HYDROCARBON
PROCESSING

Improve compressor reliability with advanced chemical treatments

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Although many olefin plants are making big investments in hardware and metallurgy to improve compressor performance and to extend run lengths, the reliability, efficiency and throughput capacity of the CGC are still key influences on plant profitability.

Keywords:

The cracked gas compressor (CGC) is the critical system in modern ethylene plants. This compressor drives gases from the crackers for downstream separation. Few plants can afford the luxury of backup compressor trains. Any downtime or reduced capacity of the CGC negatively impacts olefin facility profits. Under this highly competitive environment, even fewer ethylene operators can afford the thousands or even millions of dollars per day in lost revenues due to unplanned shutdowns to clean and repair CGCs.

Significant design advancements have developed more robust systems. Although many olefin plants are making substantial investments in hardware and metallurgy to improve compressor performance and to extend run lengths, the reliability, efficiency and throughput capacity of the CGC are still key influences on plant profitability. As engineering designs have improved, more attention is directed to preventing costly fouling of these critical systems with innovative chemical treatments.

Background

The purpose of the CGC is to compress the gases from the cracker for separation in downstream units. Due to the low boiling points of the light gases, very low temperatures are required for separation at feed-stream pressures. **Fig. 1** is a basic schematic for a five-stage compressor train.

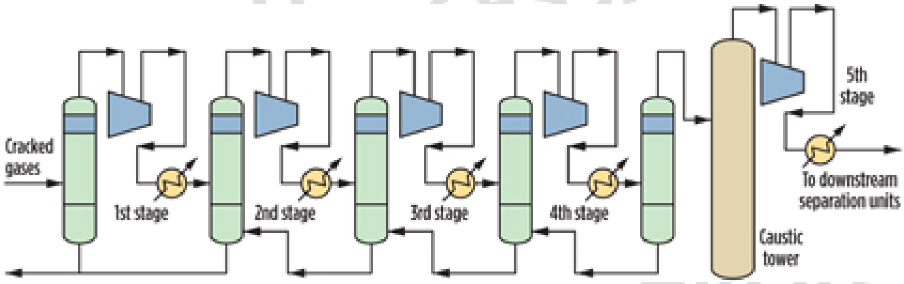

Fig. 1. Typical compressor train schematic.

Fouling origins

Compressor fouling problems are common. They are particularly troublesome in gas crackers due to the low volume of aromatic gasoline formed during cracking. Aromatic hydrocarbons are useful because they help keep fouling precursors in solution for easy removal. Liquid crackers have an inherent advantage due to higher aromatics production; however, these crackers also experience extensive fouling. The fouling rates in liquid crackers processing a variety of feedstocks such as heavy naphtha, gasoil (GO) and atmospheric GO residues have increased substantially.

Costs associated with CGC fouling are high, and they can increase exponentially as conditions deteriorate. **Result:** The reliability of CGCs remains a serious issue in spite of improvements in design and system metallurgy. Therefore, olefins plants are exploring new techniques to optimize compressor performance and run length. Many operators are discovering that chemical additives can offer attractive advantages for fouling control.

Feedstock

Gas crackers usually crack ethane and/or propane, whereas liquid crackers usually crack naphtha. The increasing volumes of shale gas and advantageous pricing have shifted more ethylene plants to rely heavily on natural gas feedstocks. However, this pattern is changing due to competition and growing demand for natural gas. Several ethylene producers are responding by turning to heavier, cheaper feedstocks such as GO and residues to improve profitability and to operate their systems at more severe conditions, thus increasing throughput. Variations in feedstock properties, higher cracking severity, and operations near design capacity accelerate polymerization reactions that lead to compressor fouling.

Unsaturates formed during the cracking process are reactive species, and levels found in effluent gas vary depending on the feedstock. Although some heavier components are eliminated in the quenching operation, the cracked gas still contains virtually all the C_4s and most of the C_5s and C_6s, along with some heavier fractions in the gaseous phase. This stream also contains appreciable amounts of highly reactive di-olefins and acidic compounds that are subject to oxidation and/or polymerization. Unsaturates contribute to free radical generation via thermal reaction or Dies-Alder mechanism or oxidation at the high temperatures found in the compressors, forming polymers. These polymers tend to accumulate in the compressor discharge lines, casing and after-coolers.

Most of the world's ethylene producers rely on wash oil and wash water as a mitigation strategy. Wash-water injection reduces the compressor discharge temperature, which helps control fouling. Conversely, water injection also leads to erosion and corrosion of the compressor wheels and blades.

Wash oil is used in a similar manner but works in a different way. It serves as a solvent that dissolves some polymers, thus allowing them to be removed from the system.

For maximum effectiveness, wash oil should be highly aromatic (60%) and have a boiling range of 175°C to 315°C. Most important, it must be free of styrene, naphthalenes and diene compounds. Wash oil that meets these specifications is increasingly more difficult to obtain locally, and shipping adds significant cost. High cost and short supplies are discouraging the use of wash oil. A number of ethylene producers have found that high-quality wash oil and wash water alone cannot provide sufficient fouling control.

Potential fouling factors

Fouling is a continuous process driven by free-radical chain propagation, oxidative and catalytic polymerization, and Diels-Alder reactions. The polymers initially formed by these reactions are soluble in aromatic streams unless they undergo continued polymerization. These factors promote polymerization reactions in CGCs:

- High concentrations of monomers, including dienes formed by high-severity furnace operations
- High compressor-outlet temperatures
- Organic peroxide-induced fouling caused by oxygen intrusions

- Return/recycle stream contamination by peroxides and other polymerization catalysts from LLDPE and HDPE plants.

Fouling increases with the number of these influences present within the system. **Fig. 2** illustrates that it is essential to control as many of these factors as possible to manage the fouling rate before it can begin to grow exponentially. Failure can make it extremely difficult or impossible to control compressor fouling.

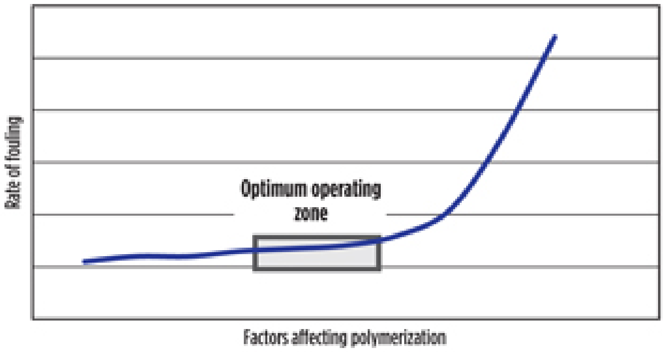

Fig. 2. Relationship between fouling rate and factors influencing polymerization.

Fouling within a compressor train is seldom uniform, and some areas are more susceptible than others. Fouling is worse in hotter areas along the wheels near the discharge, discharge piping, after-coolers and diffusers. Medium-pressure (MP) casing fouling is worse than high-pressure (HP) casing fouling because the concentration of reactive dienes and other monomers increases as condensation occurs in these stages, and the reactive monomers from the gas phase tend to dissolve (or diffuse) into liquid hydrocarbons that condense during compression.

Once in the liquid phase, the reactive monomers may undergo polymerization where typically monomers with reactive double bonds such as butadiene, styrene, isoprene and vinyl acetylene, react and polymerize. The condensation of lighter hydrocarbons can make the problem worse. Polymers forming in the compressors, if not depositing on the machine, will likely accumulate on the tube sheet or in the shell side of the after-coolers.

Continuous exposure to high temperatures supports poly-merization. As the reactions between the monomers proceed, large polynuclear aromatic compounds form. As the polymer grows, it loses solubility, begins to cross-link, dehydrates and transforms into brittle and insoluble coke deposits.

At this point, no aromatic stream, wash oil or dispersant will solubilize the polymers or prevent their deposition. Increased wash-oil injection may dislodge some of the polymers and allow them to move within the compressor. Some will accumulate in the after-cooler inlets or in knock-out pots, resulting in high pressure drops.

Experience in a number of plants indicates that polymer deposition on after-cooler surfaces has a significant impact on plant run-length. Such deposits limit throughput and increase power consumption, eventually forcing a shutdown. Few olefin plants have spare exchangers or bypass routes available, so after-cooler exchangers must be protected from fouling (**Fig. 3**).

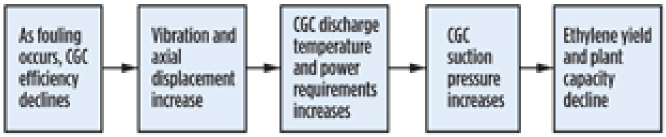

Fig. 3. CGC fouling process.

A certain amount of fouling is inevitable, but it can be controlled. The key is to control fouling as it initiates during the polymeric chain propagation rather than to implement a treatment program for an already-fouled system. During the initial polymerization steps, the polymers are more likely to be hydrocarbon soluble.

Advanced mitigation techniques

Conventional chemical mitigation techniques involving traditional antifoulant/dispersants and wash oil have limited value. Conventional dispersants work by physically removing some deposits from the fouling site. However, they cannot prevent solids generation. They are ineffective on the insoluble polymers, metal precursors, peroxides and free radicals that contribute to the fouling. In addition, dispersants can have costly negative side-effects.

These compounds have an affinity for water; when added in the CGC system, they can migrate with the wash water. Once in the quench-water circuit, their surface-modifying properties can create tight emulsions that make it more difficult to separate hydrocarbons from process water. Dispersants may also cause operational upsets and enhance after-cooler fouling by moving foulants from one location to another—the so-called “cleanup”’ effect.

An innovative chemical treatment program can prevent fouling by inhibiting reactions. This unique formulation contains a true inhibitor and a highly effective antioxidant. The true inhibitor reacts with monomers before they can form insoluble polymers, and the antioxidant-reduced oxidative polymerization. Compatible metal chelators or passivators are added as conditions warrant.

This unique formulation traps and inhibits free radicals by making the precursor or reactive species inert, thus retarding the polymerization reaction rate and reducing solids generation by altering the formation of insoluble molecules. The method attacks the polymerization/fouling processes in the initial phase where it is easiest to control and dramatically reduce solids generation. The treatment has allowed some compressors to run efficiently for five to six years with minimal fouling in the MP and HP casings and after-coolers.

The new fouling control program contains no metals and less basic nitrogen than amine-based antipolymerants currently available in the market. This is important because traditional high-nitrogen chemistry reacts to form insoluble salts under acidic conditions, as when hydrogen sulfide (H_2S) is present, essentially trading one fouling problem for another and contributing to the after-cooler pressure drops that can eventually force unplanned shutdowns. A new antipolymerant is effective in the presence of H_2S and does not form insoluble salts regardless of system pH.

Monitoring tools optimize performance

Monitoring is important when any treatment program used, but it is essential for optimum CGC treatment. Pressures, temperatures, flowrates, and wash-water and wash-oil injection rates (if any) are the keys to understanding compressor performance. Monitoring these parameters allows calculating the theoretical efficiency of the compressor system as well as after-cooler pressure drop limits. Other important performance indicators include machine vibration, knock-out drum polymer content and turbine energy consumption.

Fouling is a complex process. Both gradual trends and sudden changes in these parameters can imply developing problems. Solutions require an understanding of root causes that may not be immediately obvious. Proprietary models and sophisticated simulation tools can be used to explain complex interrelationships between changes in feedstock and furnace operating conditions and their impact on the composition of cracked gas entering the compressor.[1] Such tools can be used to evaluate how flow variations in recycle/purge streams influence cracked-gas composition and the effects on compressor efficiency. The end result is a set of realistic performance improvement targets based on a complete understanding of what is actually happening within the system.

The chemical composition analysis of fouling deposits provides a wealth of additional information. Organic and inorganic content can be identified, along with any corrosion products that may be acting as fouling catalysts. A full elemental analysis can identify impurities, and the carbon-to-hydrogen ratio indicates the extent of polymerization in the compressor train as well as the nature of those polymers.

The analysis allows treatment to be fine-tuned for maximum performance, but each analysis is only a snapshot of a dynamic process. Other proprietary assessment tools can address this problem by allowing online sampling in real time, using a retractable screen that can be inserted and withdrawn as often as necessary for sample collection and analysis.[2]

Case 1: Fouling example

A 400,000-tpy (400-Mtpy) olefins gas plant cracked a mixed feedstock consisting of 80% ethane and 20% propane. The quench-water tower overhead was compressed in a four-stage centrifugal unit driven by a steam turbine operating at 1,500 psig and 950°F. The second-stage CGC after-cooler design was unusual in that the process side was on the tube side of the exchanger. This intercooler was susceptible to fouling and had unacceptably high-pressure drops. During normal operations, the plant used wash water at about 0.7% of gas flowrates to maintain compressor discharge temperature at 194°F and also injected wash oil weekly (80%–90% aromaticity) at about 0.1% of the charge gas flowrate.

Problem. The plant experienced an unplanned shutdown approximately 18 months after a previous planned turnaround. Unfortunately, this plant had no backup reboiler. Reasons for the unplanned shutdown included:

1. Stage 2 pressure drop approached after-cooler design limits (from 7 psig to 26 psig)
2. Stage 2 polytrophic efficiency decreased 8%–10% below start of run (SOR)
3. Stage 3 polytrophic efficiency decreased 5%–8% below SOR
4. Operating capacity declined 30%–50%.

Considerable fouling was observed in the second-stage after-cooler during the unplanned turnaround. Because the compressor had been cleaned during the planned turnaround 18 months previously, the plant expected little fouling and, therefore, did not inspect or clean it. Conventional dispersants had been used to wash off the polymers formed in the second and third compressor stages in an attempt to eliminate polymer deposits in CGC casings and discharge lines.

Evaluation and recommendations. Foulant samples were collected and sent to a third-party specialty chemical research division to identify the fouling precursors and mechanisms. Based on that analysis, the specialty chemical company recommended a multifunctional antifoulant to control fouling where the problem was most serious, in compressor stages 2 and 3. Dosing hardware and portable feed tanks were rushed to the site. Due to the rapid pressure drop increase, it was recommended to install assessment tools to facilitate polymer sample collection (**Fig. 4**) and analysis so that treatment could be optimized and fine-tuned as conditions changed.[2] Fouling declined and plant performance improved dramatically.

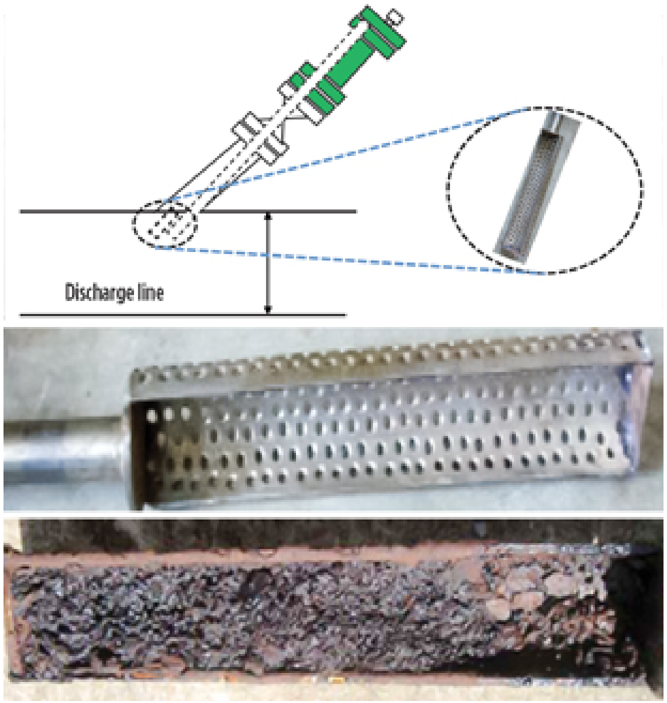

Fig. 4. Proprietary online fouling monitoring system with retractable filter and example of retractable filter with deposit sample.[2]

Sample analysis. Data summarized in **Table 1** indicate that although some polymerization continued to take place, the severity of polymerization decreased with treatment, as indicated by polymer molecular weight and degree of cross-linking. Further analysis showed that the deposit consists mostly of non-cross-linked polymers. Treatment was successful in controlling polymerization.

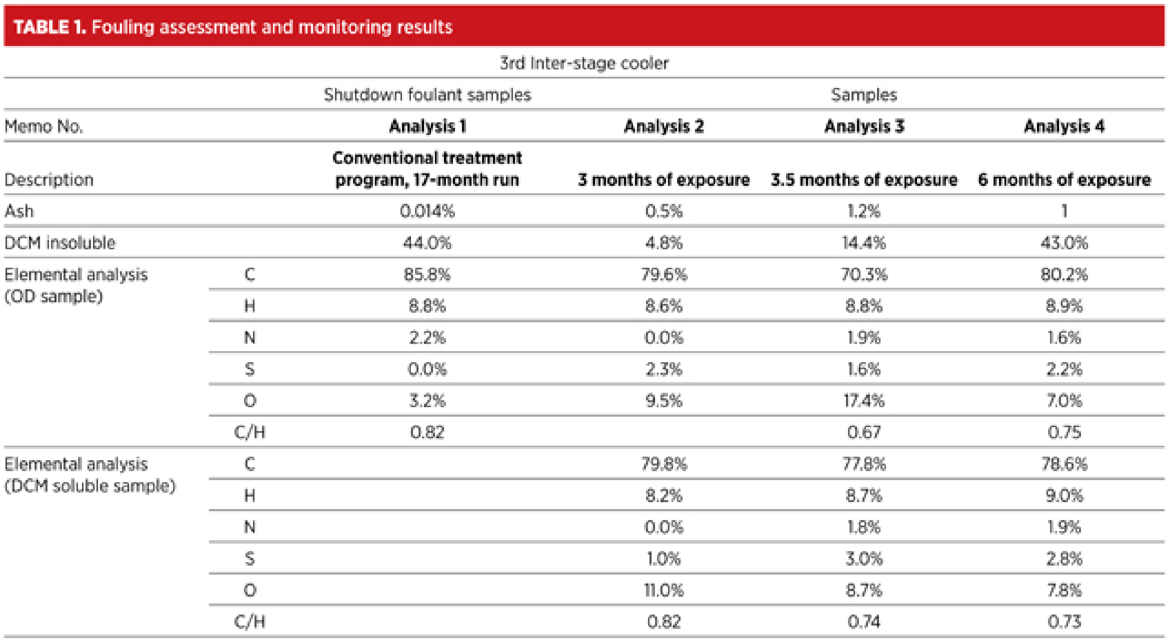

TABLE 1. Fouling assessment and monitoring results

		3rd Inter-stage cooler			
		Shutdown foulant samples	Samples		
Memo No.		**Analysis 1**	**Analysis 2**	**Analysis 3**	**Analysis 4**
Description		**Conventional treatment program, 17-month run**	**3 months of exposure**	**3.5 months of exposure**	**6 months of exposure**
Ash		0.014%	0.5%	1.2%	1
DCM insoluble		44.0%	4.8%	14.4%	43.0%
Elemental analysis (OD sample)	C	85.8%	79.6%	70.3%	80.2%
	H	8.8%	8.6%	8.8%	8.9%
	N	2.2%	0.0%	1.9%	1.6%
	S	0.0%	2.3%	1.6%	2.2%
	O	3.2%	9.5%	17.4%	7.0%
	C/H	0.82		0.67	0.75
Elemental analysis (DCM soluble sample)	C		79.8%	77.8%	78.6%
	H		8.2%	8.7%	9.0%
	N		0.0%	1.8%	1.9%
	S		1.0%	3.0%	2.8%
	O		11.0%	8.7%	7.8%
	C/H		0.82	0.74	0.73

Foulant samples were initially collected quarterly.[2] When the pressure drop across the second-stage intercooler stabilized, the sampling interval was lengthened to six months (**Fig. 5**). Pressure drop remained stable and sample collection was discontinued when analysis 4 indicated that the fouling was under control.

In this case, a monitoring program and additives improved fouling control and increased plant run-length while achieving substantial energy savings.

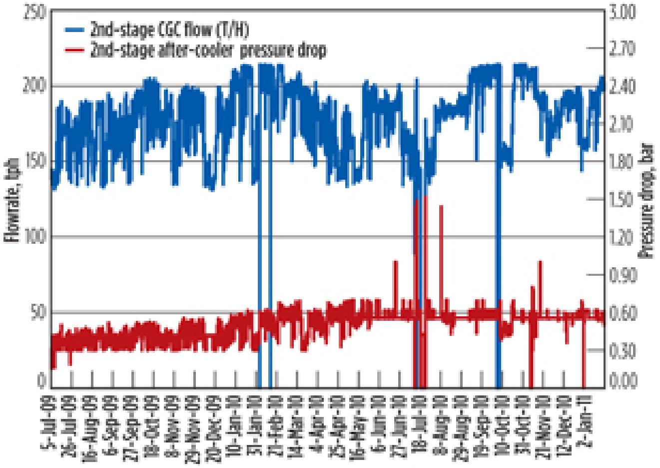

Fig. 5. Second-stage after-cooler pressure drop trends.

Case 2: Treatment interruption increases fouling

A 400 Mtpy-ethylene plant, using a mixture of ethane and propane feedstock, experienced fouling problems in the CGC unit. Evidence of severe fouling was found when the system was disassembled during a shutdown in September 2010, and a third-party specialty chemical company was approached for recommendations. A site survey revealed several problems:

- Decreasing plant throughput
- Increasing energy consumption (specific steam volume)
- High axial displacement in the MP-stage compressor
- Increasing CGC discharge temperatures in all stages
- Increasing wash-oil consumption.

Successful antifoulant trial. Following a turnaround in 2010, the plant approved a six-month antifoulant trial program, and treatment was initiated in January 2011. Several CGC parameters were monitored daily:

- Axial displacement
- Specific steam consumption
- Compressor discharge temperatures
- Polytrophic efficiency.

The treatment program successfully controlled axial displacement and vibration in all three monitored compressor stages. The data indicated steady-state performance within compressor design parameters. Steam consumption per ton of ethylene stabilized below pretreatment consumption levels. Discharge temperatures remained below operating targets and polytrophic efficiency increased during the trial (**Fig. 6**).

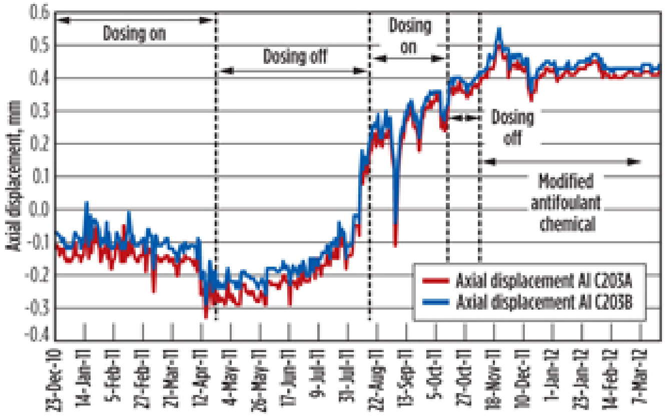

Fig. 6. MP compressor axial displacement trends.

When the trial was complete, plant management decided to halt the dosage and to monitor performance without treatment for comparison purposes. The situation remained relatively stable for three months. Later, indications of fouling reappeared in July, and the situation degraded rapidly and became more difficult to control.

The axial displacement increased, steam consumption began to climb and the polytrophic efficiency declined markedly. As discharge temperatures increased, polymer deposits accumulated at rising rates on compressor internals, causing potentially damaging vibration and a rapid increase in axial displacement that soon exceeded the design limit for the MP compressor stage.

Compressor loading reduced to prevent shutdown. The treatment resumed at the plant's request in August 2011. However, the axial displacement was so severe that vibrations were almost impossible to control, and the polytrophic efficiency continued to decline. Management decided to halt the antifoulant dosing again and reduce compressor loading by 20% to 30% to prevent the compressor from going offline and shutting the plant down completely.

The reduced compressor loading forced the plant to operate below normal capacity, thus lowering gross revenues as steam and wash-oil consumption increased operating costs. Unfortunately, the next planned shutdown was many months away.

Capacity increased with modified treatment. To improve operating economics and keep the plant running until the next planned shutdown, third-party specialty chemical technicians reformulated the antifoulant with enhanced surface modifiers and dispersants to increase antifoulant activity in the compressor after-coolers and disperse the organics and corrosion byproducts (**Fig. 7**). When the modified program was implemented in November 2011, the axial displacement declined and then stabilized slightly above design targets.

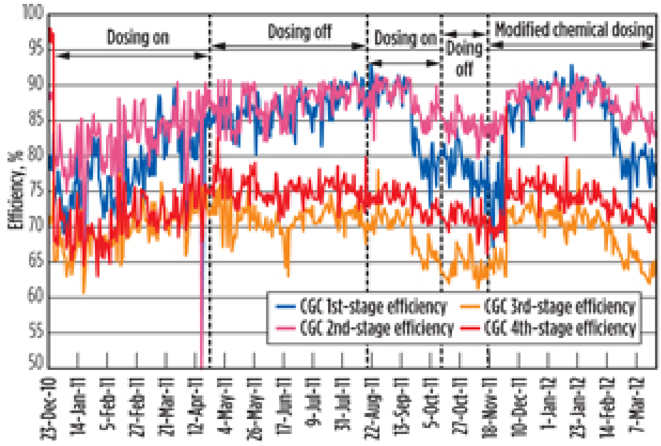

Fig. 7. Plant-monitored polytrophic efficiency trends.

Although the situation was still far from ideal, the stabilized system allowed the plant to increase throughput approximately 10%, increasing revenues and avoiding an extremely costly unplanned shutdown. The resulting efficiency improvement reduced operating costs for steam and wash oil, further improving plant profitability. The modified treatment was resumed after the planned turnaround in April 2012, with excellent results. Wash-oil consumption was reduced by 30%, axial displacement stabilized within design limits, and specific steam consumption declined substantially.

Results. The modified treatment allowed a 10% increase in load over the five-month period preceding the planned shutdown scheduled for March 2012. It also increased ethylene production by 4%. At an average market price of $1,400/metric ton, the 15 additional tons of ethylene added $21,000 to the plant's bottom line.[3]

Average steam consumption declined, thus reducing energy costs. The plant required approximately 1 ton of steam to generate 140 kW of energy at a cost of $50/ton (**Fig. 8**). The additional steam required when treatment was discontinued between April and August cost the plant nearly $33,000. Restarting the treatment program offset virtually all of that additional expense by generating more power with less steam, saving the plant approximately $31,000.

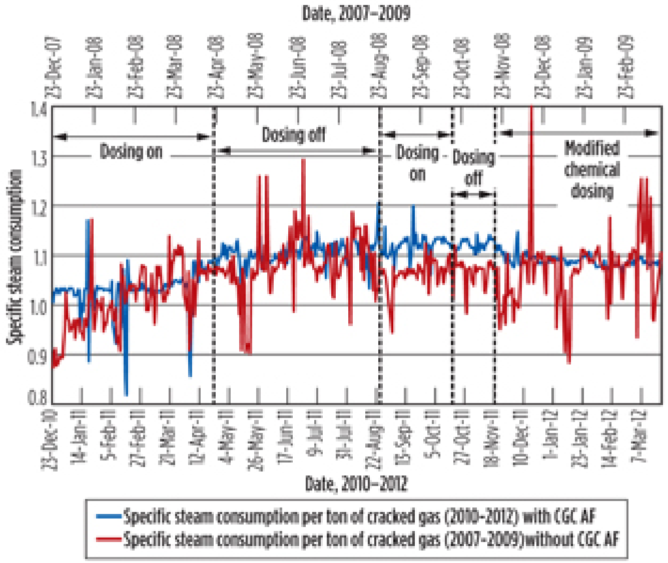

Fig. 8. Specific steam consumption patterns.

The plant purchased approximately 25 tons of wash oil annually at a cost of around $2/kg. The wash-oil savings under the modified treatment program are estimated at approximately 20%, a savings of $10,000 on an annualized basis.

Performance observation

Even the very best antifoulants are preventive tools. Fouling is a continuous process. Once fouling accumulates, it is extremely difficult to stabilize, let alone to remove by chemical treatment. In this case, the decision to halt the first treatment regimen allowed fouling to resume and worsen. Although the second treatment regimen helped to stabilize the partially fouled system, accumulations occasionally broke free, causing compressor imbalances and increasing axial shifts. The on-again, off-again treatment is risky. When fouling symptoms are observed, the treatment with an effective antifoulant should be initiated as quickly as possible and maintained consistently.

Case 3: Mixed-feedstock cracker compressor fouling

Within six months after a specialty chemical company began compressor antifoulant treatment in 2008, the olefin plant changed its feedstock from 100% naphtha to 60% naphtha and 40% LPG. The treatment allowed the plant to meet a 2012 turnaround schedule established before the subsequent feedstock changes. The operating issues were compressor fouling, decreased polytrophic efficiency and throughput limitations due to increasing suction pressure. Following the treatment program, plant reliability improved. More stable operations were possible with less fouling. The olefin plant could increase throughput capacity and conserve steam consumption. More importantly, the plant was able to meet the targeted five-year run length with clean compressors. CGC efficiency inevitably declines over time as the system wears and deposits accumulate. Controlling fouling deposits is essential, given the critical role played by CGCs and their impact on plant revenues and operating costs. **HP**

Notes

[1] Compressor Advanced Simulation Software (COMPASS)

[2] Fouling Assessment Tool (FAT)

[3] Average market price according to ICIS

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