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New Technology for High Temperature Furnace Fouling Control

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Introduction

Baker Petrolite has invested in a long-term research project to understand residual stream heater fouling mechanisms, and how to control these fouling mechanisms. This bench scale work has led us to the development of new treatment strategies for high severity applications such as visbreaker and coker heaters. The performance of these new fouling control strategies in mitigating heater tube fouling was further demonstrated in a pilot scale delayed coker unit.

Applications of this new technology in commercial delayed cokers have significantly increased unit throughputs by extending heater run lengths, while reducing the frequency and cost of coil decoking procedures. Unlike approaches used in the past, this new Baker Petrolite technology has proven to be effective controlling high temperature resid heater fouling.

Customized treatment programs are derived by using proprietary feedstock characterization and analysis methods, and comparisons with extensive feedstock characterization data which have been developed for a wide range of coker unit feedstocks.

This treatment approach provides the flexibility to address the specific fouling mechanisms associated with a particular coker furnace. It will inhibit fouling due to:

- Thermal degradation of the oils
- Asphaltene destabilization
- Precipitation of solids or other inorganic materials from residual feedstocks
- Catalytic fouling due to metals in the feed or on heater tube surfaces

Use of this technology can provide a refiner with significant economic benefits by:

- Increasing furnace run lengths – time between start up and when skin temperature limitations are reached, or the time between start up and shut down due to economic loss limits being reached
- Increasing throughput by allowing longer runs at maximum rates, or increasing heater throughput attainable compared to previous unit runs
- Increasing yields by allowing longer runs at target transfer line temperatures, or going to higher transfer line temperatures while maintaining fouling rates within target ranges
- Improving refinery economics by allowing feedstocks with a more severe fouling potential to be processed:
    - Deeper cut, higher density vacuum tower (VTB) bottoms
    - Reduced or eliminated vacuum gas oil dilution of VTB or coker gas oil recycle rates
    - Higher asphaltene content in crude oil and coker feed
    - Higher coker feed acid content due to higher levels of naphthenic acids in crude blends
    - Higher metals contents or inorganic solids loadings in coker feed

Shorter than desired run lengths of coker and visbreaker furnaces can cost refiners tens of millions of dollars per year in unrealized revenue, where heater fouling limits unit throughput or run length. In many cases, the capacity of bottoms upgrading units limits a refiner's capacity to process lower cost heavy crudes, which offers additional economic incentives for refiners to maximize thermal conversion unit throughputs.

Causes of Residual Stream Heater Tube Fouling

Heater tube coke formation is caused by a combination of high oil film temperatures and high oil residence times, plus the inherent instability of the hydrocarbon stream being processed.

There are various heater modifications or operational adjustments unit engineers can make to control these conditions and mitigate fouling. The optimal operating envelope for a furnace involves many factors, including equipment design, fluid velocities, firebox controls, pressure, temperature, burner fuel and BTU content, instrumentation, operational control and routine and preventative maintenance.

The final operating envelope employed by the refiner is ultimately based on unit and refinery economics. Most operating philosophies fall into one of two general categories:

- <u>Running the Coker Furnace</u> – from start up, maintaining maximum throughput and transfer line temperatures until a furnace tube skin temperature limit is attained on any TI (temperature indicator)
- <u>Operating the Coker Furnace</u> – from start up, adjusting the furnace operation to control fouling rates (as measured by the refinery) at or below a target rate, for example a 1.0°F tube skin temperature increase per day

Most of the adjustments made in the second operating mode above involve incurring economic penalties compared to start-of-run conditions. These economic penalties may not be as significant as taking major throughput decreases or shut downs to spall or de-coke the furnace. These adjustments are usually continued, or increased, until the negative economic impact is no longer sustainable. The adjustments used to increase furnace run length include:

- Reducing charge rates to the furnace
- Reducing the transfer line temperature
- Amount of vacuum gas oil "drop" to VTB, or coker gas oil recycle to coker feed
- Increasing feedstock API gravity via crude blend changes or reduced flashing in vacuum column
- Reducing feedstock asphaltene or TAN content via crude blending

Nearly all delayed cokers and visbreakers operate somewhat differently. However, regardless of the "operational severity" of the furnace, if the amount of foulant and the rate of deposition within the furnace tubes are reduced, run lengths will increase. Baker Petrolite's research team focused on understanding and controlling the "feedstock severity" factors that have a significant impact on the fouling rates in coker and visbreaker furnace tubes.

Controlling Feedstock Fouling Tendencies

With its focus on feedstock chemistry, rather than operational control of fouling rates, the Baker Petrolite research team had to investigate and develop answers to several key questions about high temperature fouling phenomena:

1. What are the major fouling mechanisms leading to material deposition and coking in the furnace tubes?
2. What chemical additive functionalities are necessary to inhibit or mitigate the fouling mechanisms identified?

3. Can chemical additives with the proper functionality survive sufficiently long to achieve the necessary performance in a high temperature furnace?
4. Are there sufficient evaluation tools and/or analytical methods available to reliably measure the fouling potential of feedstocks in high temperature furnaces?
5. Can these tools be used to determine the relative fouling tendencies of feedstocks, so that prospective chemical mitigation program candidates can be pre-qualified?

Fouling Mechanisms

The stages of furnace fouling are widely known in the industry. The initial loss of heat transfer (U-value decline) at start-up is often generally associated with catalytic fouling. Steady state fouling occurs for the majority of the run that is associated with thermal fouling. There is also bulk fouling that can occur due to any inability to maintain steady state conditions, operational upsets, or other conditions causing rapid fouling in the furnace tubes. Understanding the mechanism(s) occurring during these fouling periods is critical to seeking an effective fouling mitigation or control process.

The conditions in furnaces typically allow multiple mechanisms of fouling to occur. The temperatures in a coker furnace are above the auto-cracking temperature for hydrocarbons. As the asphaltenes crack they become less soluble in the hydrocarbon, phase separate and can precipitate from the oil. The asphaltene – resin interaction is also disrupted due to the extreme conditions in the furnace. This will promote asphaltene agglomeration, which can also lead to precipitated material in the furnace tubes. Any organic material that precipitates onto the furnace tubes will rapidly undergo dehydrogenation to form coke due to the high tube skin temperatures. Solids and inorganic materials can contribute to furnace fouling as well. Many metals are known to catalyze cracking reactions. Solid particles, whether inorganic or coke particles can act as nucleation sites for organic material to build on and once the particle becomes too large for the resid to support it will drop out of the oil onto the equipment surface.

The mechanisms vary in intensity during each phase of furnace operation. The predominant mechanism at any given time depends primarily on the foulants existing in the feedstock, or potentially formed under severe thermal stress. During furnace start up the coking rate is relatively high, as clean metal surfaces act to attract or catalyze coking. This catalyzed coking reaction is commonly known as catalytic fouling. Catalytic fouling results in a layer of foulant or coke rapidly depositing in the furnace tubes, and results in an additional layer of material heat must transfer through before it can effectively heat the oil. The initial stage of fouling can result in a 40% loss of the of heat transfer coefficient allowed from start of run to tube de-coke, dramatically shortening furnace run length.

As the unit continues to operate and after this layer of foulant is deposited on the surface of the tubes, catalytic fouling subsides as the major mechanism and thermal fouling takes over as the major mechanism. Thermal fouling or steady state fouling tendency is determined by the thermal stability of the oil or the stability of the asphaltenes and resins in the oil. This stage is characterized by the precipitation of thermally converted asphaltenes or coke, where the deposition rate exceeds the removal rate (due to velocity) from the furnace tube.

The potential fouling severity of a delayed coker or visbreaker feedstock is dependent on the amount of inorganic contamination, the amount of metals that comprise the inorganic component, and the stability of the asphaltenes and resins in the stream. The higher the contamination levels the higher the potential fouling rate. The higher the concentration of asphaltenes, and the greater the instability of those asphaltenes, the higher the fouling potential of a specific feedstock will be.

Critical Chemical Additive Functionalities

With an understanding of the potential mechanisms of the coker and visbreaker furnaces, the critical functionalities of any chemical fouling control additive package can be determined.

A successful high temperature, heater coke suppressant program must:

1. Withstand high temperature at tube wall surface
2. Have polar alignment to active coking sites
3. Provide steric blocking to hinder coke formation
4. Provide increased asphaltene solubility or stabilization
5. Disperse inorganic particles

Failure to address any one of these functionalities in a chemical additive coke suppressant program can prevent achievement of the desired operational/economic performance improvements.

Feedstock Evaluation Tools

Developing the evaluation tools necessary to understand feed stream fouling tendencies and to allow the selection of suitable additive functionalities and dosages is a key to achieving desired fouling control program performance. The evaluation tools developed for commercial MILESTONE and VisTec programs are critical in overcoming the industry's past chemical additive program deficiencies, providing the "step forward" needed to help ensure chemical additive program success.

For example, the Baker Petrolite heater fouling control R&D team evaluated the suitability of conventional industry feedstock characterization methods for predicting heater tube fouling rates. It turns out that standard feedstock Asphaltene/Resin and Saturates/Aromatic ratios on coker charge streams did not necessarily correlate well to the actual fouling rates experienced in coker furnaces, as illustrated in Table 1.

Coker Feed Type	Furnace Run Length	Asphaltene/Resin Ratio	Saturates/Aromatic Ratio
Canadian	2.4 Months	0.348	2.63
Midwest	5.0 months	0.325	3.85
West Coast	9.0 Months	0.458	2.94

Table 1: Run Length vs. Asphaltene/Resin and Saturates/Aromatics Ratios, Selected Coker Feedstocks

Baker Petrolite developed the Coking Stability Index (CSI) to measure furnace feedstock stability. The CSI is a comparative test that is a better predictor of coker furnace fouling tendency with a given feedstock, as measured by furnace run length. This is illustrated in Table 2.

Coker Feed Type	Furnace Run Length	CSI	Asphaltene/Resin Ratio	Saturate/Aromatic Ratio
Canadian	2.4 Months	**99.5**	0.348	2.63
Midwest	5.0 months	**137.1**	0.325	3.85
West Coast	9.0 Months	**192.0**	0.458	2.94

Table 2: Run Length vs. CSI, Asphaltene/Resin and Saturates/Aromatics Ratios, Selected Coker Feedstocks

The Baker Petrolite CSI test is used to measure the stability of asphaltenes in furnace feeds via the determination of the onset of asphaltene flocculation point using a solvent titration method. The CSI system uses a solids detection method utilizing a near infrared (NIR) laser to determine the onset of asphaltene flocculation. The apex of the curve corresponds to the point of asphaltene precipitation and provides a relative measure of the stability of the feedstock. The higher the CSI, the more stable the coker feed. This method can be used to evaluate the stability of furnace feeds that will be subjected to high temperatures. Example CSI profiles for various feedstock types are shown in Figure 1.

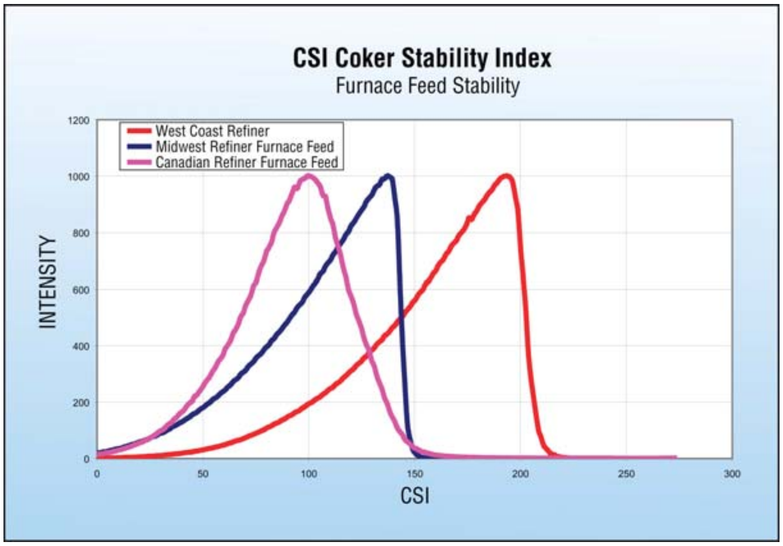


Figure 1: Example CSI Profiles for Various Coker Feedstocks

In addition to determining feedstock asphaltene stability, further analytical testing is performed on feedstock and deposit samples to provide insight into suspected inorganic fouling mechanisms. Bench top fouling simulation studies are also used to evaluate chemical additive performance with respect to coke suppression and fouling deposit volume.

All of these feedstock properties are benchmarked vs. an extensive database of characterization information developed for a wide range of unit feedstocks. These proprietary characterization methods and benchmarking processes are used to develop custom chemical treatment programs for specific unit feedstock types. The efficacy of the selected additive program is then confirmed with additional CSI testing. (Figure 2).

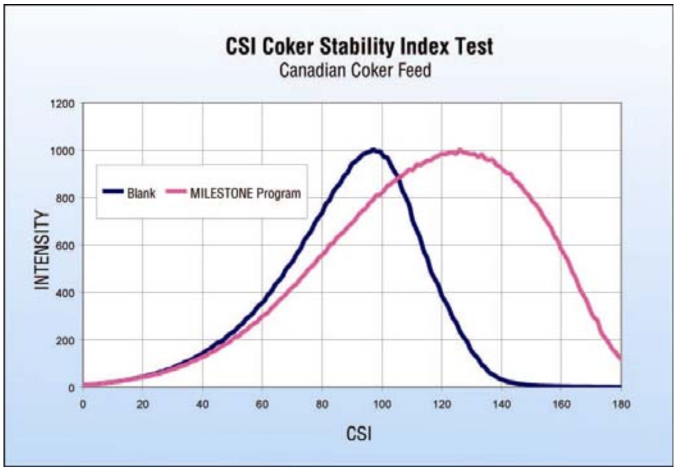


Figure 2: Effects of MILESTONE™ Additives on Coker Feedstock Asphaltene Stability

Positive performance of the recommended chemical treatment program (shifting the stability index to a more stable reading) translates very well to positive program performance in a high temperature furnace.

Failure of the selected program to achieve positive performance in the CSI tests indicates the fouling potential of the feedstock may be too severe to be effectively controlled by high temperature chemistries. Baker Petrolite will not advocate use of a chemical fouling control program unless positive dosage responses are observed in the CSI performance testing.

Pilot Plant Studies

Since 1998, Baker Petrolite has been an active participant in an ongoing delayed coker Joint Industry Research Project with a number of petroleum refining and process licensing companies at the University of Tulsa. This JIP has investigated several facets of delayed coker operation, using the U.S. Department of Energy pilot scale delayed coker unit, including the study of high temperature fouling. Test runs conducted by the JIP using Baker Petrolite products confirmed that Baker Petrolite's new fouling control strategies significantly reduce coker heater fouling rates for the feedstocks tested.

A Commercial Evaluation of MILESTONE Heater Fouling Control Technology

The new Baker Petrolite approach to controlling heater tube fouling with chemical additives was shown to be effective in both bench scale and pilot plant testing. An early field test was conducted at an East Coast Refinery early in 2005.

In late 2004, Giant Refining Company's Yorktown, Virginia refinery experienced delayed coker furnace fouling that dramatically shortened the furnace run length (the time between de-cokings by pigging) that had been achieved in the past. In January 2005, Baker Petrolite and Giant Refining initiated a chemical fouling control program, later to be termed MILESTONE Heater Fouling Control Technology. This successful MILESTONE program continues at Giant Yorktown to date.

The Giant Yorktown coker furnace is composed of four furnace coils with two coils on either side of the furnace. Half of the furnace (2 coils) can be taken out of service for decoking while the other half remain in operation. Key operating points before September 2004:

- Fouling rates targeted at 1°F/day maximum skin temperature increase on each coil
- Opportunity crudes and operational problems accounted for most fouling excursions (>1°F/day)
- Pigging is the primary de-coking method and was considered a cost effective option to controlling fouling at or beyond target ranges
- A high naphthenic acid crude was added to the crude blend in January 2004
- Between January 2004 and September 2004, fouling rates were considered acceptable

The coker then had a turnaround in September 2004. After the turnaround, a primary change in unit operations was to double the rate of high naphthenic acid crude in the blend. Two weeks after the coker started up, excessive fouling in the coker furnace was observed with the following effects:

- Coil fouling rates increased such that skin temperature increases ranged from 5 – 10+°F/day.
- Operational efforts to control the fouling rate included:
    - Reducing unit charge rate
    - Reducing transfer line temperature
- Pigging intervals increased from over 100 days to a range of 19 to 53 days

The economic cost of fouling increased significantly, due to decreased heater run lengths, reductions in unit feed rates, and increased maintenance costs associated with additional pigging events.

A third party coking consultant was brought in to review coker operations, and in particular the coker furnace. Both pre-turnaround and post-turnaround coker charge samples were analyzed for contaminants. No problems were found with unit operations and no contaminants were detected by lab analysis.

Operational efforts to reduce fouling led to additional economic losses, including unit charge rate reductions of 500 to 5,000 BPD, and decreasing transfer line temperatures by 8°F, which reduced fouling rates but resulted in conversion losses.

These reductions in charge rates and transfer line temperature were unacceptable.

Baker Petrolite analyzed the feeds going to the coker furnace and proposed the implementation of a MILESTONE heater fouling control program.

MILESTONE Technology Evaluation

Giant's technical personnel were not fully confident of the ability of the MILESTONE program to deliver significant value on this coker furnace operation. Giant's senior engineer took steps to make sure that the operations that led to the high fouling rates would be matched when the coker came up from a January 2005 pigging/decoking procedure. The concern was that operational or feedstock changes could provide positive results that could be mistakenly attributed to the chemical fouling control program.

All previous operational variables were maintained at levels which resulted in very high fouling rates just before shut down/pigging:

- Crude Blend
    - The same crude oils, blended at the same ratio
    - Same VTB (coker feed) TAN levels
- Maintain the same desalter stability and efficiency
- Same coker charge rate
- Transfer line temperature kept at previous level
- The upstream naphthenic acid corrosion control program was held at pre-shutdown dosages

In this way, the evaluation of the MILESTONE program was assured to be a fair test of the chemical treatment program's capabilities.

MILESTONE Technology Performance

The first criterion for success was whether furnace tube skin temperature increases could be controlled, thereby increasing run lengths.

Target: The pre-turnaround fouling rate of 1°F/day
Results: Using MILESTONE™ additives, tube fouling was reduced to 0.3 – 0.4°F/day tube skin temperature increases

Target: The fouling control program had to extend the run length well in excess of 4 week pigging intervals, while allowing charge rate and coil outlet temperatures to return to normal
Results: The program began to deliver a projected 6 month run length

After one month of operation with MILESTONE™ additives, and no unacceptable increases in heater tube skin temperatures, the refinery began to gradually increase furnace coil outlet temperatures. Within three months coil outlet temperatures had been returned to normal. Furnace charge rates were then gradually increased and were successfully returned to normal levels within 2 months.

Figure 3 shows that coker unit throughput was returned to "normal" rates, and then continued to be increased to higher than normal levels, while maintaining the tube fouling rate to less than 1.0°F/day skin temperature increases.

Coker Charge Rate 12/1/2004 to 6/2/2005

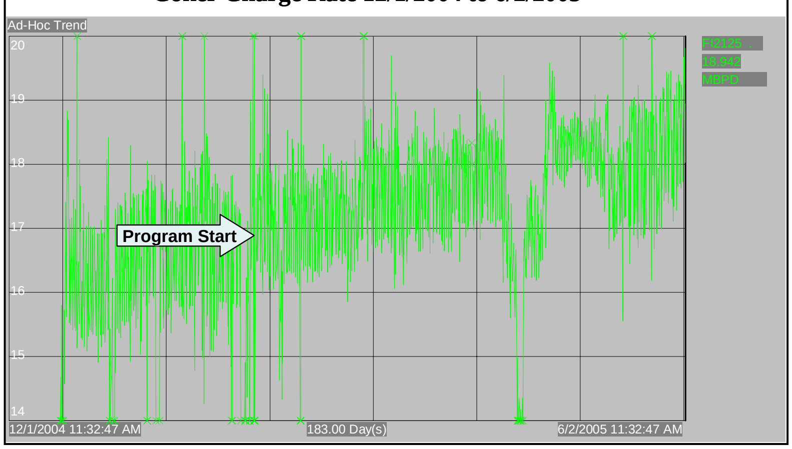
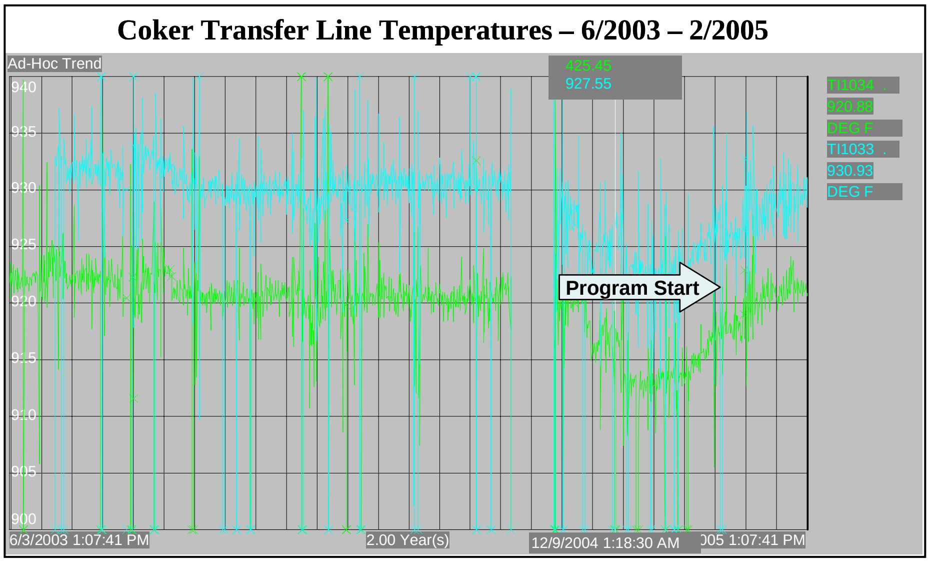


Figure 3: Coker Charge Rate vs. Time

The outage shown in Figure 3 was not due to furnace tube fouling; this was due to a plant maintenance issue.

Figure 4 shows that the transfer line temperature was returned to the range used prior to reducing firing due to furnace tube fouling in December 2004. Furnace tube skin temperature increases were still maintained below the 1°F/day at this higher transfer line temperature.



<u>Figure 4</u>: Coker Furnace Transfer Line Temperature vs. Time

Conclusions

Baker Petrolite has undertaken a comprehensive R&D effort to (1) develop an understanding of the mechanisms involved in high temperature coker and visbreaker fouling, (2) develop the methodologies to evaluate feedstock severity, (3) develop products with high temperature functionality, (4) develop evaluation and control methodologies to understand chemical dosage responses and program recommendations, (5) confirm program performance on a pilot scale coker, and (6) prove program performance in a refinery delayed coker application where severe fouling conditions were being experienced.

The MILESTONE delayed coker fouling control program designed for Giant Refining was a technical and economic success. The significant "win" for this MILESTONE program is the prevention of economic losses that would have continued without the use of the fouling control program. The "technical successes" are summarized below:

1. The heater run length has been increased to record levels
2. Under severe fouling conditions of the initial trial period, 0.3 – 0.4°F/day skin temperature increases were achieved and maintained
3. With subsequent increases in charge rate and transfer line temperatures, a heater tube fouling rate of 0.6°F/day was achieved, without an increase in chemical usage (still less than the 1°F/day target)

The program has been in continuous operation on this coker since January, 2005.

Reference

[1] Falkler, T. J.; Stark, J. L. Oil & Gas Journal, Sept. 13, 2004, 102(34)