Chemical Tracers Find Elusive Leak in Hydrotreater Feed/Effluent Exchangers

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Introduction

High sulfur content in the effluent of a hydrotreater stream is a signal that the unit has a problem with either the reactor catalyst bed or the feed/effluent exchangers. Plant resources can often isolate the offending vessel by analyzing samples on-line or pressure testing exchangers off-line. These approaches take time and can be expensive when they involve a shutdown to search for the problem. At times, conventional efforts fail to locate the offending vessel. On-line techniques, such as radioisotope tracers, have been used for many years to leak test these exchangers. These techniques avoid the maintenance and lost production costs of a search during a shutdown. But, every technique has its limit and some leaks are too small for the previously available techniques. A new service using stable chemical tracers has been employed to find very small leaks.

Statement of the Problem

A Mid-West Refinery in the U.S. operates a Naphtha Hydrotreater with a bank of four feed/effluent exchangers. See Figure 1.

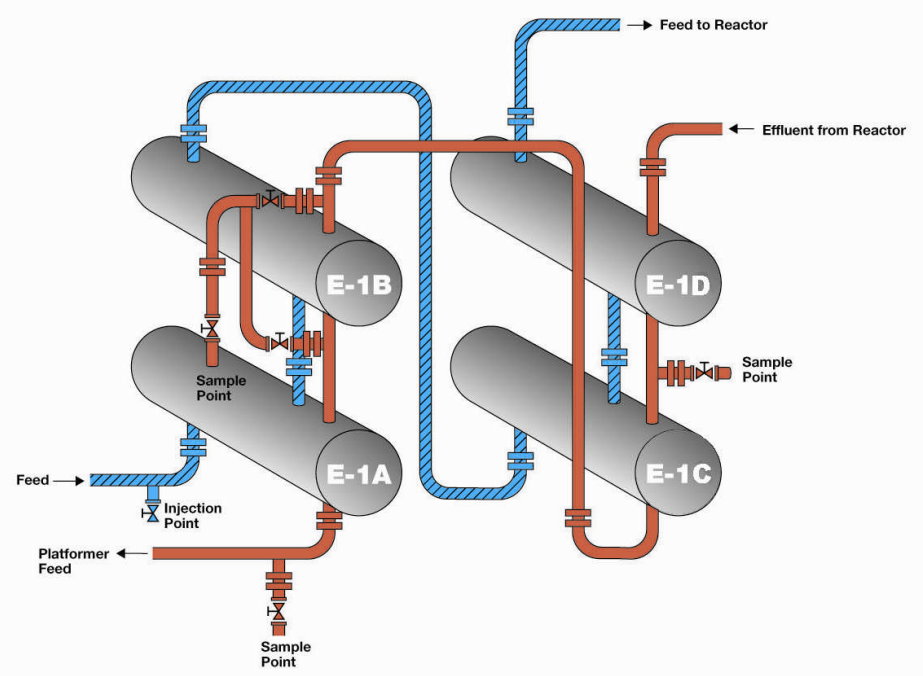

Figure 1 – Four Feed/Effluent Exchangers in the Naphtha Hydrotreating Unit

The flow though the Hydrotreater varies from 5,000 to 10,000 bbls/day. The effluent from the reactor is cooled by the exchangers and then sent as feed to the Platforming Unit. Results of Platformer Feed sample analysis showed that sulfur levels, which had been staying between 0 to 2 ppm, were now fluctuating between 2 and 10 ppm. Figure 2 shows a distinct trend to higher sulfur levels. Plant personnel had tried to determine which exchanger was leaking by sample analysis, but had been unsuccessful. They contacted Tracerco to gain assistance in identifying the leaking exchanger before taking an outage to fix the problem.

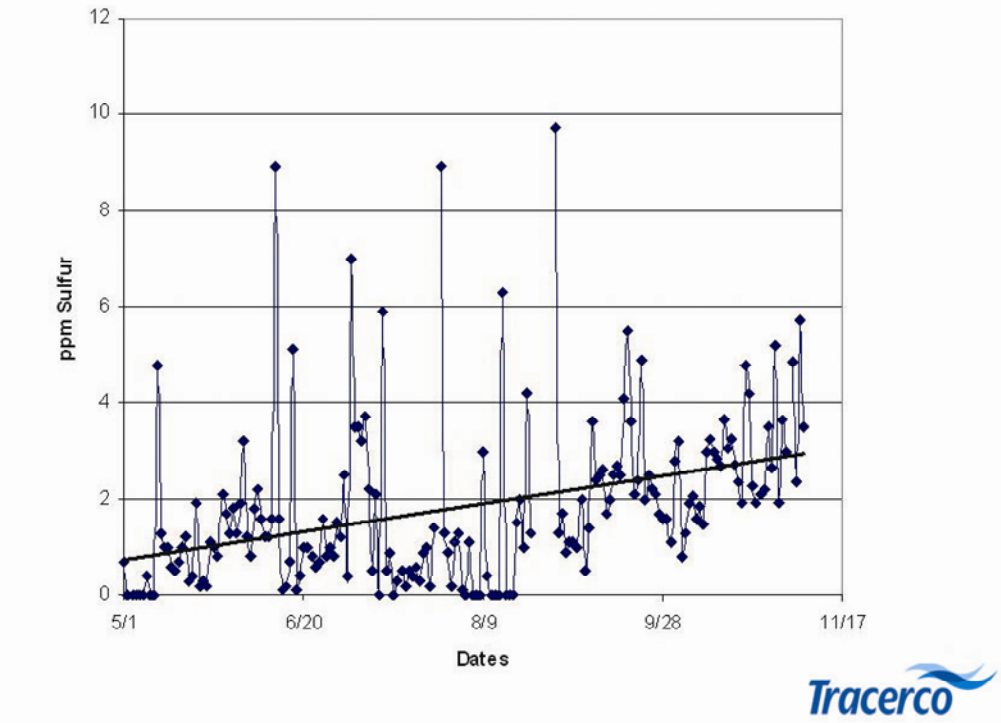

Figure 2 Platformer Feed Sulfur Levels

The Solution

Tracerco has a long history of performing on-line heat exchanger leak tests using radioactive materials as tracers. The standard technique is to mount radiation detectors on the feed and effluent lines of each exchanger and inject a radioisotope tracer that is compatible with the feed stream. As the tracer flows through the exchangers with the higher-pressure feed stream, the detectors on the feed piping will respond to the passage of the tracer, producing bell-shaped Gaussian response curves on the computer. If one of the exchangers has a leak, the leak to the effluent side will be at the same concentration of tracer as its percentage in the feed. Though diluted by the effluent, the detectors on the effluent exit lines will respond, producing a response curve on the computer. By comparing the area under the leak detector response curve to the area under the feed detector response curve, the percentage leak can be approximated.

The limitation of this technique is in its sensitivity. This technique is the easiest and quickest way to perform an on-line leak test if 0.5 percent or more of the feed is leaking into the effluent. Sometimes, the sensitivity can be improved to 0.2 or even 0.1, but the more typical limit is 0.5 percent.

Smaller leaks can be found with radioisotope tracers by a sampling technique. The tracer material and the injection procedure are exactly the same as before, but instead of mounting detectors on the feed and effluent lines, sample points on the effluent lines have to be established. Sample points generally consist of a sample cooler where hot effluent is condensed/cooled and collected in sample containers. The samples are counted with a very sensitive radiation detector. The each sample can be counted for several minutes. Compared to the on-line tracer technique where the tracer material flashes past the detector in a few seconds, much smaller amounts of radiotracer can be measured in the samples. This technique has been used to find leaks as low as 100 ppm. Unfortunately, finding smaller leaks than this would require the injection of so much radiotracer that disposal of the radiotracer becomes an issue, as well as the safety of the crew performing the leak test.

To address the need to find leaks smaller than 100 ppm, Tracerco researched chemical tracer techniques. Tracerco identified a range of compounds, some of which are compatible with organic and some with aqueous streams, that are chemically and thermally stable, and can be readily recognized in samples by specialized gas chromatography. These chemicals can be found in hydrocarbon samples at concentrations as low as 1 part per billion (ppb).

The four feed/effluent exchangers each had a sample point, which meant the tracers could be injected into a single injection point. See Figure 1. Each exchanger was tested with a separate tracer. This allowed a two man crew to test the four exchangers. One tracer could have been used, but all four exchangers would have to have been sampled at the same time, requiring a five man crew. It was more cost-effective to use two people and four tracers.

Because the effluent stream contained hydrogen sulfide (H_2S), the decision was made to collect the samples in stainless steel sample cylinders instead of using a sample cooler. Hydrogen and H_2S would have been continuously released to the atmosphere while collecting the samples with a sample cooler. Ten sample cylinders were mounted to a manifold at the first sample point. As the tracer was injected, the first sample cylinder was opened and closed in 10 seconds. The other nine sample cylinders were opened and closed at 10 second intervals. The sample cylinders were then removed from the manifold and immersed in an ice bath to condense the naphtha and tracer. Each cylinder was depressurized through a tube containing activated charcoal and then the naphtha in the cylinder was collected in plastic bottles.

The activated charcoal tubes and the sample bottles were sent to the Tracerco lab for analysis. The results showed that three of the sets of samples were negative. The set of samples for the E-1B exchanger showed tracer in samples 5 through 10. See figure 3.

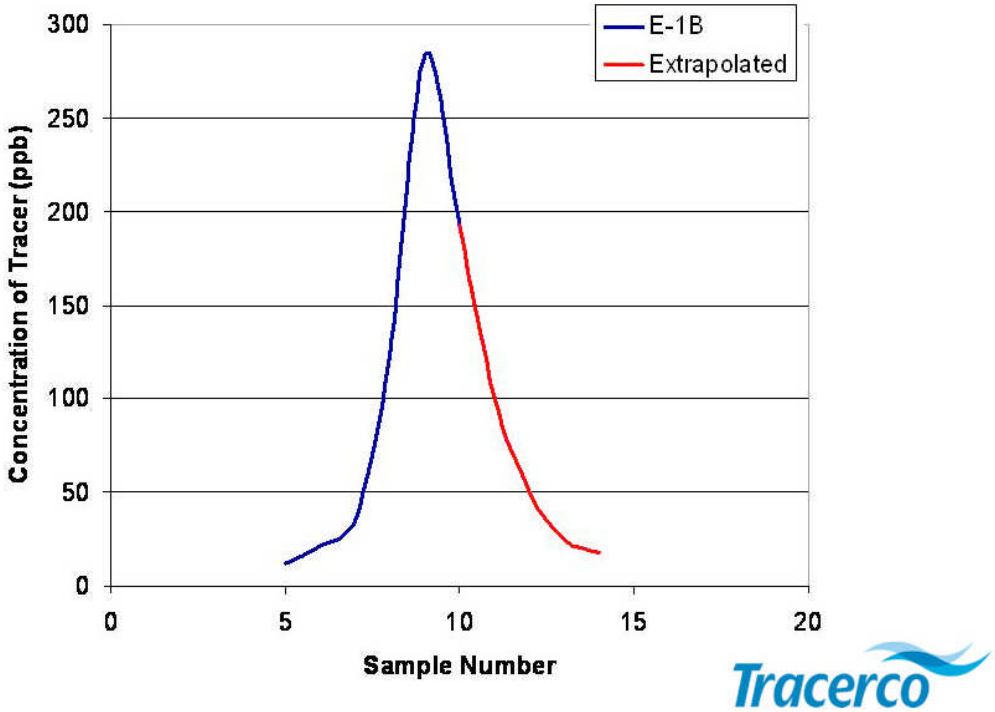

Figure 3 Chemical Tracer Response Curve

Unfortunately, the tracer was slower coming through the exchangers than had been expected. The ninth sample had the highest reading and the tenth sample was the first sample on the trailing edge of the response curve. If another 10 samples had been caught, there would have been tracer in samples 11 through 13, at least, and probably in a few more. The trailing edge of a response curve is usually more drawn out than the leading edge.

For this analysis, however, the conservative approach was applied and a short trailing edge was extrapolated. The average concentration for the samples was determined and the grams of chemical tracer that passed the sample point while the samples were being collected was calculated. When this result was divided by the total grams of chemical tracer that was injected, the resulting percentage leak was revealed. The results indicated that the rate of leakage of the feed into the effluent was 0.0044 percent or 44 ppm at the time of the test.

At a convenient time for the refinery, the unit was brought down and the E-1B exchanger was pressure tested with water. One tube had an obvious leak and four other tubes had small leaks. The tubes were plugged and the unit was brought back on line. The sulfur levels returned to the 0 to 2 ppm level.

Conclusion

The plant personnel were able to avoid the lost production from a longer shutdown and the maintenance costs of opening and hydrotesting the other three exchangers. This project demonstrated the capabilities of the new approach to leak testing exchangers. Ultra Low Sulfur Diesel Hydrotreaters operate at such low sulfur specifications that very small leaks in the feed/effluent exchangers can result in off-specification effluent. With the new chemical tracers that are now available, leak rates as low as 5 ppm can be detected.

Resumes

Troy Witherill was graduated from the University Of North Dakota with a B.S. in Chemical Engineering in 1992. He has worked for Ashland Petroleum Company, Basis Petroleum Inc., Murphy Oil USA, Inc., and Countrymark Cooperative, LLP in various technical and process engineering and supervisory roles.

Dave Ferguson was graduated from Texas A&M University with a B.S. in Chemical Engineering in 1980. He has worked for Olin Corporation, Dow Chemical, Iris Power Engineering, Tru-Tec Services, and Tracerco in various research, engineering, commercial, and management roles.