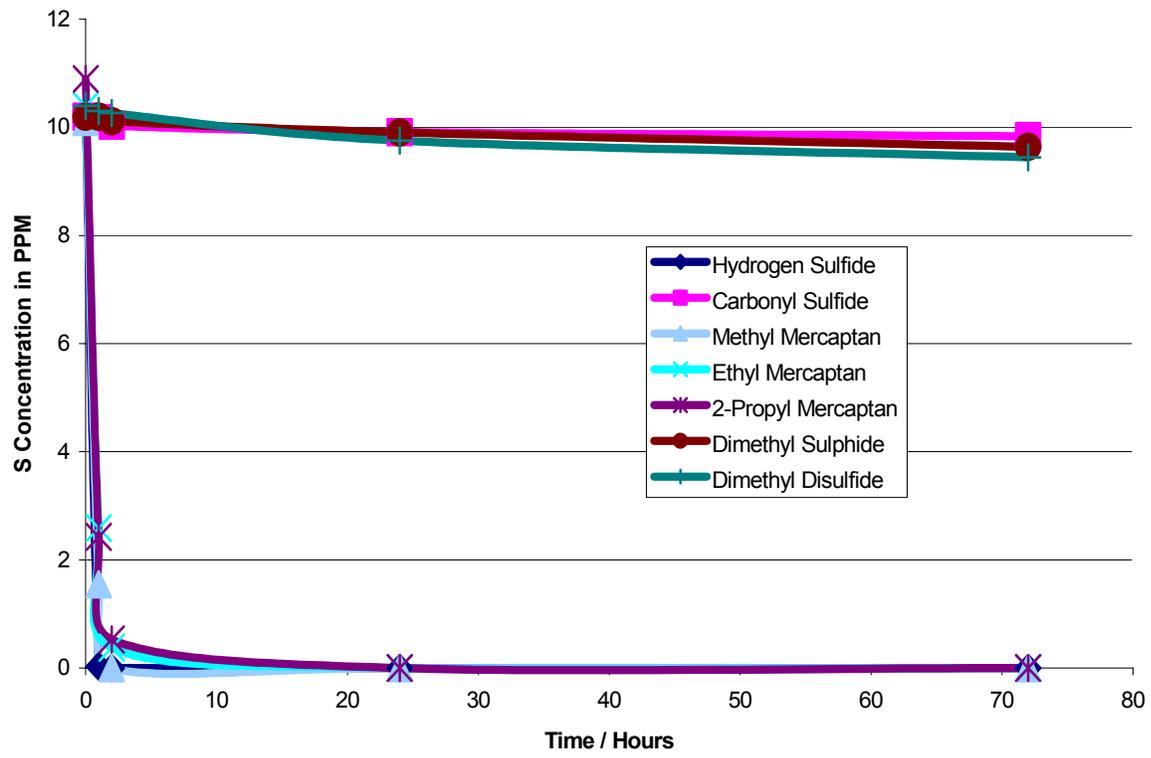
[Fig.5] Passivation of sulfur species onto a stainless steel cylinder

Aluminium
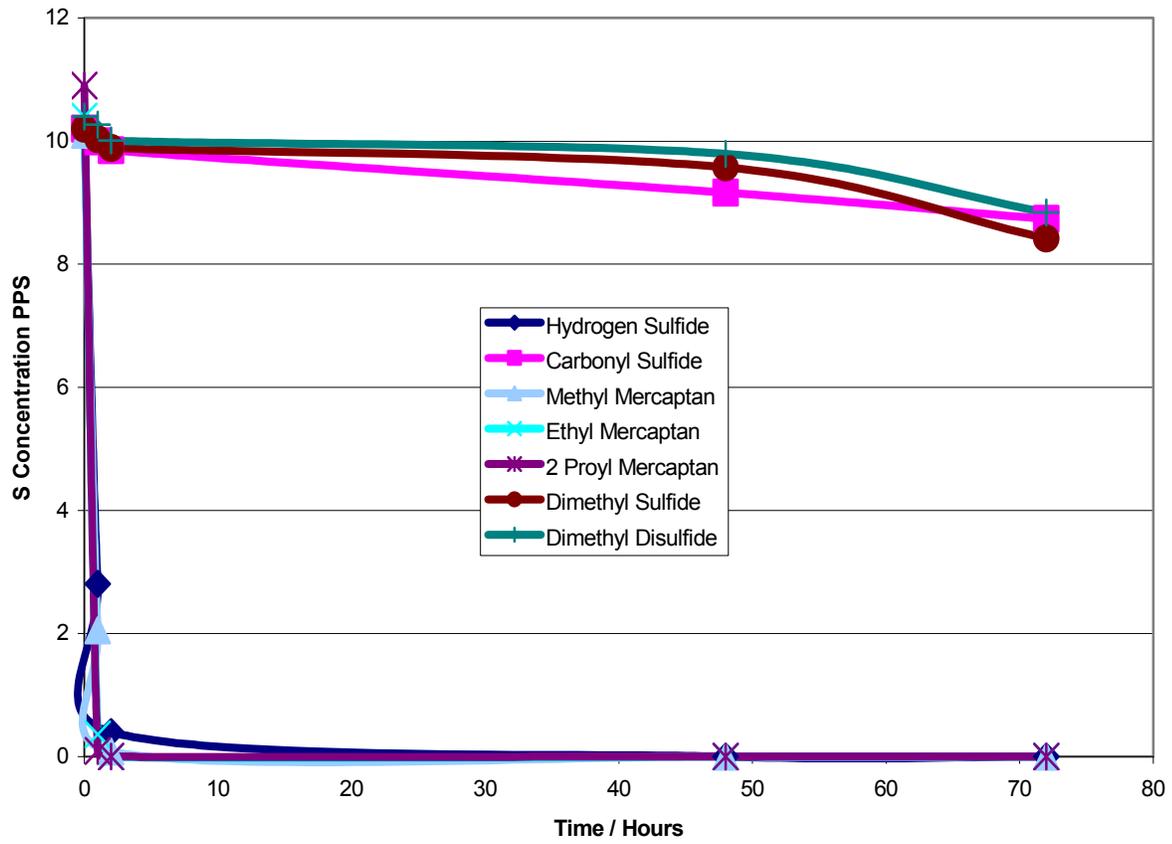
[Fig.6] **Passivation of sulfur species onto an aluminium cylinder**
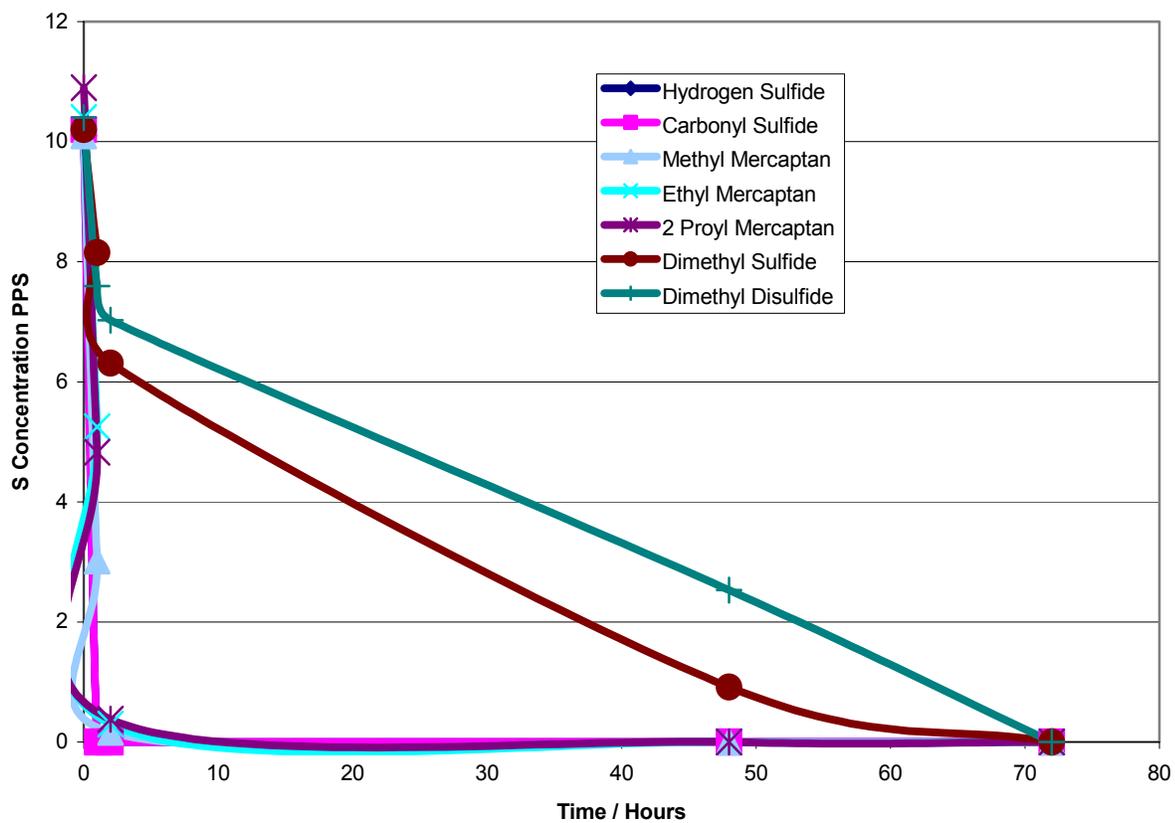
[Fig.7] Passivation of sulfur species onto a carbon steel cylinder

Teflon-Lined Aluminum

(Chart axes: Y-axis "S Concentration PPS" ranging 8 to 12; X-axis "Time / Hours" ranging 0 to 80)

Legend:
- Hydrogen Sulfide
- Carbonyl Sulfide
- Methyl Mercaptan
- Ethyl Mercaptan
- 2 Proyl Mercaptan
- Dimethyl Sulfide
- Dimethyl Disulfide
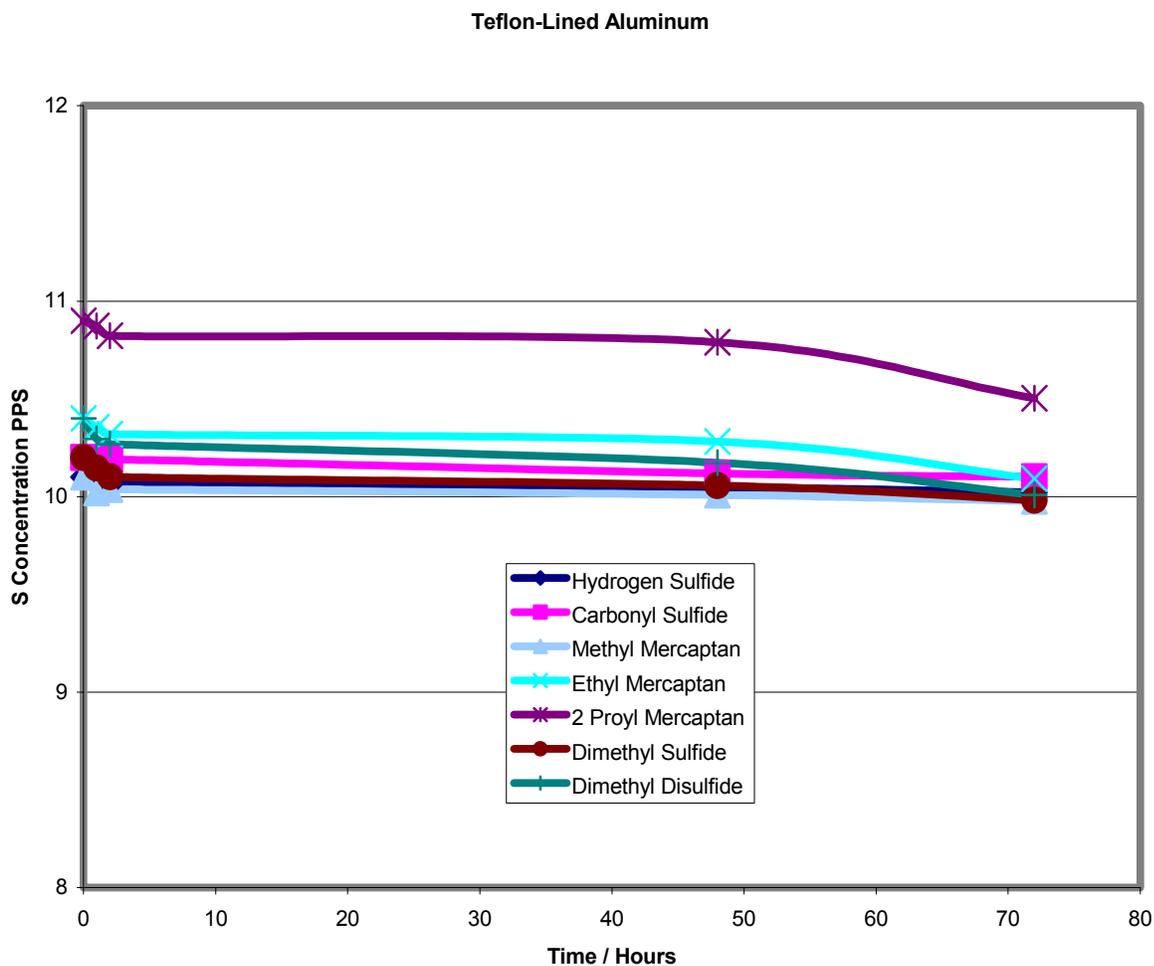
[Fig.8] Passivation of sulfur species onto a Teflon-Lined alumina cylinder

From the results above it is clear that prior to sampling a gas or liquid hydrocarbon, whether for treater design or to monitor absorbent performance, the analyst should have some understanding of the sulfur compounds present in the source to be sampled. Comparing respective adsorption rates for each of the sulfur species indicates that hydrogen sulphide is the most reactive with carbon steel, stainless steel and aluminium containers. Within 1 hour of starting the study, most of the hydrogen sulphide was passivated in both carbon steel and stainless steel with aluminium losing over 70% of the hydrogen sulphide through passivation within 2 hours. Only the Teflon-lined cylinders held 99% of the hydrogen sulphide after 72 hours.

The Teflon lined aluminium cylinder showed the best passivation resistance towards all of the sulfur compounds, however both carbonyl sulphide and dimethylsulfide levels were unaffected by both stainless steel and aluminium linings. After 72 hours, the stainless steel and aluminium lined cylinders still maintained 85 to 90% of the initial levels of the carbonyl sulphide and dimethylsulfide.

Clearly there is a choice in sample cylinder material to be made prior to attempting any analysis via remote sampling. An initial NGL feed description is important in deciding the most effective cylinders to adopt but from the study the most effective material of choice was the Teflon lined aluminium.

Sampling

  It is recommended that NGL samples be taken at plant site using the water displacement procedure described in GPA-2166. In this case water is used as a piston to maintain compression of volatile liquid hydrocarbons in the NGL but can equally be used in sampling heavier cuts such as gasoline and condensates.

  Checks should be made to ensure there is an adequate flow of product at the sampling point, valve positioning should be considered to ensure the appropriate location has a readily accessible valve. Verify that valves are in good working order prior to manifold attachment. Make note on sample cylinder tags if anything is observed that could compromise the results of the testing.

  After end caps are removed from the sample cylinder, Teflon tape should be applied to the cylinder as well as the end of the manifold to be connected to the sample source. After attaching the sample cylinder to the source, a purging of the product through the cylinder should take place by opening the inlet valve. Purging should proceed for 30 seconds. The relief valve on the manifold should be closed.

  With the cylinder held vertically, the top valve should be opened to full line pressure from the sample source. The bottom cylinder valve should now be opened to allow for the water to exit the cylinder. The water should leave at a rate of 100 cc per minute [slightly faster than a drip]. Water should be displaced into a volumetric cylinder so that 80% outage can be determined.

  When 80% of the water is displaced the bottom valve should be closed after which the top valve should be closed. The valve to the sample source should not be closed until after both cylinder valves are closed. The cylinder should then be disconnected from the manifold. The balance of the water should remain in the cylinder [to be expelled later in the testing laboratory].

  Care should be taken in avoiding over tightening of the end caps when recapping. Sample tag information including date, sample location, sample point pressure and temperature, plant site name and address and any other relevant notations regarding the sampling procedure should be detailed and fixed to the cylinder.

Container transit

  Before transporting liquid hydrocarbon samples to a laboratory for analysis it is recommended that you consult the "IATA Dangerous Goods Regulations", 43rd Edition, and the "Hazardous Materials Compliance Pocketbook" for current information on the shipping of hazardous materials.

  The International Air Transport Association (IATA) Dangerous Goods Regulations provides agencies and telephone numbers around the world, for information on international product transport. This manual will provide information such as:
1) Limitations
2) Classification
3) Product Identification
4) Packaging Specifications and Performance Tests
5) Marking and Labelling Information
6) Documentation and Handling of Hazardous Materials
7) List of Packing Suppliers around the World

  The Hazardous Materials Compliance Pocketbook provides information relating to every known category of chemical shipped, as well as:
1) How to Identify Hazardous Material Shipments
2) How to Comply with the Law
3) ID Cross Reference
4) Hazardous Materials Table
5) Emergency Phone Numbers

In addition to these two publications, each shipper should consult their local Ground and Air Transport (FedEx, UPS) company to determine the proper paperwork, which will need to accompany every shipment. The Department of Transportation (DOT) also provides updated information and guidelines for domestic transportation of Hazardous Materials in the United States. Consultation with these agencies will provide the shipper with adequate information on the safe and unabated guidelines for allowing these products to be safely transported around the world.

Key Laboratory Steps to Design a Customized Desulfurization System

Upon receipt of the NGL for analysis, the testing laboratory will implement several key sequential steps to ensure that sample integrity is maintained and that as much information as possible, is collated to help fully characterize the NGL. They steps required to be taken by the laboratory are outlined in Fig.9

| Sample logging and preparation | → | NGL analysis | → | Analytical review of results | → | Product screening and selection |
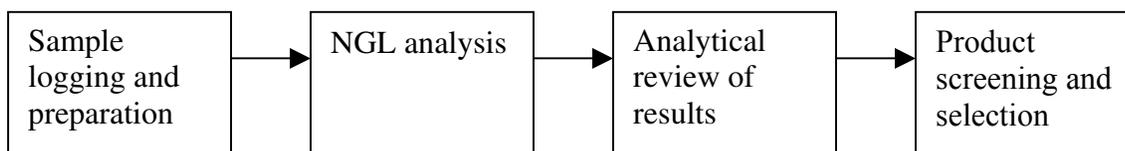
[Fig.9] Laboratory NGL analysis

Sample logging and preparation
After a sample is received in the laboratory, it is logged and given a reference number to track its progress from receipt through to analysis completion. The sample cylinder is tagged with the date of receipt and a simple description. As per the notation recommended in the Plant Sampling Section, any sampling vagaries stated on the cylinder tags from the field should be noted down and recorded.

NGL analysis
sulfur analysis is carried out using a sulfur chemiluminescence instrument. [Fig.10], providing the type and level of sulfur species present. An output of traced peaks with specific retention times relating to particular sulfur species eluting through a column is produced. Either a thermal conductivity chromatography instrument or a flame ionization chromatography instrument performs hydrocarbon fractional analysis of the NGL. Instrument calibration runs are performed on standard solutions and a cylinder pressurising followed by water submersion effectively checks for leaks. Any plant-derived description of the NGL is recorded in a logbook to compare with lab-generated data; discrepancies between the two can indicate a possible cylinder leak.

[Fig.10] Sulfur chemiluminescence detector

Analytical review of results

The data obtained from the analysis is divided into two parts; hydrocarbon fractionation and sulfur speciation. Duplicate analyses are taken to check the precision level of each data set. Results are compared against any relevant information received from the customer pertaining to the NGL and compared to library data from analyses made on the same plant or similar. All results are certified and logged. The sulfur speciation for the NGL will largely determine the sulfur absorbent[s] selected as candidate[s] for lab or plant trial. Specific metal oxides have affinities toward different sulfur contaminants and formulations of such metal oxides are chosen according to the duty required, prior test work and commercial experience.

Product screening and selection

After complete NGL characterization, one or more candidate absorbents are selected for laboratory reactor testing or plant slipstream trials. The choice of whether to test in the laboratory or in the field will depend upon available time, plant site location, the availability of a similar or the same NGL feed, the availability of analytical instrumentation and the associated costs involved. Ideally, on-plant slipstream trials are used to test candidate absorbents since exact conditions are available; pressure, temperature, specific NGL etc. though often, laboratory testing is easier and more commonplace. Fig.11 shows a typical lab absorbent test reactor.

[Fig.11] Absorbent test reactor

Although not as useful as on-site slipstream trials, laboratory test reactor programs are essential in screening absorbents either with NGL shipped from the field or with "simulated" NGL containing the appropriate sulfur compounds by injection.

When testing in-lab or on-site, certain variables should be monitored and fixed to ensure that valid conclusions can be drawn when ranking candidate absorbent performance with specific applications in mind. If a plant application demands an operating temperature below 150 ^{o}F, that should be the temperature ceiling of the test work. Liquid hourly space velocity and feed stream residence time should be set to achieve optimum absorbent performance. If a fixed sized vessel is available at the plant, the test feed flow-rate should not exceed a design maximum for the volume of absorbent to be tested.

Field study – Duke Energy Field Services Patrick Draw Facility, WY

In 2002 Duke Energy Field Services approached Johnson Matthey to request the design of a customized desulfurization absorbent bed for their Patrick Draw fractionation facility in Wyoming. The Patrick Draw Gas Plant processes gathered gas so that it meets pipeline specification. The residue gas is delivered to the pipeline and the recovered liquids are fractionated on-site to make ethane, propane and a mixed product. The propane is sold as finished product to refinery and petrochemical plant customers. The ethane is either sold as residue gas or sold as liquid product into a pipeline for delivery to chemical plants. The remaining liquid mixed product is also sent to pipeline.

The application at Patrick Draw required for a reduction in total sulfur concentration in an NGL stream from approximately 15 ppmW to 6 ppmW. Several positions in the plant flow sheet were identified as spatially suitable for vessel installation and a slipstream treater was despatched to the plant-site to test candidate absorbents at two specific locations across the facility; one to treat the de-ethanizer bottoms at a lower temperature and one to treat the depropanizer bottoms at a higher temperature. Since total sulfur removal is more effective at higher temperatures, it was decided to test the most appropriate absorbent[s] on the higher temperature depropanizer bottom feed fraction. The temperature at this point in the flow sheet was 230 ^{o}F.

Several samples were taken using Teflon lined cylinders according to the method previously described. A complete analysis was carried out on the samples including hydrocarbon fractional analysis [Fig.12] and sulfur speciation and concentration [Fig. 13].

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CERTIFICATE OF ANALYSIS
CONDENSATE FRACTIONAL ANALYSIS
DYCAT 158 TREATER STUDY

LAB NUMBER………… CR-1379

STUDY NUMBER…… CR-1

DATE SECURED…… 7-15-2002

DATE TESTED……… 7-18-2002

SAMPLE TEMPERATURE……… 235 F

SAMPLE PRESSURE…………… 225 PSIG

FLOW RATE, MCFD…………… 4 LVPH

COMPANY…………… DUKE ENERGY FIELD SERVICES

WELL………………… **PATRICK DRAW GAS PLANT**

SAMPLER…………… DUKE ENERGY FIELD SERVICES

SAMPLE OF………… **DEPROPANIZER BOTTOMS**
TREATER INLET ON 7-15-2002.

LOCATION…………… ROCK SPRINGS, WYOMING

FIELD………………… PATRICK DRAW

COUNTY……………… SWEETWATER

COMPONENT	MOLE %	Wt. %	Liq. Vol. %
NITROGEN…………………………	0.000	0.000	0.000
METHANE…………………………	0.000	0.000	0.000
CARBON DIOXIDE………………	0.000	0.000	0.000
ETHANE………………………….	0.000	0.000	0.000
PROPANE……………………….	1.069	0.714	0.859
iso-BUTANE……………………	27.749	24.423	26.485
n-BUTANE………………………	33.291	29.300	30.624
iso-PENTANE……………………	11.213	12.251	11.974
n-PENTANE………………………	9.083	9.924	9.599
HEXANES…………………………	11.756	15.341	14.103
HEPTANES +……………………	5.839	8.048	6.356
	100.000	100.000	100.000

SPECIFIC GRAVITY @ 60/60 F, calculated……………………………………… **0.6105**

TRUE VAPOR PRESSURE @ 100 F, calculated……………………………….. **43.70**

AVERAGE BOILING POINT, F, calculated………………………………………. **62.707**

AVERAGE MOLECULAR WEIGHT……………………………………………….. **66.039**

BTU / GALLON OF LIQUID, as Liquid………………………………………….. **106,811.6**

CUBIC FEET OF GAS / GALLON OF LIQUID, as Ideal Gas………………… **28.80**

Lbs / GALLON OF LIQUID………………………………………………………… **5.090**

JAMES A. KANE, PRESIDENT

[Fig.12] Hydrocarbon fractionation of depropanizer feed

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CERTIFICATE OF ANALYSIS
EXTENDED SULFUR FRACTIONAL STUDY
DYCAT 158 TREATER STUDY

COMPANY…………..DUKE ENERGY FIELD SERVICES

LAB NUMBER………CR-1379   **STUDY NUMBER…..**CR-1B

DATE SAMPLED….. 7-15-2002   **DATE TESTED………** 7-18-2002

SAMPLE IDENTIFICATION…… DEPROPANIZER BOTTOMS AT TREATER INLET   **DYCAT 158**
                                      PATRICK DRAW GAS PLANT
SAMPLE PRESSURE………… 225 PSIG   **SAMPLE TEMP……** 235 F

METHOD OF ANALYSIS……… SCD CHROMATOGRAPHY   **SAMPLE METHOD…**GPA-2166

METHOD NUMBER………….. ASTM D-5504   **SAMPLE CONTAINER………..** TEFLON CYLINDER

LIGHT END COMPONENTS   **RESULTS, PPM/VOL**

CARBONYL SULFIDE (COS), PPM……………………………..	0.989 PPM
HYDROGEN SULFIDE (H2S), PPM……………………………..	2.147 PPM
CARBON DISULFIDE (CS2), PPM……………………………..	2.836 PPM
DIMETHYL SULFIDE (CH3)2S, PPM………………………….	0.159 PPM
DIMETHYL DISULFIDE (CH3)2S2, PPM……………………..	LESS THAN 0.001 PPM
SULFUR DIOXIDE (SO2), PPM……………………………..	LESS THAN 0.001 PPM
METHYL SULFIDE (CH3)S, PPM……………………………..	LESS THAN 0.001 PPM

TOTAL LIGHT END SULFURS, PPM……………………………. 6.131 PPM

MERCAPTAN COMPONENTS

METHYL MERCAPTAN, PPM…………………………………….	1.970 PPM
ETHYL MERCAPTAN, PPM……………………………………….	2.461 PPM
iso-PROPYL MERCAPTAN, PPM……………………………..	1.178 PPM
tert-BUTYL MERCAPTAN, PPM……………………………..	0.315 PPM
sec-BUTYL MERCAPTAN, PPM……………………………..	1.024 PPM
PENTYL AND HEAVIER MERCAPTANS, PPM………………..	2.625 PPM
2-METHYLTHIOPHENE, PPM………………………………….	0.041 PPM
3-METHYLTHIOPHENE, PPM………………………………….	0.103 PPM
THIOPHENE, PPM…………………………………………….	0.822 PPM
BENZOTHIOPHENES, PPM……………………………………..	LESS THAN 0.001 PPM
TOTAL ALL OTHER THIOPHENES, PPM……………………..	0.153 PPM

TOTAL MERCAPTANS AND THIOPHENES, PPM……………….. 10.692 PPM

TOTAL ALL SULFURS, PPM………………………………. 16.823 PPM

ALL UNITS EXPRESSED AS PPM/VOLUME

JAMES A. KANE, PRESIDENT
AMERICAN MOBILE RESEARCH, INC.

Fig.13 Sulfur speciation and concentration of depropanizer feed

After examining the feed in detail, paying particular attention to the type and level of sulfur compounds present, Johnson Matthey selected **two** absorbents from their range with the potential to deliver optimum sulfur removal. The two absorbents selected were designed to perform with maximum efficiency at the 230 $^\circ$F temperature on depropanizer bottoms at a flow rate yielding a Linear Hourly Space Velocity [LHSV] of 4 hr^{-1} * across the absorbent.

* LHSV = Flow rate in m^3 per hour / available fill volume of absorbent in vessel in m^3

Absorbents A and B were then tested under identical conditions [Fig. 14] to determine which would be the most suitable at removing as much sulfur as possible from the depropanizer bottoms.

LHSV	4
Temperature	230°F
Pressure	225 psig

Fig.14 Depropanizer bottoms test conditions

The results of the test program can be seen in [Fig.15]
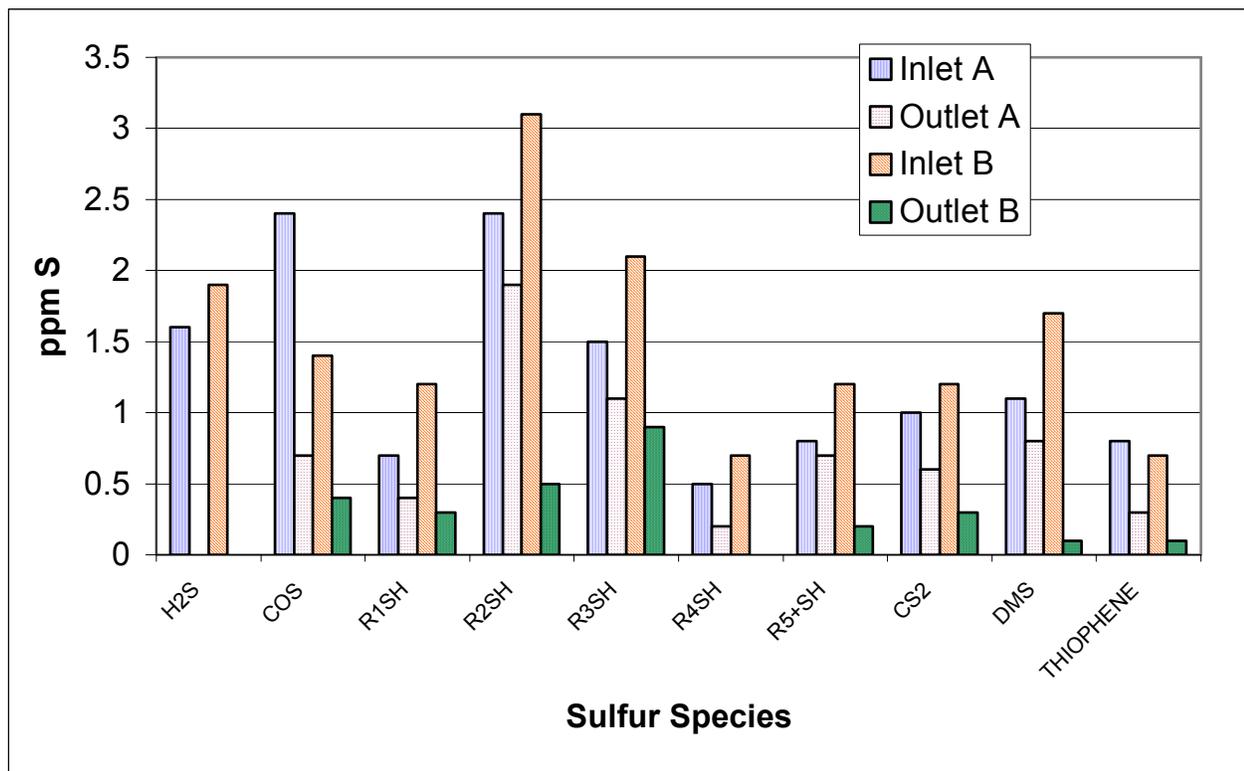
Fig.15 Absorbents A & B: Comparative sulfur removal efficiency after 24 hours

S species	H2S	COS	R1SH	R2SH	R3SH	R4SH	R5+SH	CS2	DMS	Thiophene
Inlet A/ppm	1.6	2.4	0.7	2.4	1.5	0.5	0.8	1.0	1.1	0.8
Outlet A/ppm	0	0.7	0.4	1.9	1.1	0.2	0.7	0.6	0.8	0.3
% S removal	**100**	**71**	**43**	**21**	**27**	**60**	**13**	**40**	**27**	**63**
Inlet B/ppm	1.9	1.4	1.2	3.1	2.1	0.7	1.2	1.2	1.7	0.7
Outlet B/ppm	0	0.4	0.3	0.5	0.9	0	0.2	0.3	0.1	0.1
% S removal	**100**	**71**	**75**	**84**	**57**	**100**	**83**	**75**	**94**	**86**

Fig.16 Absorbents A & B: % sulfur removal after 24 hours

After 24 hours of comparative testing although absorbents A & B showed similar efficiencies removing H₂S and COS, B was clearly more active at removing each of the other eight sulfur species. It was decided to reject absorbent A and extend the testing of absorbent B. Absorbent B was tested in the field a further 20 days with inlet and outlet S monitoring continuing for 504 hours in total. [Fig.17] shows the results of the testing of absorbent B after 504 hours.
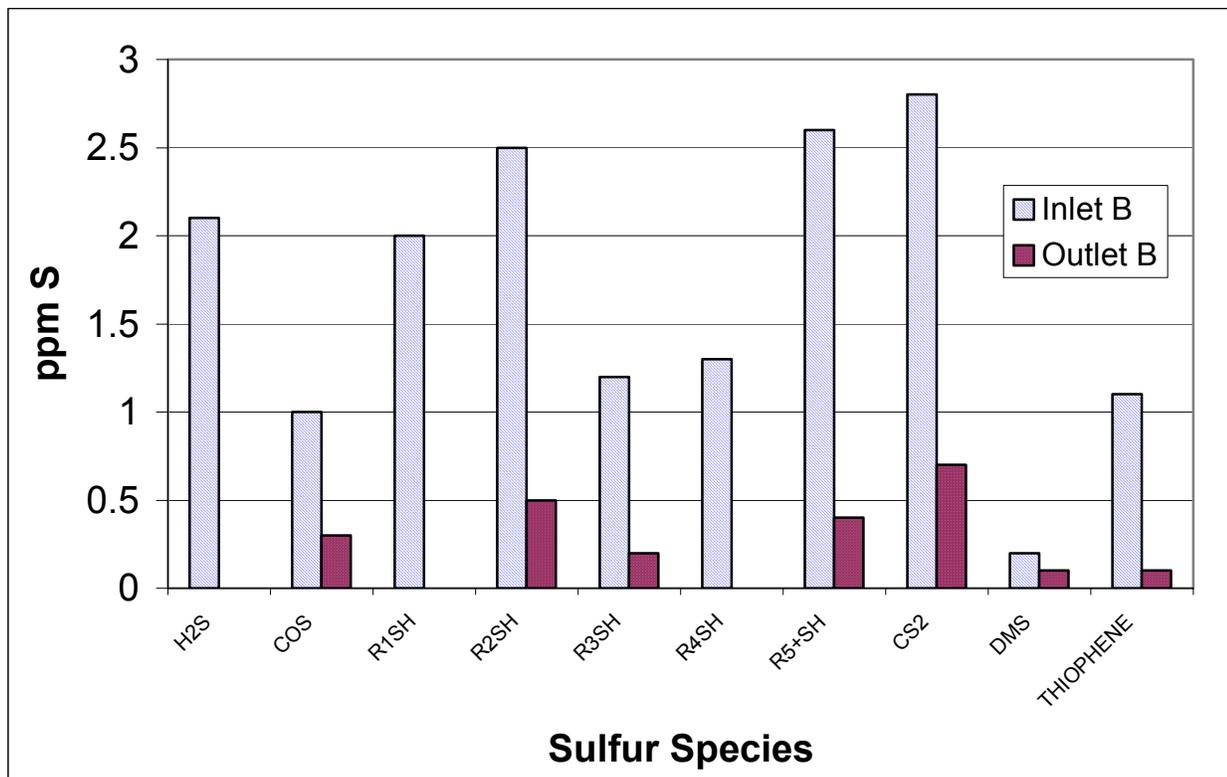
Fig.17 Absorbent B: sulfur removal efficiency after 504 hours

S species	H2S	COS	R1SH	R2SH	R3SH	R4SH	R5+SH	CS2	DMS	Thiophene
Inlet A/ppm	2.1	1.0	2.0	2.5	1.2	1.3	2.6	2.8	0.2	1.1
Outlet A/ppm	0	0.3	0.5	0.5	0.4	0	0.4	0.7	0.1	0.1
% S removal	100	70	75	80	67	100	85	75	50	91

Fig.18 Absorbent B: % sulfur removal after 504 hours

The sulfur removal efficiency of absorbent B is the same after 504 hours as after the initial 24 hours [within reasonable experimental error]. The absorption performance of B is most impressive on when removing H2S and butlyl mercaptan and also very effective on ethyl mercaptan, pentyl plus mercaptans and thiophene. From a total content of 16.8 ppm, total sulfur levels are effectively reduced down to 3.0 ppm within the 504-hour test. The specification of 6 ppm total sulfur is easily met and there is evidence to suggest the 6 ppm specification outlet of absorbent B would continue well in excess of 504 hours.

After 504 hours Duke Energy requested a termination of the test after the data proved that absorbent B was consistently passing the specification required.

Conclusions

- Key sequential steps are required when considering the choice of absorbents opposite specific sulfur removal applications.
- Sample container selection is important bearing in mind that different container materials adsorb or passivate different sulfur species to different degrees leading to false [low] apparent sulfur levels in the NGL sample in question
- Changes in sampling procedure can lead to inaccurate sampling and NGL sample integrity cannot then be guaranteed
- On-site testing of absorbents is preferable to in-laboratory testing with a greater degree of realism coming with actual feedstock and conditions
- The affinity of sulfur species' towards absorbents varies depending upon both treatment conditions and the absorbent in question

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