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Ethylene Plant Cracker Gas Compressor Fouling

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ETHYLENE PLANT CRACKED GAS COMPRESSOR FOULING

By Sheri Snider, Nalco Company

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INTRODUCTION

Nalco Company has been monitoring and treating process gas compressors in ethylene plants for more than 15 years. This paper provides an overview of process gas compressor fouling including economics, locations, mechanisms, control methods, and monitoring. Compressor train corrosion and fouling control case studies are also presented.

ECONOMIC CONSEQUENCES OF FOULING

Fouling in a cracked gas compressor can negatively affect plant economics. Figure 1 illustrates that initial efficiency loss (the declining red line) does not increase costs significantly if there is adequate turbine capacity; increasing the turbine speed (blue line) prevents lost production. However, once the turbine is limited, any additional loss in efficiency results in reduced throughput (black line, "Capacity") and a dramatic increase in the total cost of operation (TCO).

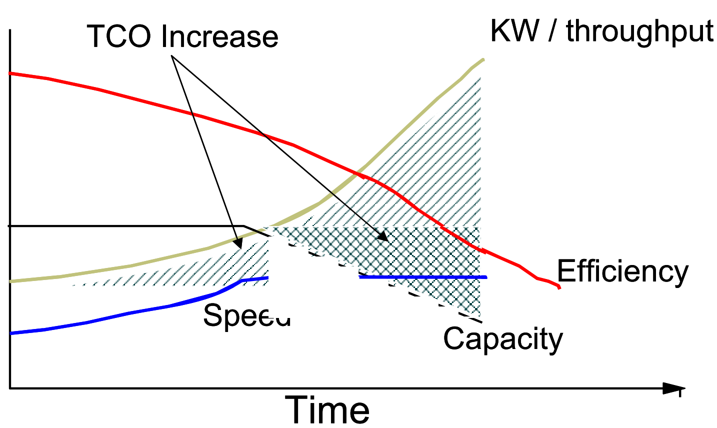


Figure 1: Economics of Process Gas Compressor Fouling

In addition to energy cost and production loss, a fouled compressor may require an unscheduled shutdown. Even before shutting down, a fouled machine is usually operated at higher-than-desired suction pressure, in order to maintain the desired discharge pressure. This affects unit economics, increasing the first stage suction pressure increases the furnace pressure and lowers selectivity towards ethylene.

COMPRESSOR FOULING LOCATIONS

Figure 2 shows the internals of a compressor. Fouling can occur in the inlet guide vanes, wheels, diffusers and balance line.

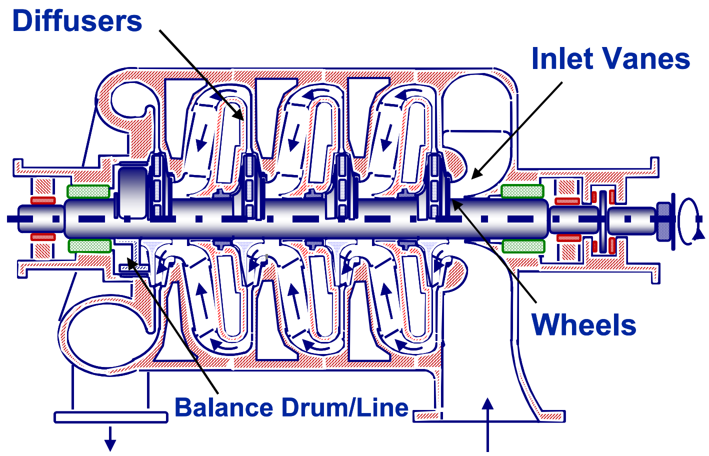


Figure 2: Compressor Fouling Location – Stage and Balance Line

Figure 3 reveals how fouling and wear in the labyrinth seals between the wheels can reduce stage efficiency. Labyrinth seals prevent gas from leaking from a higher-pressure wheel to a lower-pressure wheel. The teeth create turbulence and resistance, and as a result the gas is slowed. As the teeth become fouled or damaged, there is less resistance, so gas leakage increases. From a monitoring standpoint, this is observed as a loss in efficiency.

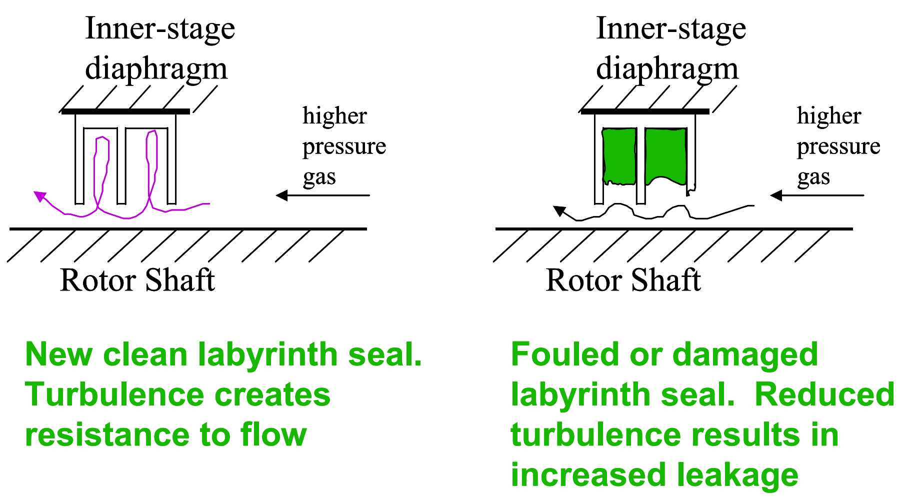


Figure 3: Compressor Fouling Location – Labyrinth Seals

Another potential location for fouling is the stage discharge line. An example is illustrated in Figure 4.

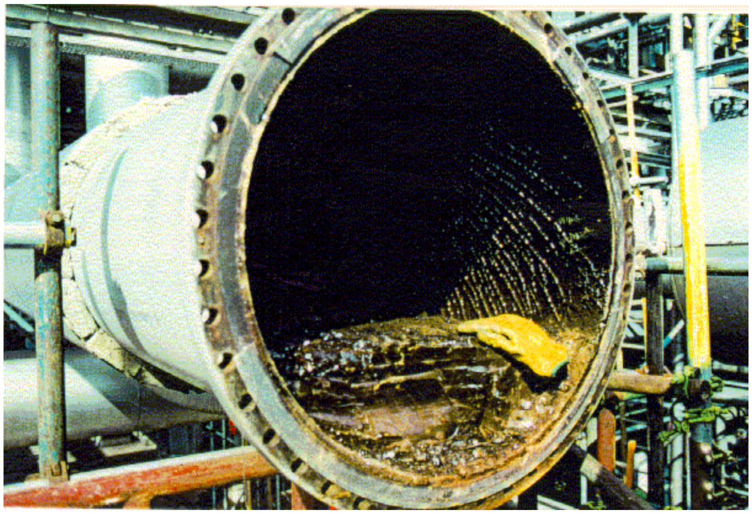


Figure 4: Compressor Fouling Location – Discharge Line

The stage intercoolers are typically designed with the cracked gas on the shell side where polymer may collect on the bundle at the inlet to the exchanger. Once polymer starts to collect at the inlet, the exchanger starts to act like a filter. Polymer deposition creates a pressure drop that lowers the overall performance of the compressor. This is typically observed in our monitoring as an increase in intercooler pressure drop (dP). A photo of a fouled intercooler is provided in Figure 5.

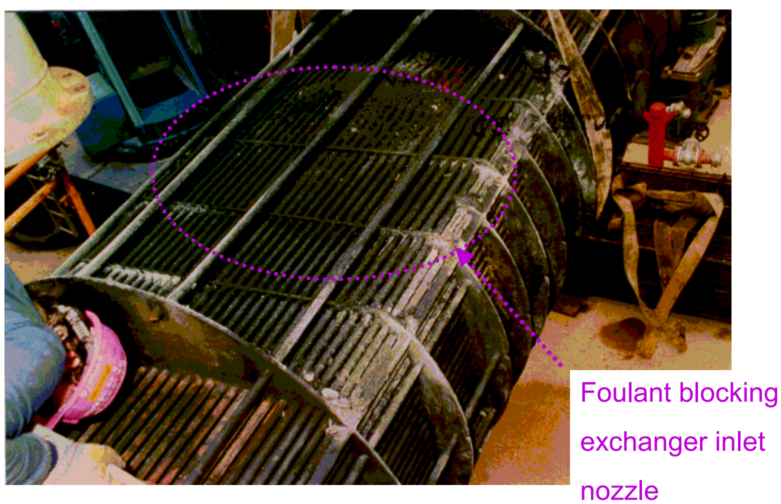


Figure 5: Compressor Fouling Location – Stage Aftercooler

It is important to understand that fouling in a compressor may affect vessels upstream or downstream of the compressor.

The liquids that are knocked out in the early stages typically are routed back to the quench system. Polymers may contribute to emulsions or fouling in the quench system. The liquids knocked out in the later stages are often routed to the light ends fractionation section, potentially increasing polymer deposition in these towers.

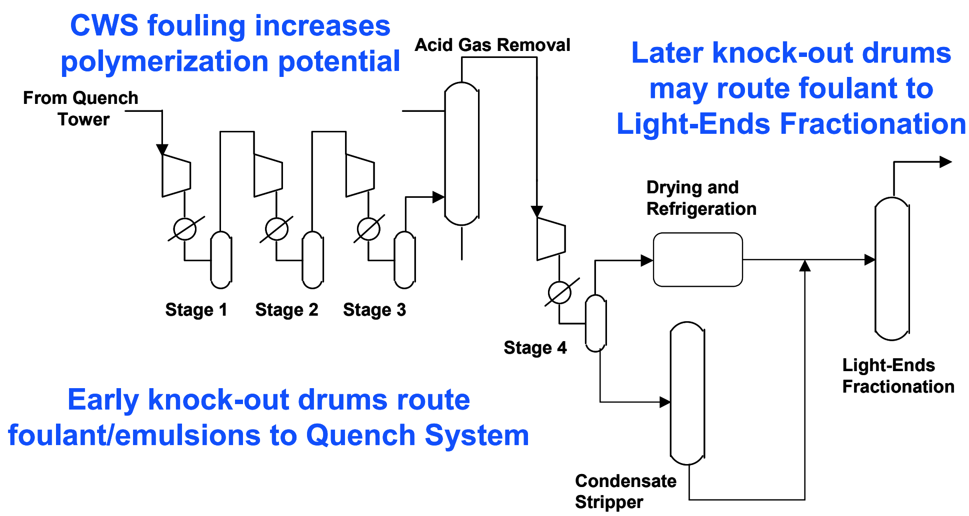


Figure 6: Compressor Fouling – upstream and downstream impacts

Process Gas Compressor Fouling Mechanisms – Chemical Mechanisms

Many papers have been written that discuss fouling mechanisms occurring in process gas compressors. Most agree on three mechanisms; free radical polymerization, Diels-Alder condensation, and the thermal degradation to coke.

In free radical polymerization, monomers with reactive double bonds, such as butadiene, styrene, isoprene and vinyl acetylene (Figure 6), react to make polymer. In a compressor, the reactive monomers from the gas phase dissolve (or diffuse) into liquid hydrocarbons that condense during compression. Once in the liquid phase, the reactive monomers may undergo free radical polymerization as illustrated in Figure 7.

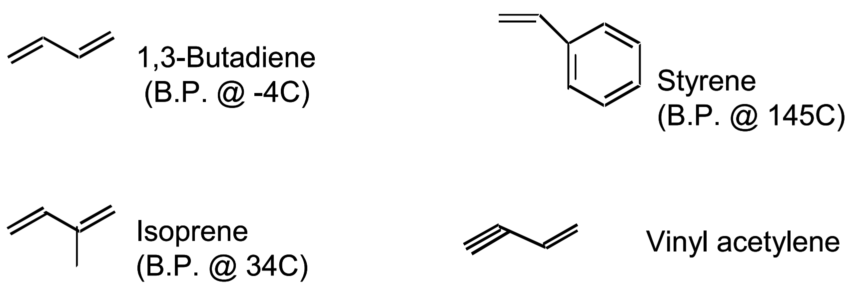
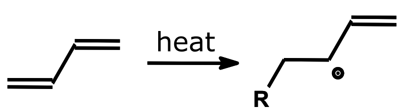


Figure 6: Monomers that undergo free-radical polymerization.

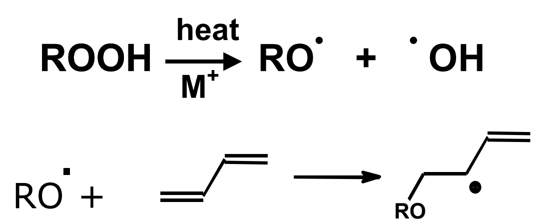
Free radical polymerization, shown in Figure 7, begins with the initiation step, in which a radical is formed via hydroperoxide decomposition (if there is an oxygen source, heat or a metal catalyst) or heat. Once the unstable radical forms, it will quickly react with a monomer, generating a new radical. The new radical continues to react with monomer (propagation). As the polymer chain grows, the molecular weight of the polymer increases until the polymer becomes insoluble. The polymer then lies on piping and process equipment (compressor wheel, discharge piping, etc.), as discussed previously.

Initiation:

Thermal Initiation:



Hydroperoxide Decomposition Initiation:



Propagation:

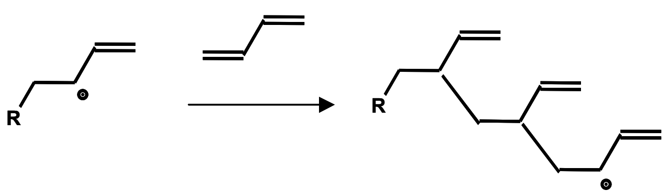


Figure 7: Free Radical Polymerization — Initiation and Propagation Steps

Fouling kinetics will not be discussed in depth in this paper; but it is important to emphasize the relationship between temperature and the rate of polymerization. The relative rate constant of peroxide initiated free-radical polymerization is illustrated in Figure 8. Notice that rate increases exponentially with temperature. There is a greater potential for compressor fouling at higher discharge temperatures.

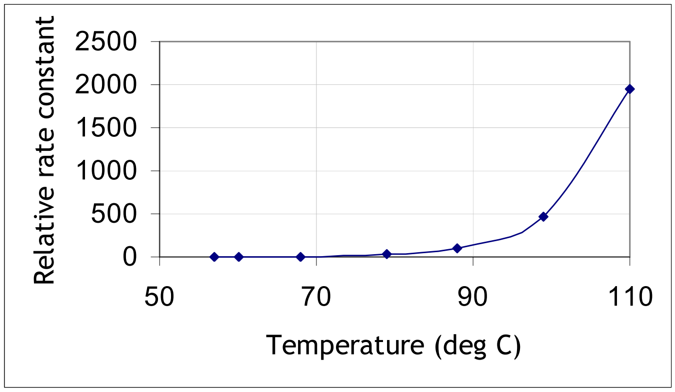


Figure 8: Relative rate constant of peroxide decomposition versus temperature.

Whether the polymer is formed via free radical mechanism or via Diels-Alder mechanism, as shown in Figure 9, over time the precipitated hydrocarbons will reduce to a coke-like substance as illustrated in Figure 10. The cyclic monomers continue to react with other cyclic, dienic or acetylenic monomers to form polynuclear aromatic (PNA) material. The PNA will dehydrogenate over time to a form a coke-like substance commonly found when compressors are opened for inspection.

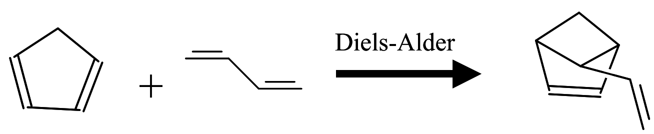


Figure 9: Diels-Alder condensation of cyclopentadiene and butadiene

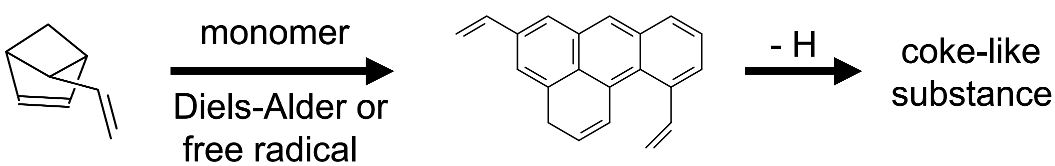


Figure 10: Thermal degradation and dehydrogenation to a coke-like substance

Process Gas Compressor Fouling Mechanisms – Physical Entrainment

In addition to the polymerization reactions described above, there may be physical sources of fouling in the compressor. Many ethylene producers use wash oil to mitigate fouling in a compressor; but poor-quality wash oils may introduce impurities that may deposit in the compressor. If there is foaming or entrainment in the caustic tower, caustic may get carried into the next stage of compression, causing salt deposits. Corrosion can also affect compressor fouling. By-products of corrosion, such as iron oxide and iron sulfide, can deposit in the compressor and related piping and equipment.

Process Gas Compressor Fouling – Nalco Fouling Severity Matrix

Once the compressor fouling mechanisms are fully understood, it is easy to predict how changes in ethylene plant design or operation will affect compressor fouling. For instance, high cracking severity in the furnaces produces more fouling precursors, such as butadiene and styrene. Operating at production rates above design capacity results in higher compressor operating temperatures and therefore higher fouling rates.

In addition, the compressor is often an ideal place to return various recycle streams from polymer plants and refineries. However, these recycle streams may contain fouling precursors, oxygen or peroxides, or other components that can adversely impact compressor operation and fouling.

Nalco created a fouling severity matrix (Figure 11) to incorporate several factors contributing to process gas compressor fouling. As one may expect, four stage process gas compressors in gas crackers tend to have the highest fouling potential.

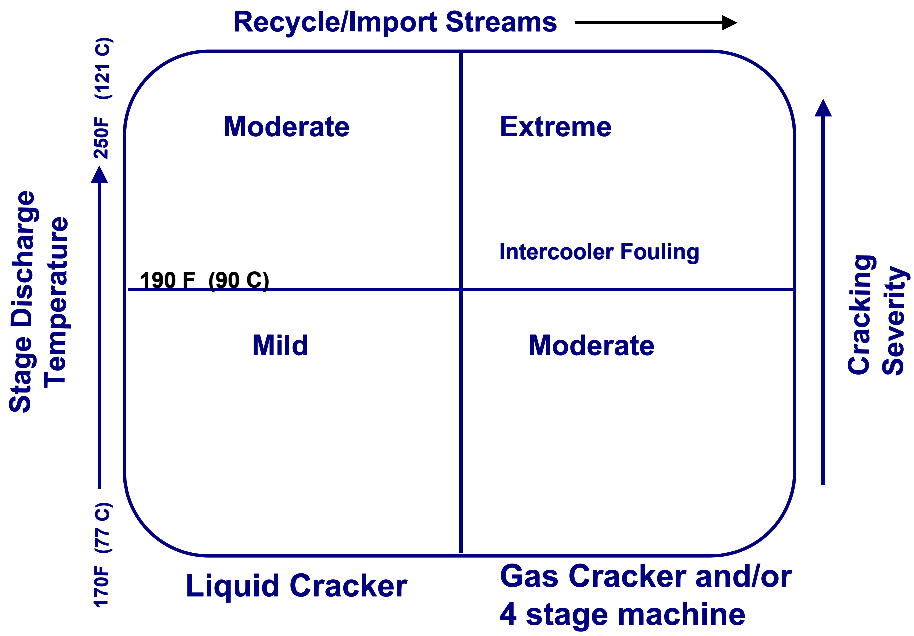


Figure 11: Nalco Fouling Severity Matrix

Liquid crackers generate a lower concentration of fouling precursors and have more heavy hydrocarbons condensing in the machine that act as solvents for polymer. These crackers tend to have lower fouling severity than gas crackers.

Five-stage machines tend to have lower discharge temperatures than four-stage machines, so they tend to have lower fouling severity.

If a compressor has a history of intercooler fouling, Nalco places this compressor in the “extreme” fouling severity category, regardless of temperatures and feed slates. Intercooler fouling is very difficult to control and, in order to meet runlength goals, the compressor will require more attention (performance monitoring) and an aggressive fouling control program.

Identifying where the compressor sits on the Fouling Severity Matrix and understanding the impact compressor fouling has on the ethylene plant throughput and runtime between turnarounds will lead to identifying the most cost effective fouling control method.

PROCESS GAS COMPRESSOR FOULING CONTROL

This section of the paper discusses the many methods used to control process gas compressor fouling in the ethylene industry. The methods discussed include coatings, wash oil, water injection, antifoulants and few common design and operating considerations.

Process Gas Compressor Fouling Control – Coatings

Compressor coatings are used in the industry to reduce corrosion and foulant deposition in process gas compressors. Coatings are typically applied to the diaphragms and rotor assemblies during scheduled maintenance downtime. Since the coatings are pH sensitive, consult the coating vendor before coating a stage downstream of the caustic tower, especially if carryover is a concern. Also, if reducing wash oil is used to justify the cost of coating, consider the impact on the intercoolers, as wash oil is a key component of intercooler fouling control.

Process Gas Compressor Fouling Control – Wash Oil

There are two methods for applying compressor wash oil: continuous injection and intermittent high-volume flushing. Continuous injection keeps the compressor surface "wet" and continuously moves polymer through the system; however, continuous wash oil treatment may be costly if wash oil is purchased. High-volume washes typically consume less wash oil, but polymer builds up slowly between flushes. There is a risk of removing polymer unevenly causing vibrations and there is a greater potential for downstream effects from the short-term slug of liquid in the system.

Whether purchased from a supplier or provided internally, a high-quality wash oil stream should have a high degree of solvency for polymer. The best wash oils in the industry have an aromatic content above 80 percent. An initial boiling point greater than 392°F (200°C) will ensure the wash oil remains liquid, allowing it to dissolve and scour polymer from the metal surfaces and minimize the deposition of entrained solids. The wash oil should be low in monomer content and free of polymer and solids itself, so a distilled product is best.

Process Gas Compressor Fouling Control – Antifoulants

Over time, ethylene producers have increased furnace cracking severity and the runtime between scheduled turnarounds. Minimized fouling and the resulting efficiency loss in process gas compressors have been important for achieving desired production capacity and runlength goals. As a result, there has been an increase in antifoulant usage in compressors. Of the approximately 280 ethylene plants in the world, about one-third currently use antifoulants for fouling control.

Antifoulants reduce the impact of fouling in various ways. Inhibitors reduce free-radical polymerization rates. Dispersants reduce polymer deposition. Metal deactivators, if of the proper type, prevent catalysis of hydroperoxide decomposition. When needed, corrosion inhibitors minimize the corrosion mechanism and thereby the formation of corrosion by-products.

Several examples of improved compressor performance through the utilization of Nalco antifoulants are provided in a later section of this paper.

Process Gas Compressor Fouling Control – Water

Many ethylene producers add water to the process gas compressor in order to lower the gas discharge temperature and the gas volume. Water vaporizes in the compressor stage, absorbing some heat of compression. This results in lower stage discharge temperatures. The drop in gas temperature causes a drop in gas volume, volume being directionally proportional to temperature ($PV=ZnRT$). As expected, the decrease in temperature reduces fouling rates and is a key component of fouling control when discharge temperatures without water are greater than 220°F (104°C). Water that remains liquid in the compressor stage will dissolve inorganic deposits, such as those from caustic tower carry-over.

The obvious risk of adding water to the compressor is the potential for corrosion and erosion. Figure 12 reveals the thinning of a wheel blade from continuous water injection. Injecting only the amount of water that will flash to vapor will lower the potential for erosion. Water injected into the compressor should be deaerated and free of acids or other contaminants.

For the stage of compression immediately after the caustic tower, water injection can be utilized to dissolve and flush sodium salts that have accumulated due to problems with the caustic tower operation. The quantity of water injected must be in excess of the amount that vaporizes under the local conditions, yet not be so voluminous as to damage the compressor (incompressibility of liquids). Delays in flushing the compressor after a caustic tower upset can complicate the task of on-line cleaning because the comingling of hydrocarbon-based foulant with caustic salts generates a complex matrix that is resistant to both water and wash oil.

Monitoring becomes somewhat more complicated with water injection, as the reduced discharge temperature increases the calculated efficiency. Having accurate measurements of the water flow rate to each stage will aid in monitoring compressor performance over time.

Finally, there has been some evidence of increased intercooler fouling accompanying the addition of water. Without the addition of water, the process gas enters the stage aftercooler and some of the heavier hydrocarbon components begin to condense. Polymer, carried into or just formed in the exchanger, is somewhat soluble in the liquid hydrocarbon that is present and may make its way through the intercooler and knock-out drum. However, polymer is not soluble in water. Adding water to the compressor directionally decreases the solubility of polymer in the aftercooler, which may lead to polymer deposition in the exchanger.

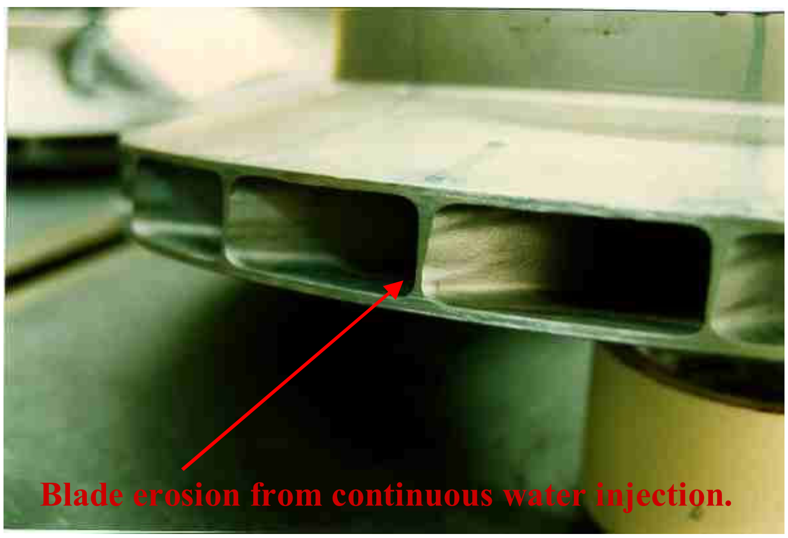


Figure 12: Erosion from water injection.

Process Gas Compressor Fouling Control – Design and Operational Considerations

Plant design and operating parameters can greatly affect compressor operation and fouling rates. The following are just a few of the design and operational considerations and how they relate to compressor fouling.

Operating above design capacity results in higher operating temperatures and consequently higher fouling rates, as well as an increased risk of knock out drum carryover and caustic carryover by entrainment. Turnarounds are an excellent time to modify knock out drum size and replace demister pads, if necessary.

Because fouling rates are a function of temperature and concentration of fouling precursors, minimize temperatures when possible. Keep the cooling water side of intercoolers clean. Keep the quench tower and quench water coolers clean to minimize the quench tower overhead temperature.

If possible, avoid routing recycle streams that contain oxygen to the compressor. Even parts per million of oxygen or peroxides in the process gas can greatly increase polymerization rates. If recycling a stream to the compressor cannot be avoided, consider the use of a compressor antifoulant to mitigate the effect oxygen has on fouling rates.

Some seal designs are more tolerant of fouling than others. An excellent source is the 2000 AIChE Paper written by Taylor, Beck and Eads (AIChE 2000, Article 85B). The writers compare stationary impeller eye and interstage seals with abradable seals. The rotating labyrinth teeth of the abradable seal are self-cleaning by centrifugal force and, therefore, are more tolerant to fouling than a stationary labyrinth seal.

There are many variations on compressor intercooler designs. Most are shell and tube with process on the shell side and cooling water in the tubes. Design variations include baffle arrangement, impingement plate options, and locations of inlet and outlet nozzles. The following paragraphs briefly discuss a few design variations and how they can affect intercooler fouling.

Since intercoolers may foul over time, intercooler designs that allow easy cleaning during turnarounds are ideal. Intercooler designs with fixed tube bundles or triangular pitch tubes make cleaning difficult and may require replacement to obtain optimal performance.

Although rare in the industry, intercoolers designed with the process gas on tube side have the least concern for process-side exchanger fouling. The drawback is controlling cooling water scaling accompanying the low water velocities through the exchanger shell.

Intercooler designs that minimize the risk of polymer build up at the inlet are less likely to have pressure drop issues due to fouling. Ethylene producers that have a history of this type of intercooler fouling may want to consider changing or removing feed impingement plates during scheduled maintenance.

Some intercooler designs have the most severe fouling in one or more baffled sections of the exchanger. Nalco has theorized that one reason for this type of fouling is trapped liquids. Most exchangers are designed so condensed hydrocarbons can pass under the baffle through a notch in the baffle; however, if polymer restricts the flow of liquid through the notch, liquid will accumulate in the baffled section. The hot liquid may then act like a small reactor in which more polymer forms, eventually restricting flow, increasing intercooler pressure drop, and lowering compressor performance. In this case, modifications to the baffle during scheduled downtime may improve future performance.

PROCESS GAS COMPRESSOR MONITORING

Monitoring compressor performance typically includes trending each stage's polytropic efficiency (or M-factor), vibration and flow corrected intercooler pressure drop over time. This section of the paper discusses these monitoring tools, and a few others, currently used by Nalco.

The best way to monitor compressor performance is to calculate the polytropic efficiency (Figure 13) of each stage and to compare this to the stage design efficiency based on volumetric flow and rotor speed. The calculations are straight-forward and computer software, such as Nalco's CompTrack, that displays performance results in easy-to-read text and graphs. The parameters required to monitor the process gas compressor in this manner are the following:

- Suction and discharge temperatures and pressures of each stage
- Compressor gas composition
- Mass or volumetric flow rate
- Rotor speed
- Performance curves (design curves) for each stage

Gas composition can be measured by sample analysis or calculated from a furnace yield model. Performance curves should be based on the current (if re-rated) compressor internals. Figure 14 provides an example of compressor performance monitoring using Nalco's CompTrack software.

Compressor performance monitoring becomes less precise when gas composition is not available. Without gas composition, the (k-1)/k factor of the polytropic equation must be treated as a constant. Inverting the pressure and temperature pieces of the equation results in the M-factor (Figure 15). The M-factor therefore increases as compressor stage performance declines. For steam crackers with nearly constant furnace feed slates and cracking severities, the M-factor is a very valuable monitoring tool.

Fouling on the process side of an intercooler causes increased pressure drop (dP) across the exchanger. Pressure drop across the exchanger is typically estimated as the difference between the previous stage's discharge pressure and the next stage's suction pressure. To best monitor intercooler performance, Nalco trends flow corrected intercooler dP's to compensate for the changes in pressure drop due to flow fluctuations.

Most ethylene producers watch compressor train vibrations closely. Increased vibration can result from fouling deposits that imbalance an impeller. High vibrations may also result from mechanical problems unrelated to fouling. Therefore, it is important to trend polytropic efficiency or M-factor in addition to monitoring vibrations (Figure 16).

When water is added to the compressor, the reduction in a stage discharge temperature will artificially increase the calculated efficiency. If the rate of water is known, the efficiency calculation can be modified using an estimated, undepressed discharge temperature. Another method, if operating only above or only below peak design efficiency, is to regress clean compressor data for a predicted discharge temperature. Deviation of the actual discharge temperature from the predicted discharge temperature is an indication of efficiency loss (Figure 17).

If the caustic tower is between stages of compression, monitoring the pH of the knock-out drum water will help determine if caustic carryover is occurring.

$$\text{Polytropic efficiency} = \frac{\ln (P_d/P_s)}{\ln (T_d/T_s)} * \frac{(k-1)}{k} * 100\%$$

T_s and T_d are stage suction and discharge temperatures in absolute

degrees R = F + 460   degrees K = C + 273

P_s and P_d are the stage suction and discharge pressures in absolute

psia = psig + 14.7   kPaa = kPag + 101.3

$k = c_p/c_v$ (Plant needs to know composition of gas to calculate k-value)

c_p = specific heat constant pressure,

c_v = specific heat constant volume, = Cp - R

R= gas constant

Figure 13: Polytropic Efficiency Calculation

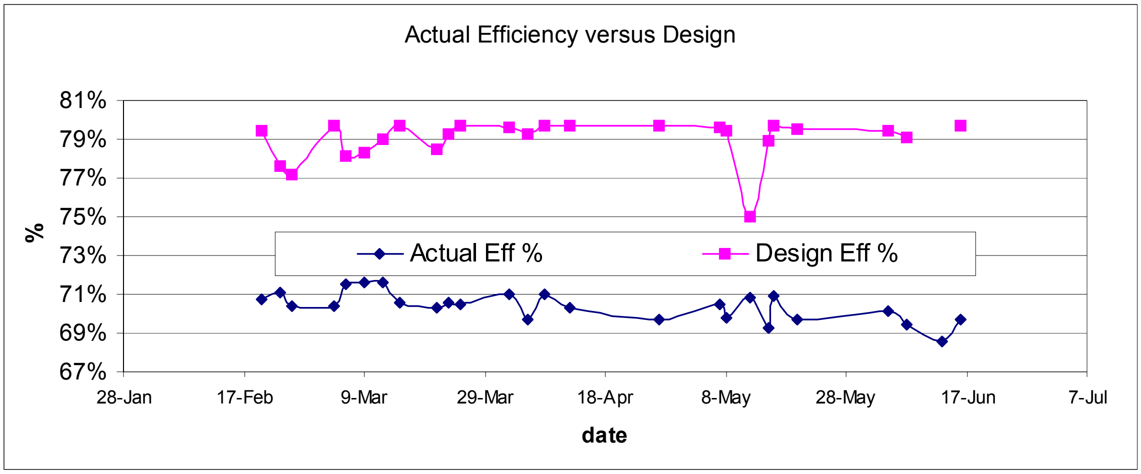


Figure 14: Actual versus Design Efficiency Trend (output of Nalco CompTrack)

$$\text{M-factor} = \ln(T_d/T_s) / \ln(P_d/P_s)$$

T_s and T_d are stage suction and discharge temperatures in absolute degrees R = degrees F + 460, degrees K = degrees C + 273

P_s and P_d are the stage suction and discharge pressures in absolute psia = psig + 14.7, kPaa = kPag + 101.3

Figure 15: M-factor Calculation

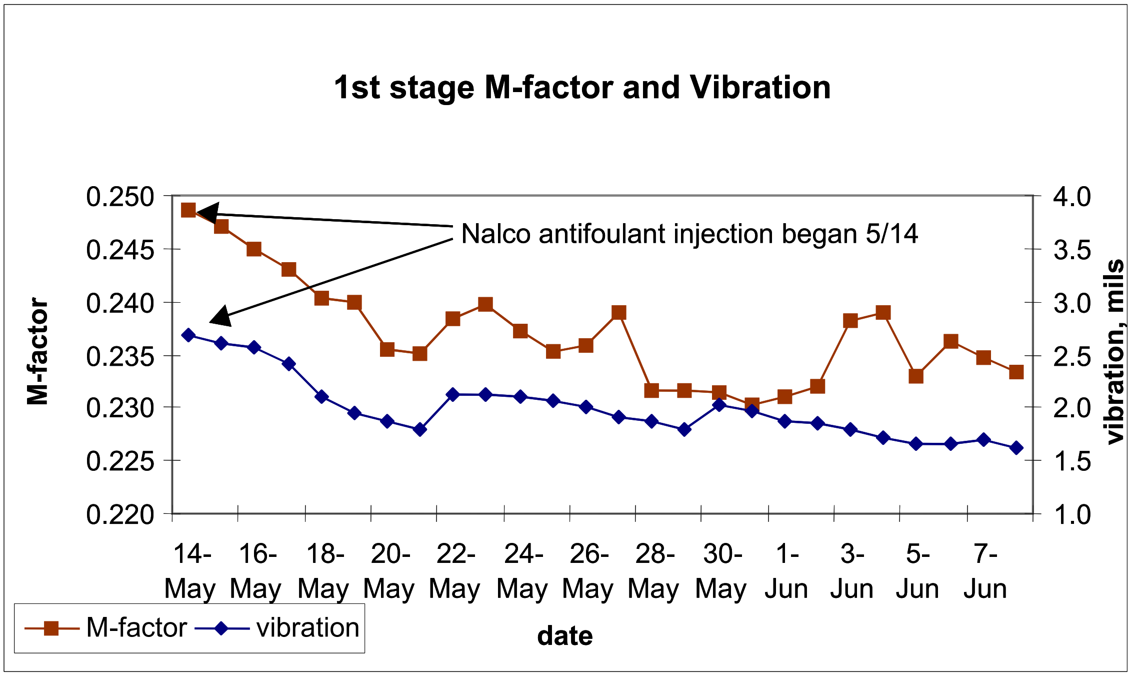


Figure 16: Vibrations and M-factor versus time

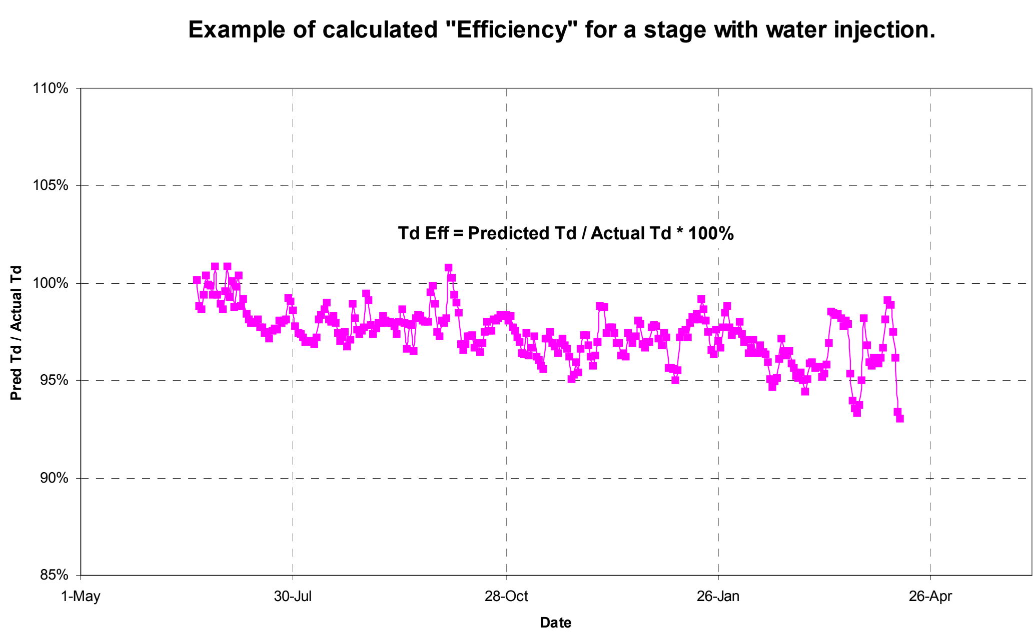


Figure 17: Using data regression to estimate a predicted stage discharge temperature and “efficiency”

PROCESS GAS COMPRESSOR CORROSION

Although there are several acidic species in the cracked gas, acetic acid is responsible for most of the corrosion in the compressor train. Both gas and liquid crackers have acetic acid in the furnace effluent; however, liquid crackers tend to have much more. A major difference between gas and liquid crackers is the ratio of dilution steam to hydrocarbon. A minor reaction pathway involving water in the furnace effluent is responsible for the generation of acetic acid; in accordance with Le Chatelier's Principle, more reactants (H20) leads to more product (acetic acid). The liquid feeds (naphtha, gas oils) can also contain naphthenic acids that crack in the furnace to give smaller acids, predominantly acetic acid. The naphthenic acid content of liquid feedstock varies, so the amount of acetic acid in the furnace effluent will vary.

The unique physical properties of acetic acid make it troublesome in several areas of an ethylene plant.

- At 80 C, it has a vapor/liquid ratio of 0.39
- It is soluble in both water and hydrocarbon phases
- It azeotropes with hydrocarbons, C5 and greater

.

Consequently, acetic acid distributes throughout the typical ethylene plant. Corrosive locations are where hydrocarbons and small quantities of water condense, such as the compressor train, the depentanizer overhead, and some fractionator overheads.

In the compressor train, metal loss from corrosion predominantly occurs in the intercoolers but can occur in the stages of compression, the knock-out drums and the piping. Adequate corrosion control and monitoring is key to preventing equipment damage.

Compressor train corrosion control typically consists of adding a neutralizing amine to the suction of each stage requiring treatment. The cracked gas entering each stage of compression is saturated with water. Some water is condensed in each aftercooler and knocked out in the suction drum prior to each stage. Nalco recommends sampling the water from each knock out drum and measuring pH and total soluble iron. An iron level above 2 ppm may warrant a neutralizer program. Currently, about one in every fifteen compressors is treated for corrosion.

Periodic sampling may be necessary in liquid crackers because acid levels can vary. In general, liquid steam crackers receive their feedstock from refineries, and evolving market conditions are leading some refineries to process crude oil with high total acid number (TAN) values. This translates to higher levels of naphthenic acids in the naphtha and gas oil feedstocks that are sold to ethylene producers. Higher naphthenic acid concentration in the feedstock causes higher concentrations of acetic acid (also formic, propionic, etc) in the ethylene unit.

EXAMPLES OF IMPROVED PROCESS GAS COMPRESSOR PERFORMANCE USING NALCO ANTIFOULANTS

Case Study 1: Vibrations reduced

The first-stage radial vibration of a four-stage process gas compressor in a gas cracker spiked to 3.8 mils. Plant throughput was reduced due to the high vibrations. Nalco began a dispersant program in the hopes of removing some of the polymer build up, thereby lowering vibrations, so the throughput could be increased.

Figure 18 and 19 display the reduction in vibrations, the M-factor, and the increase in throughput under the Nalco Comptrene™ program. Vibrations were reduced to 1.8 mils over the course of two months.

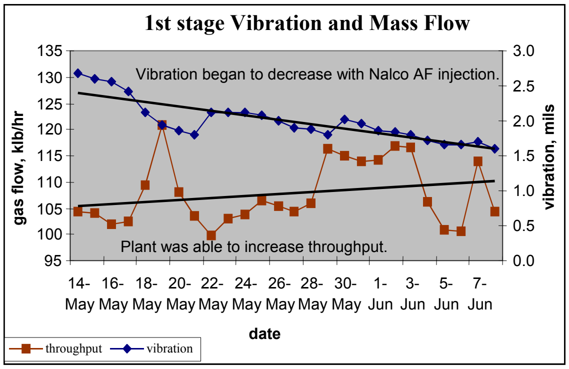


Figure 18: Vibration and Mass Flow

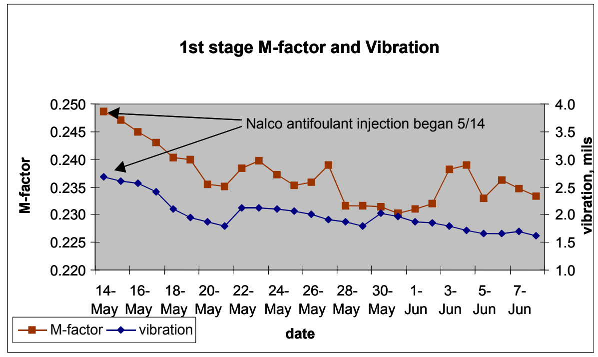


Figure 19: Vibration and M-factor

Case Study 2: High vibration reduced with Nalco dispersant.
The second stage of a five-stage process gas compressor in a liquid cracker had vibration spikes above 2 mils, and the plant was only three years into a five-year run (Figure 20). Plant engineers were concerned that because of this they would need to shutdown before their scheduled turnaround. The plant implemented a Nalco dispersant program. Over the course of several weeks, vibrations began to spike less frequently (Figure 20). Over the course of several months, vibrations were lowered to near start-of-run levels (Figure 21). The recovered compressor performance allowed the plant to achieve their five-year runlength goal.

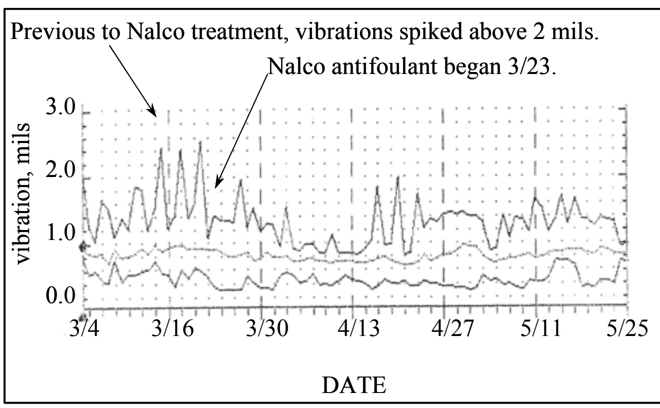


Figure 20: Case Study 2

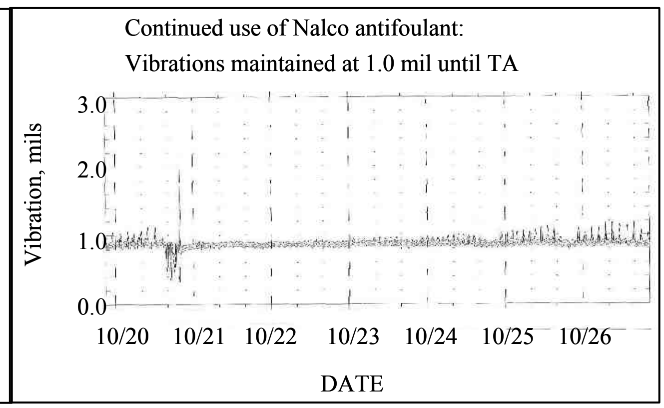


Figure 21: Case Study 2, continued

Case Study 3: Reducing Total Cost of Operation
A Gulf Coast gas cracker used expensive purchased wash oil and water injection to control fouling in their four-stage process gas compressor. Fouling was so severe in the compressor that the plant could only run one year between compressor cleanings. Nalco (known as Exxon Specialty Chemicals at the time) began working with the plant in 1990 to control fouling in the compressor and other areas in the ethylene plant.

Team efforts between the ethylene producer and Nalco resulted in a systematic reduction of wash oil and the addition of antifoulants (both dispersant and inhibitor) with each compressor run. The outcome of the antifoulant and wash oil modifications was lower efficiency losses, longer runtime between cleanings, and overall reduced treatment cost. Over the course of twelve years, the gas cracker runtime between scheduled turnarounds increased from one year to five years. Figure 22 reveals the increase in antifoulant to wash oil ratio, the decrease in lost efficiency per year and relative cost of treatment for each plant run.

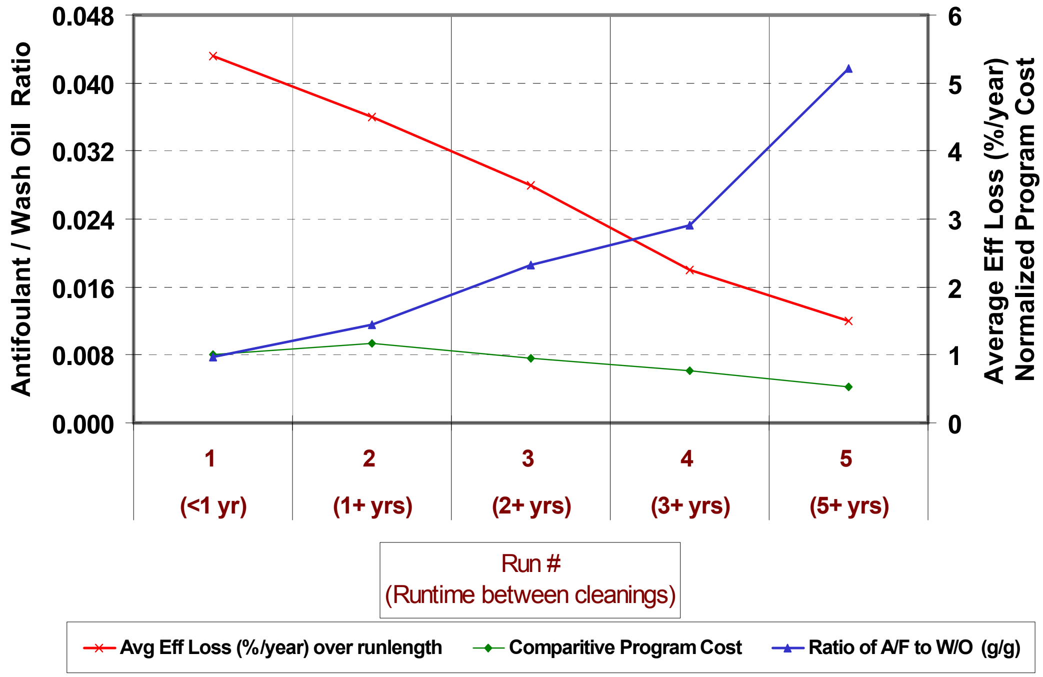


Figure 22: Case Study 3, Reducing TCO.

Case Study 4: Liquid Cracker Regains Lost Efficiency with Nalco Comptrene EC3144B.
A Gulf Coast liquid cracker estimated process gas compressor efficiency losses were costing approximately $750,000 per year. Nalco began treating the first stage of the five-stage machine with EC3144B antifoulant. Over the course of several weeks, the compressor performance improved significantly.

Figure 23 is a plot of efficiency versus volumetric flow. Data points at similar speeds were taken during several time periods and plotted. Each week of treatment with EC3144B provided a slightly higher efficiency for a given volumetric flow than the week before.

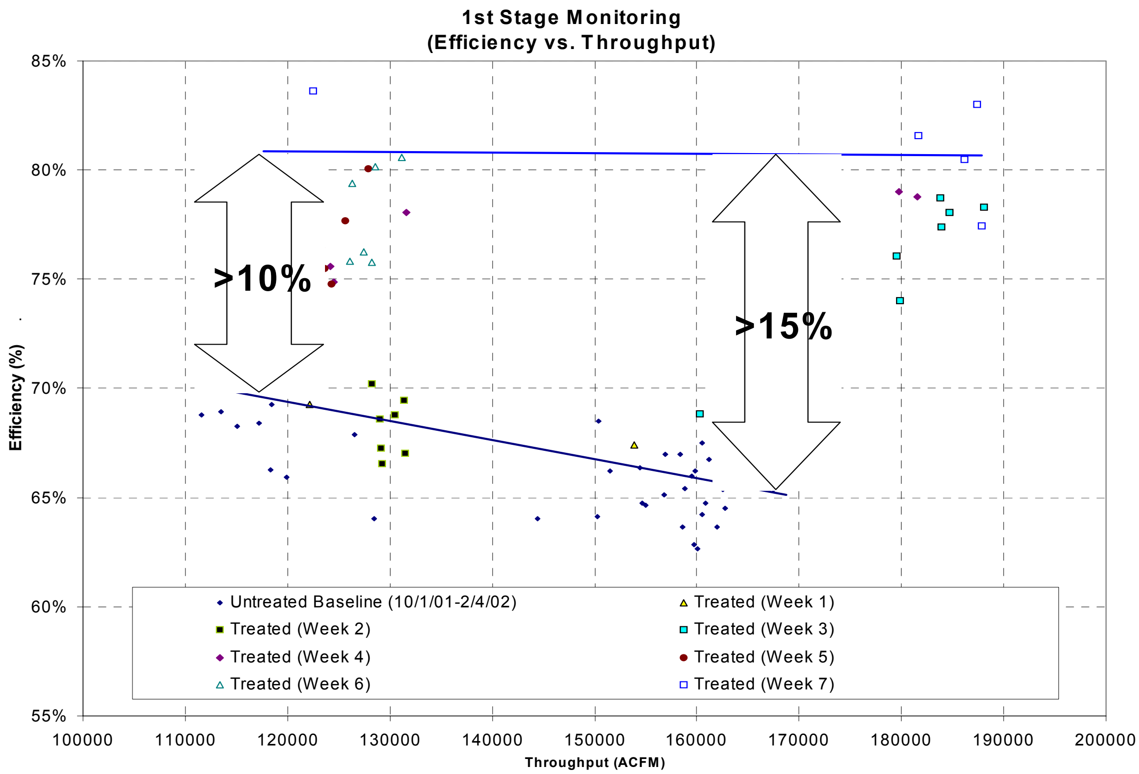
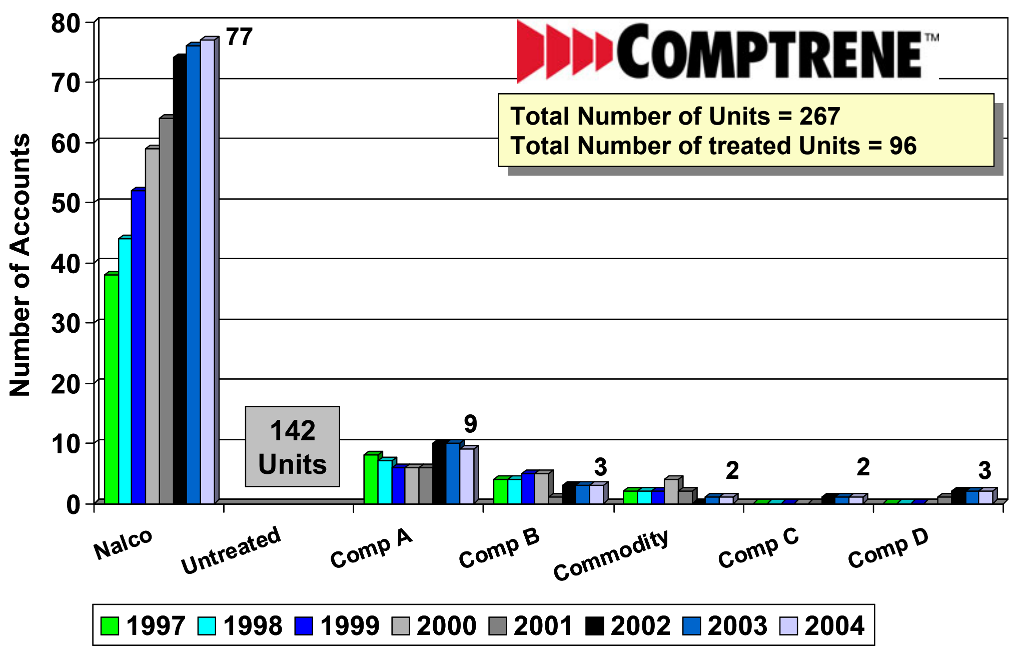


Figure 23: Case Study 4, Regaining lost efficiency.

FINAL COMMENTS

Understanding and controlling process gas compressor fouling has become an important part of increasing ethylene plant reliability and profitability. Nalco is proud to be able to work with leading ethylene producers worldwide.



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