A New Method for Closed Loop Sampling Hazardous Liquid Process Streams

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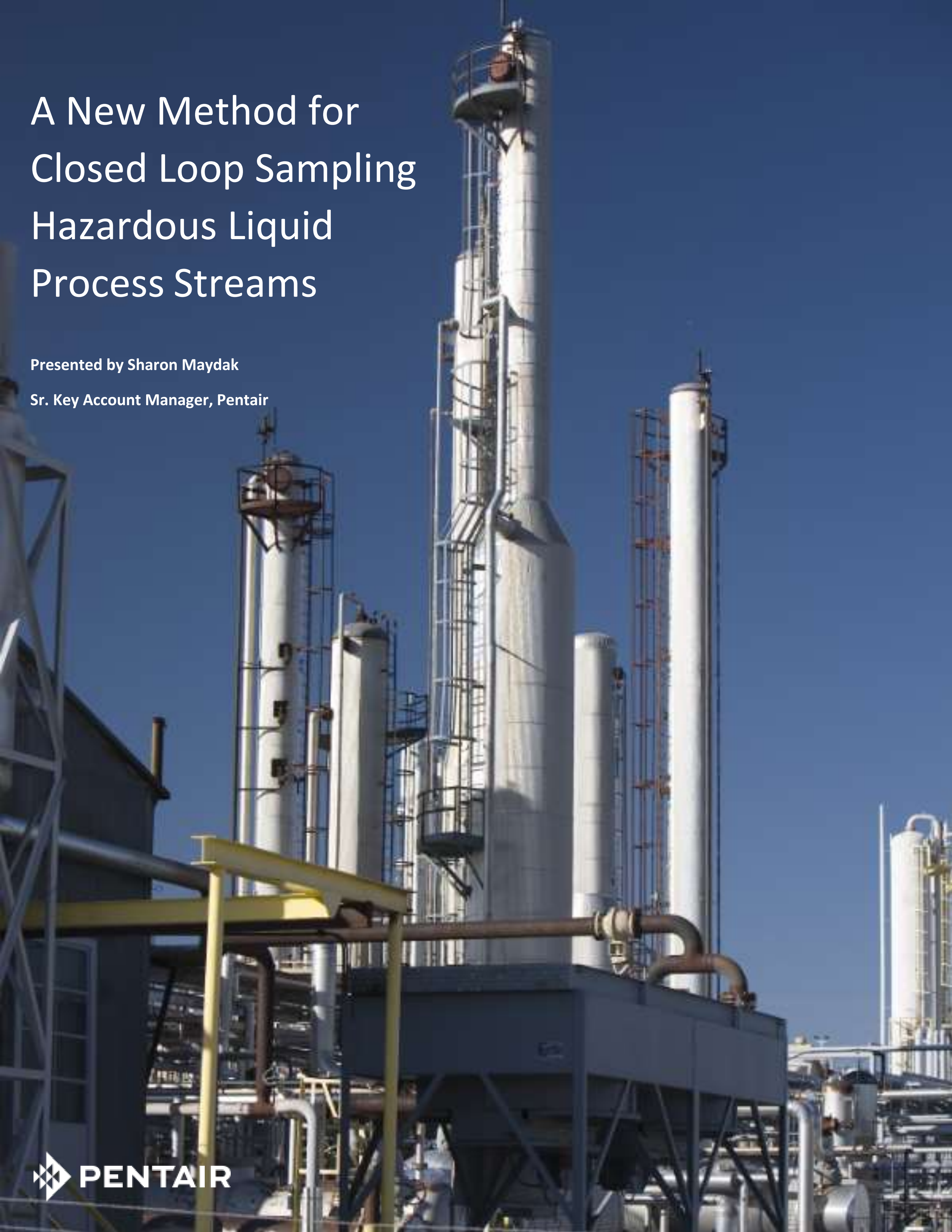

PENTAIR

A New Method for Closed Loop Sampling

Hazardous Liquid Process Streams

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ABSTRACT

Oil refineries and natural gas processing facilities face numerous challenges caused by particulate and liquid contaminants. Identifying sources of contamination can help determine where filtration may be beneficial but the necessary sampling locations can be difficult to safely achieve. This is especially true when the process stream involves rich amine, sour water, and other process fluids where H_2S is present. This paper describes troubleshooting efforts at an oil refinery to mitigate fouling issues the rich amine system. A novel closed loop sampling system that was developed by Pentair was successfully utilized in sampling efforts.

BACKGROUND

Amine systems utilized in natural gas plants and oil refineries are vital for the removal of sour contaminants from feedstocks. The quality of the amine has a strong impact on the ability of an amine system to effectively remove acid gases, H_2S (Hydrogen Sulfide) and CO_2 (Carbon Dioxide), from process streams. Unfortunately, amine systems are frequently fouled by particulates, hydrocarbons or a combination of the two, which can greatly reduce operating efficiencies in the acid gas removal process. If the concentration of the contaminants reaches high enough levels, it becomes increasingly difficult to identify the source of the contamination. Typically, the search for the source of contaminant ingression occurs in conjunction with upsets and poor efficiency, often manifesting as foaming in the absorber (contactor), plugging of absorber trays, and heat exchanger fouling.

Amine systems that are forced to deal with contamination issues incur higher than desired maintenance costs associated with cleaning of absorber tower packing/trays and heat exchangers, replacing lost amine, and recurring expenses for anti-foam injection. However, the most significant financial impact is often the capacity reduction and corresponding revenue losses incurred due to an SRU shutdown, emissions violations, or lost production due to system upsets (e.g., foaming). Filtration is a proven method to control the contaminant level in amine systems and there are naturally expenses associated with a properly maintained filter system.

Of all the costs mentioned above, the expense associated with filtration often receives the most attention. Operators will frequently focus on the microeconomics of their facilities by identifying small ways to reduce expenses to improve profitability. By doing so, they may miss the ability to take a macro-scale view and recognize the larger impact of driving increased revenue through improved process efficiency and overall plant reliability. In many cases, a small amount of expense to purify process fluids will have an overwhelmingly positive effect on profitability. Refinery amine treatment systems are often designed with a common solvent regeneration system that regenerates rich amine returned from multiple off-plot units. This can create difficulty in identifying the primary source of amine contamination and further complicate the contamination mitigation strategy. Standard practice dictates installation of a filtration system as close as possible to the source of the contamination or the equipment to be protected

Once a plant experiences a high level of contamination in their process feeds, a strategic approach is needed to fully understand the effects on process equipment and to qualify and quantify the contamination at various locations throughout the system. One of the ways this evaluation can be completed is by gathering analytical data via onsite sampling/testing which can identify the source(s) of amine contamination and allow facilities to take the best corrective action to reduce or control contaminants. Root cause analytics can also enable operators to troubleshoot and resolve process filtration inefficiencies.

The following case study provides details and results from onsite sampling/testing performed at an oil refinery with the objective to identify the source of contamination that caused poor performance and efficiency of their amine system.

CASE STUDY

A refinery typically operates multiple amine system loops which serve separate process plants across the refinery and then come together in one feed for regeneration. The subject refinery has experienced a high level of fouling on the rich amine side of the lean/rich heat exchanger for more than 5 years. This fouling has led to flow restrictions within the amine regeneration unit which ultimately caused the refinery to operate below design conditions. Accelerated loss of heat transfer in the feed/bottoms heat exchanger was experienced when a new coker gas plant was brought online and after the rich amine feed drum was replaced. The fouling issue required cleaning of the heat exchanger at shorter intervals than normal scheduled maintenance.

The engineering and operations teams at the refinery began to examine ways to identify the source(s) and the quantity of contaminants contributing to the fouling issue with the goals of preventing unscheduled maintenance events and protecting amine system performance. This effort led them to perform rich amine system solids and hydrocarbon analysis, partnering with Pentair to quantitatively determine the problem areas for iron sulfide generation and hydrocarbon content. Three key focus areas were identified for the sampling effort:

Coker Gas Oil Contactor. The current design for the coker gas oil contactor results in high rich amine loading and insufficient lean amine supply. The rich feed exiting the unit combines with other rich amine feeds before entering the stripper column for regeneration. The lean/rich amine heat exchanger mentioned previously is located after the rich amine feeds combine, and upstream of the stripper column. The reduced performance of this heat exchanger led the plant to suspect that iron sulfides present in the feed were precipitating and collecting in the heat exchanger.

Bulk Amine Contactor. This amine contactor handles the bulk of the amine feed and operates at 220 psig. However, the pressure drops down to 4 psig at the rich amine flash drum. This results in the bulk of the feed load to be placed on the back pressure control valve, which could cause two-phase flow within the piping. Two-phase flow exacerbates corrosion as the feed travels at high velocities and may entrain corrosion and iron sulfide particles from the piping walls.

Amine Flash Drum. The current flash drum was installed a few years ago. Prior to being replaced, the previous flash drum required modifications immediately after installation because the hydrocarbons were not being properly skimmed due to a design flaw. Unfortunately, this same design flaw exists in the replacement flash drum that is currently in use. Plant personnel believe that hydrocarbons are carrying over into the amine, and have considered performing a pilot study to identify if free hydrocarbons are present in the rich amine.

Once these areas were identified, refinery personnel contacted Pentair's technical services group to participate in plan development and to lead the onsite analytical tests. Through a series of meetings between the engineering team and Pentair's technical experts, two primary areas of interest were identified for sampling:

Point 1: Rich amine combined feed upstream of flash drum
Point 2: Rich amine return from bulk amine contactor

Additional sample points were pre-identified and would be used if results from the initial points were inconclusive.

The refinery is a prime leader in safety practices and strives for zero exposure of plant and contractor personnel to hydrogen sulfide, making it paramount that Pentair work closely with plant personnel to utilize a method to safely conduct the onsite test of the rich amine streams. With hydrogen sulfide in the amine, an alternative approach to bottle samples or other sampling practices that increases environment exposure to sour amine had to be utilized.

Pentair, a leader in the filtration industry for more than 35 years, designated personnel with years of onsite sampling experience in amine systems to lead this effort at the refinery. Pentair designed a closed loop gravimetric sampling system to ensure a safe sampling environment while also being easy to transport, set up, and operate. The closed loop gravimetric assembly with upstream pneumatic pump was designed and assembled by Pentair for sampling as shown in **Figure 1**.

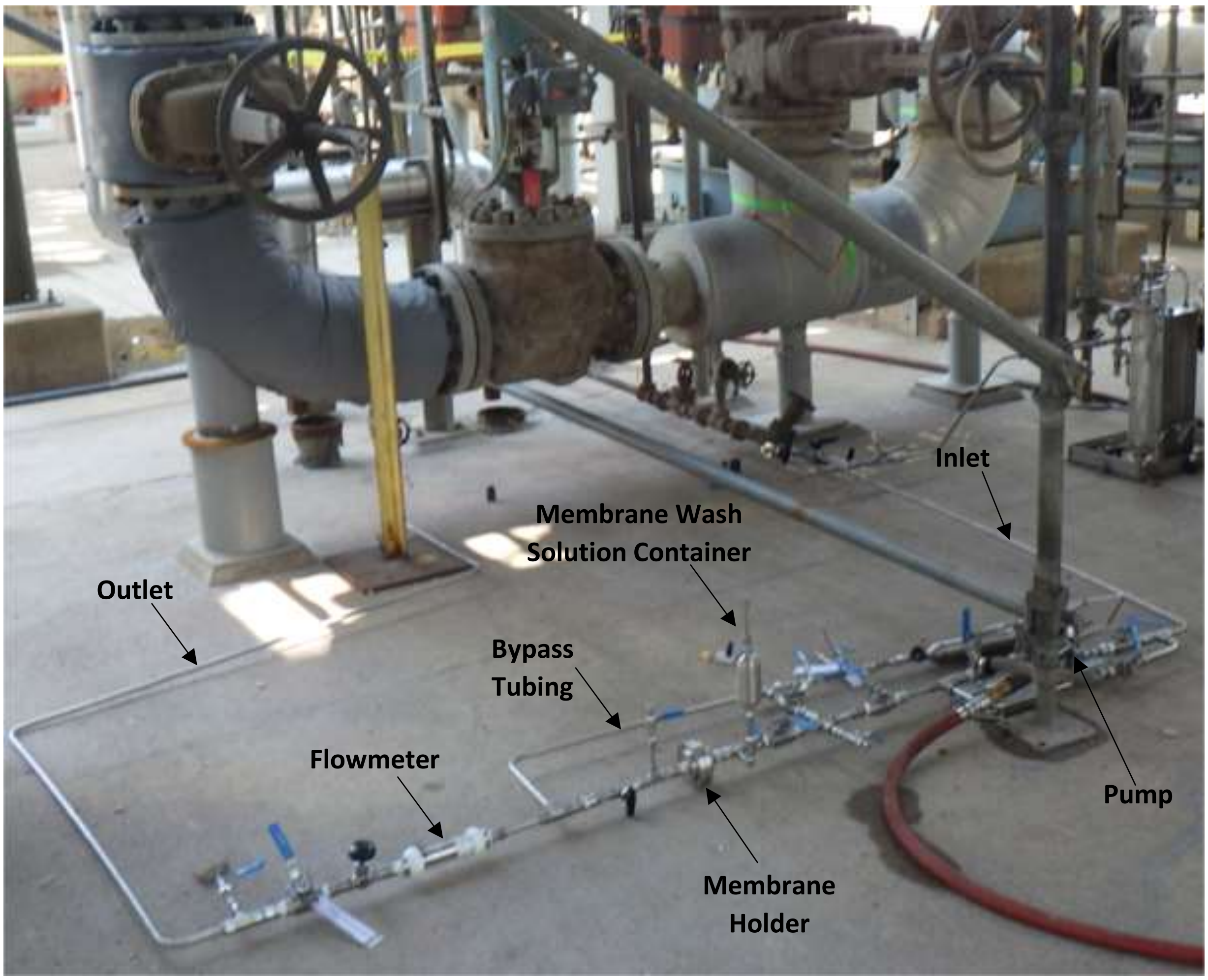


Figure 1. *Image of Pentair's Closed Loop Gravimetric Sampling System*

A pneumatic pump was selected for its inherent intrinsic safety. The flow diagram for the closed sampling loop is shown in **Figure 2**. The test assembly is made from stainless steel components and seals of material compatible with amine process fluids.

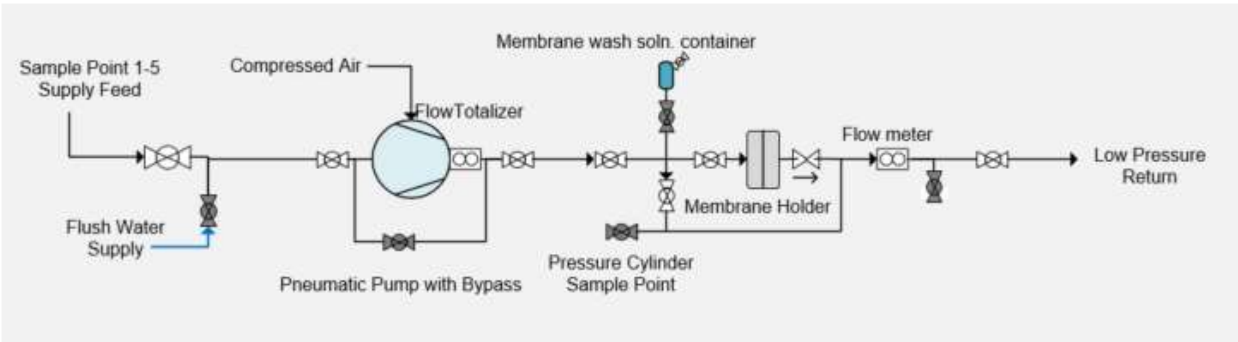


Figure 2. *PFD of Closed Loop Gravimetric Sampling System*

[Specific components can be customized per site requirements]

For onsite tests, it is important to capture data by flowing as much of the process fluid through the test system as possible. Depending on the operating pressures at the tie-in point of the test loop, it is sometimes necessary to include a pump upstream of the assembly to boost the feed pressure and push more fluid through the system.

The feed enters the assembly such that the amine can be directed through a membrane holder housing a filter membrane, or through a bypass around the membrane holder. The bypass is essential to sufficiently flush the amine through the test loop via the tie-in points. If the system is not flushed, the filter membrane will capture solids that have built up over time in the tie-in valve, which can misrepresent the contaminant concentration in the fluid stream.

Once the system is flushed, the amine can be directed through the membrane holder which contains a 0.45 μm polyvinylidene fluoride gravimetric membrane. The membrane is designed to collect all suspended solids in the amine feed for quantification. The total volume of fluid is recorded for each sample collection using a totalizing flow meter. This volume is used for the calculation of the total suspended solids once the weight of the captured solids on the membrane is determined. Additional solid characterization is performed by analyzing the solids on the membrane to determine particle size and composition.

The closed loop system also allows safe collection of liquid samples. Sample points can be outfitted with quick connect fittings for DOT approved pressure cylinders to collect rich amine samples. These pressure cylinders can be safely shipped to analytical labs, such as Pentair STAR™ Labs, for further analysis.

Upon completion of tests at each point, plant water is passed through the test loop. The bypass tubing is also necessary for the water flush because the membrane holder needs to be excluded from contact with plant water to ensure that no solids from the plant water are captured, thereby preventing mis-calculation of the actual amine solids concentration. The membrane holder path on the assembly can be rinsed with purified deionized water and stored in the membrane wash container displayed in **Figure 1**. Efficiently flushing and rinsing the system with water allows the assembly to be disconnected from the process with zero hydrogen sulfide exposure.

ANALYTICAL RESULTS

At the direction of plant personnel, the first tests were conducted at Sample Points 1 and 2. These locations were chosen as the most likely to contribute to the contamination that was fouling the exchanger. After these two tests were complete, plant personnel believed that the captured data sufficiently validated the source of the exchanger fouling and, as a result, decided not to test at additional sample points at that time.

Upon completion of the tests at Points 1 and 2, the membranes and the pressure cylinders were returned to Pentair's STAR™ Labs for additional analysis which included:

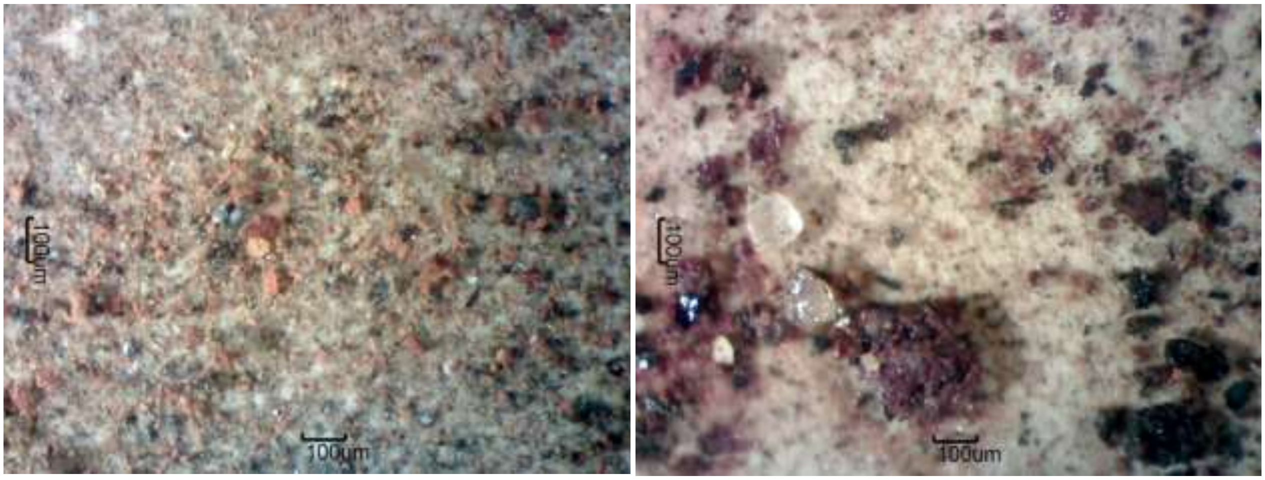
- Total suspended solids
- Elemental composition via SEM-EDS
- Particle size distribution
- Total hydrocarbon content via GC-MS

Total Suspended Solids

The total suspended solids measured from the samples collected onsite are presented in **Table 1**. The solid concentration at Sample Point 1 was 6.25 mg/L. Sample Point 2 solids concentration was significantly lower with a concentration of 1.01 mg/L. Photomicrographs of the gravimetric membranes are presented in **Figure 3**.

Table 1. *Total suspended solids results*

Sample ID	Date Collected	Volume (mL)	Total Suspended Solids (mg/L)
Sample Point 1 Combined Rich Amine Feed	7/28/2021	1,296.5	6.25
Sample Point 2 Amine from Bulk Amine Contactor	7/29/2021	3,855.6	1.01

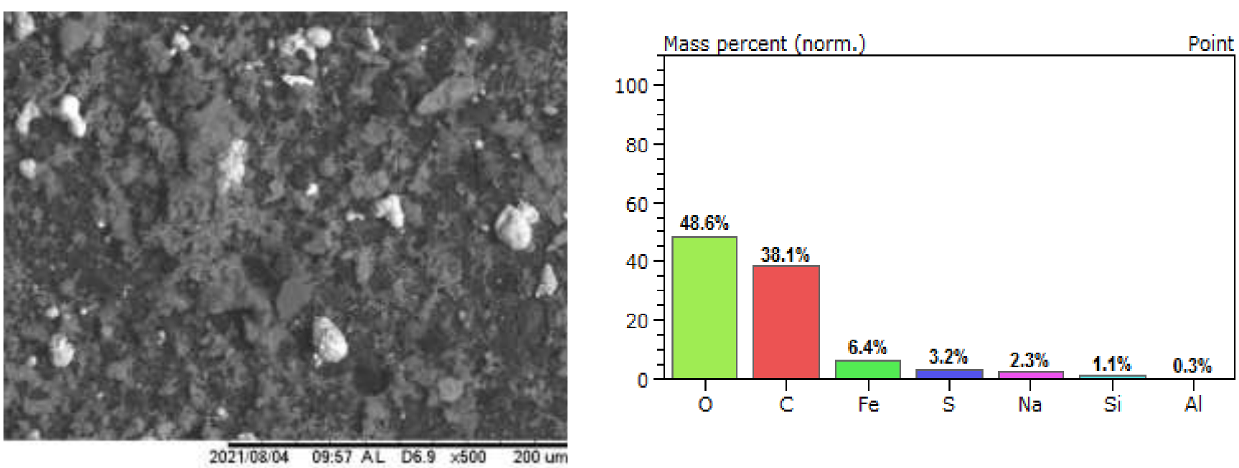


Sample Point 1 Solids *Sample Point 2 Solids*

Figure 3. *Photomicrographs of Solids Collected on Membranes*

SEM-EDS Analysis

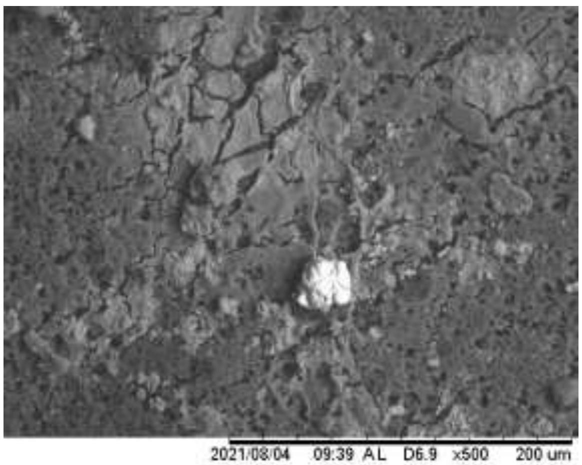
The solids collected on the Sample Point 1 membrane were further examined via a scanning electronic microscope (SEM) with energy dispersion X-ray spectroscopy (EDS) to determine the elemental composition as shown in **Figure 4**. Surprisingly, the results suggest that the solids collected may be organic, rather than the expected iron sulfide composition. Organic solids in amine units commonly originate from the inlet gas feed, amine degradation products, and from chemicals added to the process to control corrosion and/or foaming. Although the elemental composition primarily indicates organic solids are the main contaminant, iron oxides, iron sulfides and other inorganic contaminants are likely present as well.

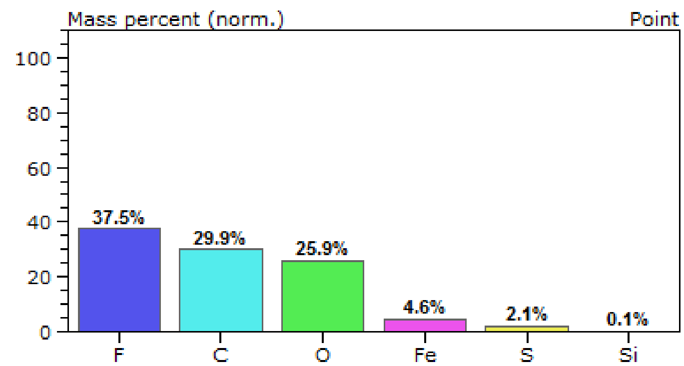


(A) **(B)**

Figure 4. *Sample Point 1 Combined Rich Amine Feed: SEM Image (A), Elemental Composition Chart (B)*

The solids seen on the Sample Point 2 membrane appear to be finer than Sample Point 1 and created a tightly packed cake in some areas of the membrane. The elements detected include carbon, oxygen, iron, sulfur and silicon. The brighter solid seen in **Figure 5** contains higher percentages of sulfur compared to the surrounding solids. These contaminants are primarily organic solids with some corrosion products. Note the fluorine and some of the carbon detected are attributable to the PVDF membrane background.





(A) **(B)**

Figure 5: *Sample Point 2 Downstream of Bulk Amine Contactor: SEM Image (A), Elemental Composition Chart (B)*

Particle Size Distribution

Solids from the membranes of each sample were re-suspended and analyzed to obtain particle size distribution data. For Sample Point 1, **Figure 6**, shows that the solid contaminants ranged up to 70 microns in size with 93% of the contaminants by volume observed to be larger than 5 microns in size.

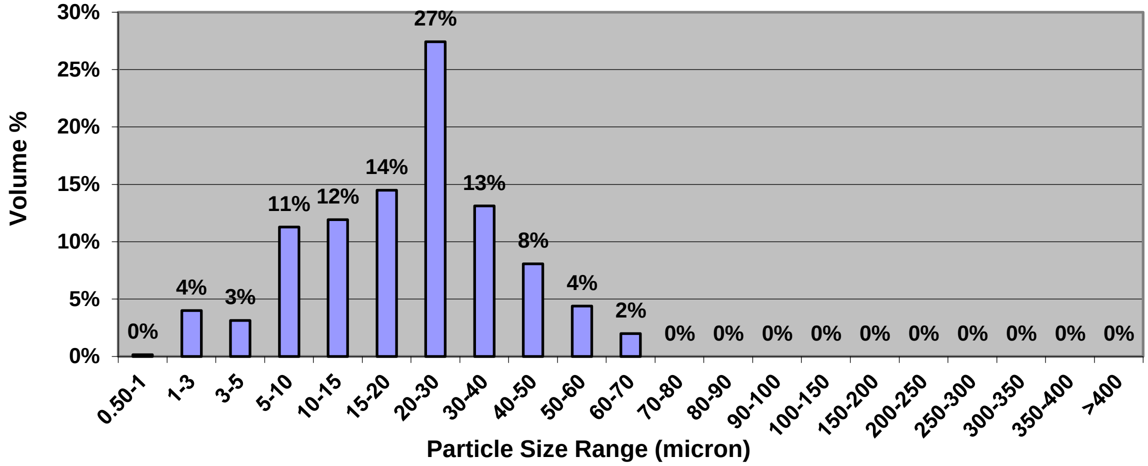


Figure 6. *Sample Point 1: Particle Size Distribution*

The solids from Sample Point 2**, Figure 7**, range up to 50 microns in size. Solids between 5-50 microns in size represents 97% of contaminant volume. Note, some larger solids were observed on the photomicrograph. It is possible that these larger solids dropped out rapidly from suspension. The solid contaminant size range may be higher (~ 300 microns).

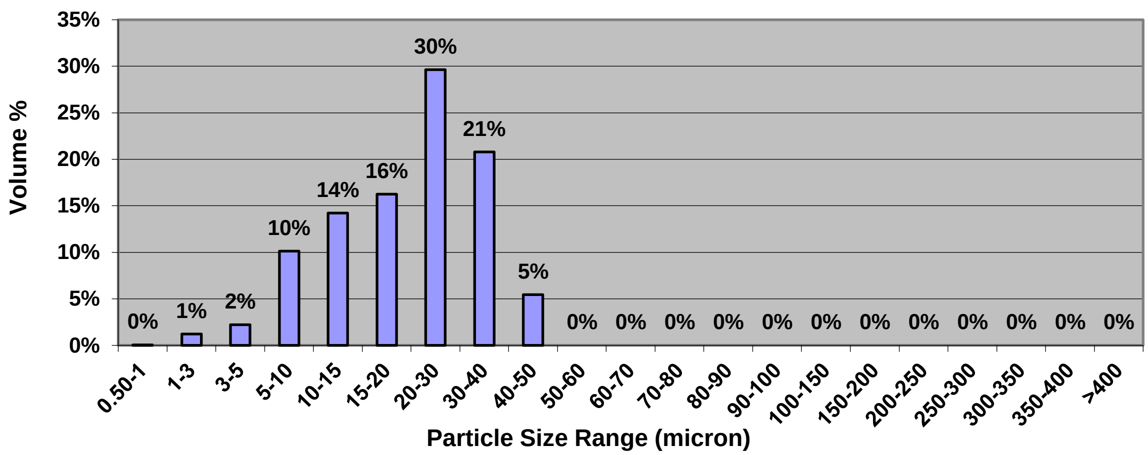


Figure 7. *Sample Point 2: Particle Size Distribution*

HYDROCARBON CONTENT

As previously mentioned, the closed loop test equipment incorporates provisions to connect pressure cylinders to collect liquid samples. For Sample Point 1, taken from the combined feed upstream of the flash drum, the hydrocarbon content was 34 ppmw. Referring to **Figure 8**, these hydrocarbons were entirely composed of BTEX (benzene, toluene, ethylbenzene and xylene) compounds, which would be soluble in the amine at process conditions. This information helped confirm that only small amounts of hydrocarbons were present at time of sampling, resulting in minimal challenge to rich amine flash drum at the time of sampling. The samples collected provide only a snapshot of data, thus further analysis would be required to confirm the ability of the flash drum to separate more significant quantities of hydrocarbon liquid. [Note: Since hydrocarbon concentration measured in the combined feed at Point 1 was low, it was decided this analysis was not necessary at Sample Point 2]

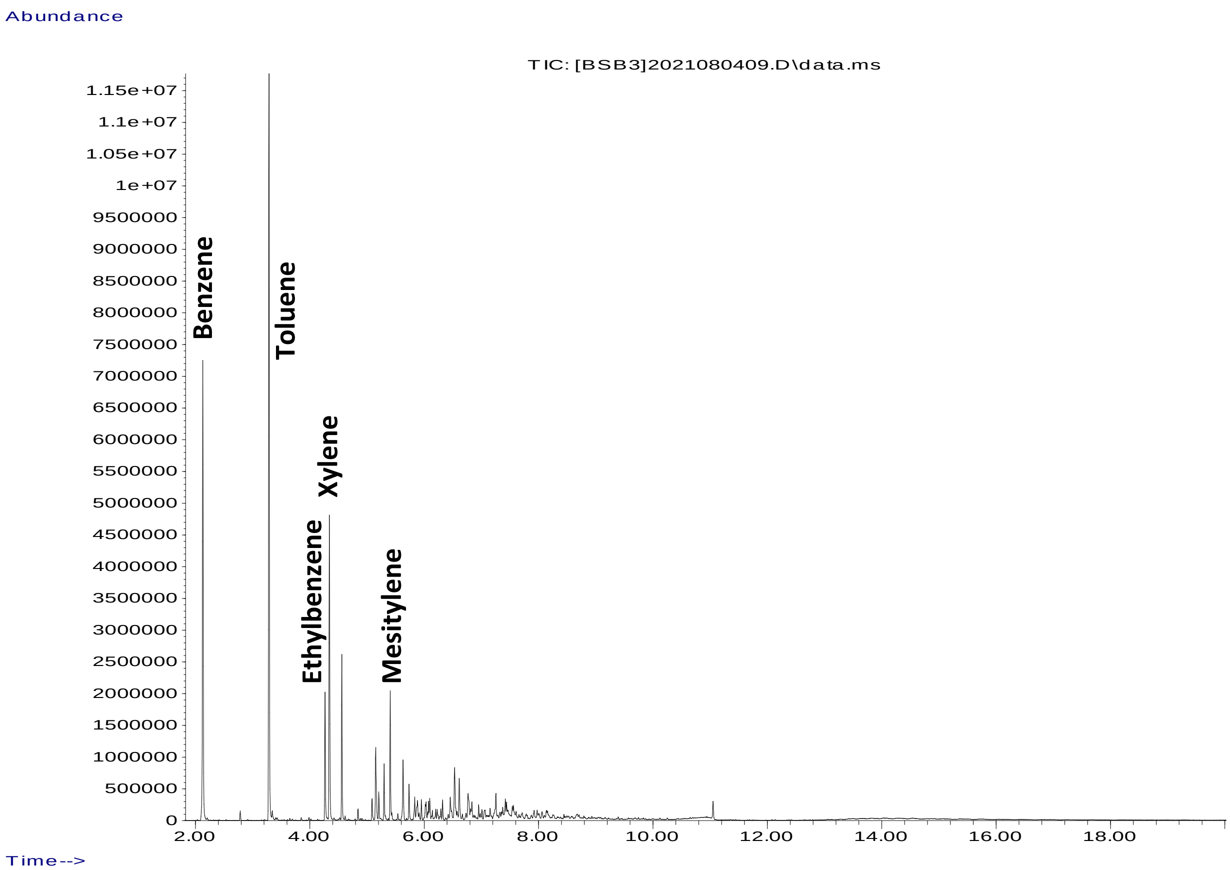


Figure 8. *GC-MS Spectrum with labeled peaks*

CONCLUSION

Amine units have an optimum operational envelope and contamination removal plays a major role in performance and efficiency. Operational challenges experienced throughout the life of a unit can be mitigated by first gaining an understanding of the sources of contaminants in the system and then using this information to guide decisions about how and where to address them – whether in the unit itself or upstream.

To help achieve and maintain peak performance, the following activities are critically important:

- Analyze the process streams for solids and liquid contaminants
- Develop an understanding of the particle size, the amount of particles (mass loading) and the morphology of the particles
- Sample over time to help understand changes within the unit

The presence of H_2S in rich amine solutions can make sampling and analysis through conventional means impossible to effectively complete in a safe manner. The refinery in this case study elected to partner with Pentair for its closed loop testing capability to safely capture suspended solids and collect liquid samples of the rich amine at minimal risk to personnel.

The data generated by this sampling effort as outlined in this paper identified that the amount and composition of contaminant influx was sufficient to have caused heat exchanger fouling and related performance issues and foaming events in the contactor. After a significant percentage of piping has been upgraded from carbon steel to stainless to mitigate a key source of corrosion, the refinery will closely monitor the performance of the amine system and re-engage with Pentair to duplicate the sampling effort for comparison to determine impact and whether other changes, such as adding filtration, are needed.

By using Pentair's closed loop sampling capabilities, it is possible to safely acquire technical information critical to evaluating the current state of hazardous liquid process streams, and to support any needed changes or improvements.