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Mitigate coke formation

A new anticoke technology sustains a noncatalytic layer on cracking tubes that reduces coking

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For ethylene cracking furnaces, coking deposits severely reduce yields and shorten the run length. Coking is a side reaction from thermal cracking; its formation ultimately increases energy consumption since tube fouling decreases unit heat transfer. Other side reactions such as carbon monoxide (CO) formation must also be controlled to maintain process efficiency for downstream sections.

Coke is formed through a complex mechanism that involves mainly catalytic surface reactions and radical reactions. This has a negative impact on product yield, energy consumption and run length. Ethylene producers are always seeking methods to retard coke formation and extend times between decoking cycles. Several methods to mitigate coke formation are available; they involve expensive offsite metallurgical modification or chemical dosing that could negatively impact downstream equipment.

A pretreatment method involves an onsite pretreatment with a chemical composition that is applied online after a decoke operation. This pretreatment forms a noncatalytic coating on the internal surface of the cracking tube. The following case histories present results from lab and pilot studies that show the impact of this pretreatment on coke and CO formation while steam cracking different feedstocks. Industrial testing results demonstrate the effectiveness of new pretreatment on mitigating coke formation for ethane furnaces. The best control of coke and CO results from the combination of pretreatment applied after a decoke followed by a continuous dosing of dimethyldisulfide (DMDS).

Coking process. In the steam-cracker ethylene production, a major ongoing challenge is reducing coke deposition in the radiant section and transfer line exchanger (TLE). Coke formation is linked to complex mechanisms involving catalytic, radical and condensation reactions. General mechanisms describing coke formation are given in the literature:¹⁻⁵

Catalytic mechanism. This mechanism involves metallic species on the internal surface of the cracking coil—iron (Fe), nickel (Ni) and chromium (Cr)—having potential catalytic activity. Filamentous coke is formed with metallic agglomerates at the propagating tips.

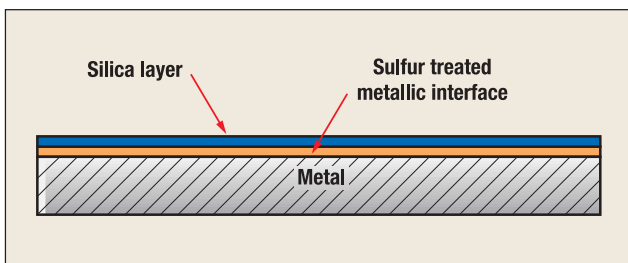


Fig. 1. Schematic representation of the pretreated treated surface.

Free-radical mechanism. This mechanism involves reactions of micro species, mainly gaseous free radicals, with the macro radicals present at the coke surface.

Condensation mechanism. This noncatalytic mechanism occurs at the metallic surface or the coke surface. Heavy polynuclear compounds present in tar and soot condense at the interface, particularly in the quench section where they dehydrogenate and contribute to the coke deposition.

Mechanical entrainment of coke. During the run, some coke formed in the radiant section can be detached. It is entrained to the quench section (also referred to as coke spalling) where it accumulates.

In the furnace, the coke deposits on the wall of the coil and prevents efficient heat transfer from the furnace to the reacting gas. To compensate for this, the external tube skin temperature is increased carefully, without exceeding the metallurgical limits. Additionally, the coil diameter is reduced by increasing deposition of the coke and raising the pressure drop across the coil. Consequently, the furnace inlet pressure must be raised. Both effects are detrimental when optimizing ethylene yield.

TLE tube fouling raises the process gas outlet tempera-

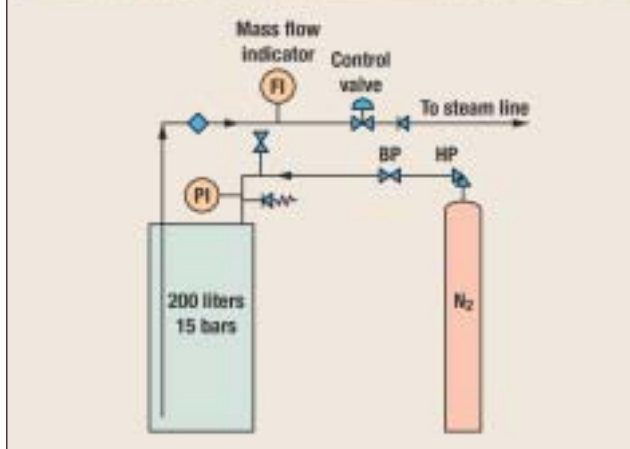


Fig. 2. Injection skid.

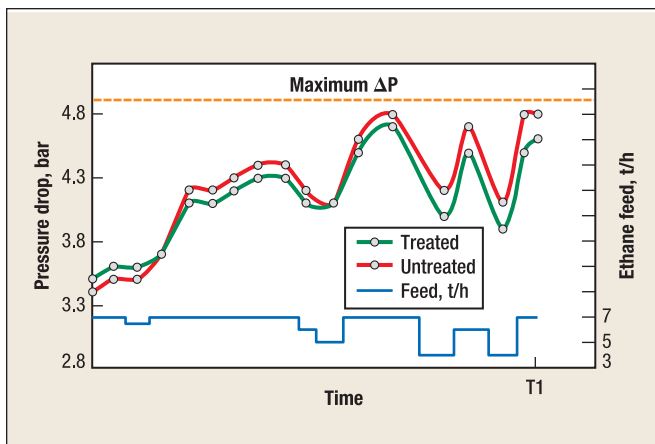


Fig. 3. Pressure drop increase and throughput vs. time for the Test No. 1 at Lacq plant (Elf Aquitaine Exploration Production France), furnace B.

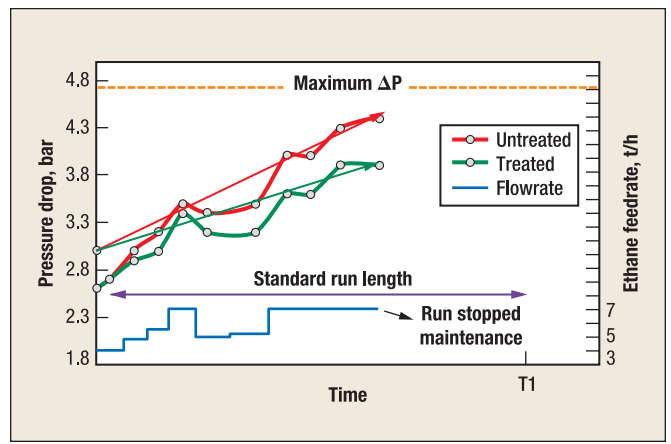


Fig. 4. Pressure drop increase and throughput vs. time for the Test No. 2 at Lacq plant (Elf Aquitaine Exploration Production France), furnace B.

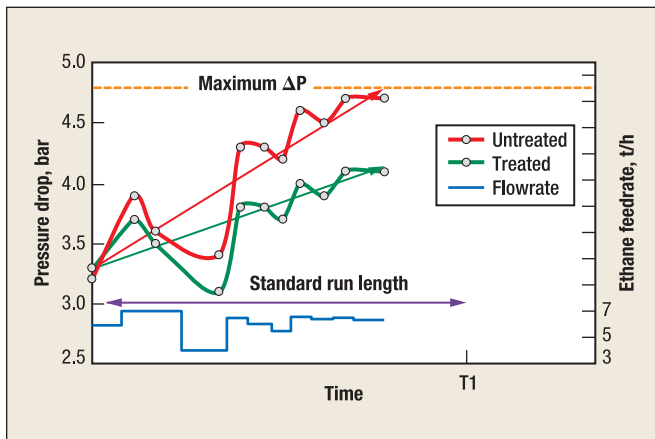


Fig. 5. Pressure drop increase and throughput vs. time for the Test No. 3 at Lacq plant (Elf Aquitaine Exploration Production France), furnace B.

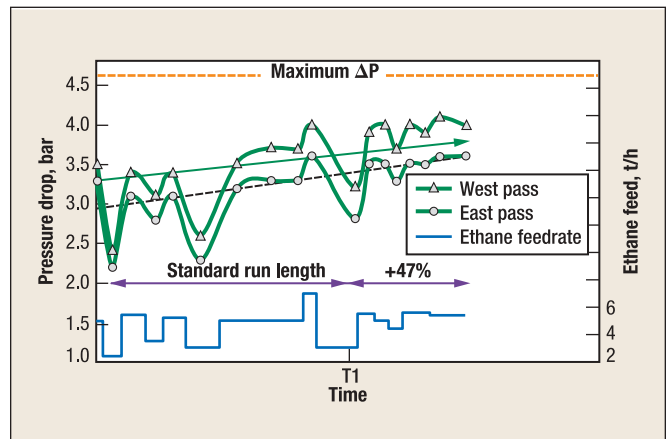


Fig. 6. Pressure drop increase and throughput vs. time for the Test No. 4 at Lacq plant (Elf Aquitaine Exploration Production France), furnace C.

ture since heat transfer is lowered. Consequently, as the TLE outlet temperature rises, less heat is recovered for steam regeneration. Further, the coke deposition increases the pressure drop. Due to all of these reasons, the formed coke must be periodically removed, by a controlled combustion with a steam-air mixture. This action requires periodically interrupting ethylene production. During the radiant coil decoking operation, some coke present in the TLE is also removed. However, after several coil decoke cycles, coke in the TLE must be removed independently by mechanical cleaning. Decoking a cracking furnace on a frequent basis does present several consequences:

- ▶ Loss of production
- ▶ Increased maintenance costs
- ▶ Reduced radiant coil tube life.

Coke reduction methods. For inhibitor dosing applications, the most commonly used chemicals are sulfur based, such as dimethylsulfide (DMS) and dimethyldisulfide (DMDS). By continuous dosing of these compounds, CO formation is drastically reduced and run length is improved. They can also have a beneficial impact on the tube carburization. Among a large family of other chemical additives, phosphorus- and tin-based compounds have been described in the literature.⁶⁻¹⁰

A major challenge in ethylene production is reducing coke deposition in the radiant section and TLEs.

Coating of tube material. Various coating materials have been recently developed.¹¹⁻¹³ These coatings are applied on the radiant coil material before installation in the steam-cracking furnace.

New metallurgy. Steel producers are developing a new metallurgy able to minimize coke formation.¹⁴

Special coil surface shaping. A spiral mixing element on the inside surface of the cracking coil has been proposed.¹⁵ This element is estimated to positively impact gas flow behavior and heat flux transfer.

Pretreatment process. A new additive and pretreatment procedure is estimated to significantly minimize coke formation.

The concept. After a decoke, the internal metallic surface of the radiant section is treated with a chemical containing sulfur (S) and silicon (Si). A noncatalytic surface is created online. Fig. 1 shows a schematic representation of the treated surface.

This additive is a clear homogenous chemical organic liquid containing a certain amount of Si and S, the remainder is carbon, hydrogen and oxygen. The boiling range of this additive is below 120°C.

General conditions for the industrial pretreatment. The

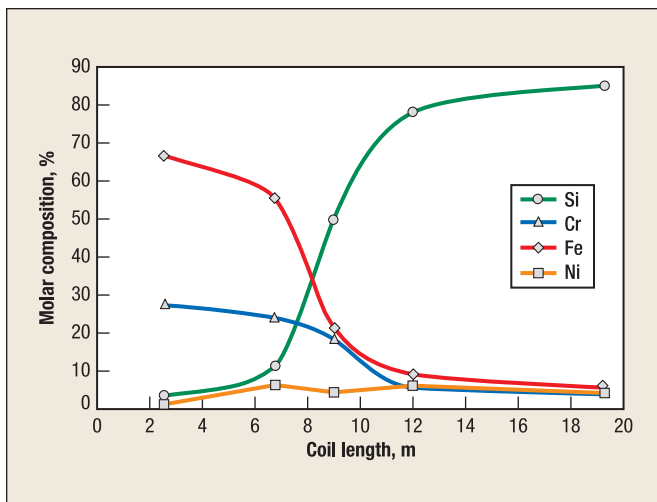


Fig. 7. Composition of the internal coil surface, furnace 2F1 J, ATOFINA Gonfreville plant, France.

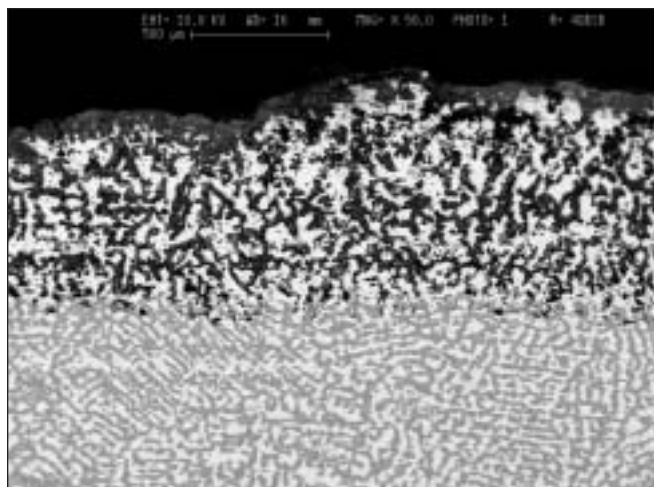


Fig. 8. Photograph of coil cuts from sample close to the outlet, furnace 2F1 J, ATOFINA Gonfreville plant, France (mag. x 50).

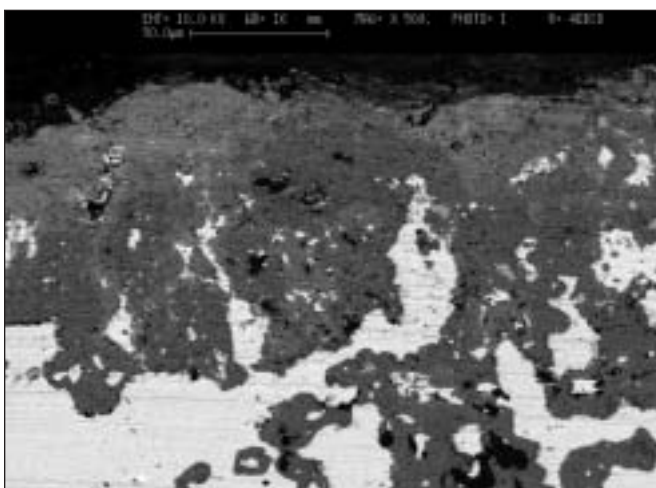


Fig. 9. Photograph of coil cuts from sample close to the outlet, furnace 2F1 J, Gonfreville plant (ATOFINA), France (mag. x 500).

pretreatment is done onsite after the decoke procedure, when the furnace is under steam flow. The additive is injected in the steam line, at the entry of the convection section, at a steam temperature above 150°C. The coil outlet temperature (COT) is in the range of 850–900°C. The average pretreatment duration is four hours. The pretreatment quantity is related to the cracking coil internal surface and adjusted gets an optimal effect.

Injection device. A typical injection skid is presented in Fig. 2. The pretreatment compound is pushed under nitrogen from a pressurized vessel equipped with a flow indicator and a control valve into the furnace steam line. This equipment is designed to perform multiple injections if necessary.

Pilot results. The impact of the pretreatment has been tested on several continuous pilot tests with different feedstocks. For propane, the coke reduction was 27%, 35% for ethane and 65% for naphtha. These results have been previously published.¹⁶ The pilot tests with propane have also shown that the pretreatment can reduce CO formation. However, the lowest level of CO was observed when DMDS was used.¹⁶

Industrial tests. A series of industrial tests were performed at Elf Aquitaine Exploration Production France's Lacq plant. The average ethane feed was 7 tph for a COT of 825°C. The conversion was in the range of 55% and the standard run length was T1 in arbitrary units, and limited by pressure.

Table 1. Pretreatment conditions for Lacq plant, furnace B

Pretreatment quantity	Pretreatment COT, °C	Pretreatment method	Anti-coke effect observed
Test 1 A	850	½ furnace	Pressure drop increase reduced by 21%
Test 2 B	850	½ furnace	Pressure drop increase reduced by 42%
Test 3 B	850	½ furnace	Pressure drop increase reduced by 50%

Table 2. Economic simulations, incremental ethylene production by pretreatment

Conditions	Runlength, day	Ethylene production, t/d	Incremental ethylene production, t/d
Case 1 Base case	43	295	–
Case 2 Pretreatment + base case	72	300	5
Case 3 Pretreatment +10% throughput	53	324	29
Case 4 Pretreatment increased conversion, throughput base case	61	307	12

The radiant section coil made of HK40 alloy, was divided into two passes, each of them being 158 m in length and an internal diameter of 11.9 cm.

Three industrial tests were performed. After decoking, one-half of the furnace (one pass) was pretreated with the coke-mitigating compound. The other half of the furnace remained untreated. By using this methodology, the fouling of the pretreated pass could be compared to the fouling of the untreated pass in similar conditions (temperature, throughput, feed quality).

Table 1 describes the process-test conditions in detail, for these three industrial tests and some results. Figs. 3–5 represent the pressure drop increase and the throughput vs. time for these three tests.

Since there are throughput fluctuations, the pressure drop reduction was estimated at a constant flowrate. In the figures, the pressure drop estimation is represented by an arrow for each pass, from start-of-run (SOR) to end-of-run (EOR). Test one was conducted with a relatively low quantity of pretreatment addi-

tion. In this test run, the pressure drop was reduced (21% reduction) as compared to the untreated pass.

In Test No. 2, the same procedure was followed as in Test No. 1, except a higher quantity of pretreatment compound was applied on the same pass. Results from Test No. 2 indicated a pressure drop reduction of 42%. This test was stopped due to a scheduled five-year turnaround. For Test No. 3, the pretreatment was similar to Test No. 2, and the pressure drop reduction for the pretreated pass was even better—50%.

Second industrial test. Another industrial demonstration was performed at Lacq, on a second furnace identical to the one previously mentioned. In this case, the pretreatment after a decoke was applied to the complete furnace (two passes) and the injected quantity was identical to Tests No. 2 and No. 3.

Fig. 6 represents the pressure drop increase and the throughput vs. time for these tests.

The pressure drop for both passes increased at a slower rate compared to a run without the pretreatment. During this test, the run length was clearly extended. The pressure limit is reached on a standard run at T1 (run length in arbitrary units). For this Test No. 4, at T1, the pressure drop was far below the limit (in the range of 80% below the limit). This clearly indicates that a significant increase in run length is possible using a pretreatment. The above industrial tests demonstrate the coke-minimization properties of the new pretreatment.

Coating formation and characterization on a furnace. The pretreatment was performed at ATOFINA's Gonfreville naphtha cracker. The average naphtha feed was 14 tph. The radiant section coil was made of Manaurite 36XM long. The furnace contains 48 U-shaped cracking coils (48 passes), each of them having a length of 18.6 m, with an exit internal diameter of 45 mm.

The complete furnace was treated under optimal conditions, similar to the quantities used for Tests Nos. 2–4 at the Lacq plant. At the end of the pretreatment, the furnace was cooled for tubing replacement. Several passes were segmented to analyze the coating. Surface analysis was done by electron microscopy techniques, X-ray, scanning electron microscopy and electron retrodiffusion microscopy. Internal coil surface and cuts were analyzed.

X-microanalysis showed Si, Fe, Ni and Cr as a function of coil length (Fig.

7). The Si increases after one-third of the coil length, reaching a constant high-silicon level from the middle to the end of the tube.

Photographs of tube cuts from the coil sample close to the outlet were taken by electron retrodiffusion microscopy (Figs. 8 and 9). The coating thickness measured in the second half of the coil was in the range of 50–100 μm . For the tube exposed to severe conditions (the outlet section), the coating also filled the pores resulting from aging (carburized layer transformed in oxides by decoke operation), below the coating layer.

These results show that the coating layer is formed preferably at the hottest section of the coil, where a high coking rate is usually observed in a classical untreated tube. Consequently, a noncatalytic layer formed online at the metallic surface.

Control of pretreatment effluents. Under the pretreatment conditions, the additive is thermally decomposed, interacting with the metallic surface to form this coating. Effluents such as hydrogen sulfide (H_2S) and silica can exit the hot section. Two types of outlet connections were used. One in which the coil outlet is connected to a vent and another where the coil outlet is connected to a fractionation section. For this later option, H_2S is classically neutralized by a caustic wash. Sampling was performed on several locations of the downstream section for silica analysis. The silicon balance showed that 80–90% of the silicon was fixed on the coil. The remaining silicon was trapped in silica form at the bottom of the primary fractionator, in the pyrolysis oil. Typically, 20–30 ppm of fine silica was identified. No effect was observed on the downstream section.

Economic impact from pretreatment. The pretreatment can positively impact the economics for an olefins facility by increasing throughput, severity of the operation, run length or combination of these factors. The economic benefits that can be achieved by minimizing coke deposition using the pretreatment, were simulated with the well-known software. This simulation was done on the following basis:

- Ethane furnace throughput—25 tph
- Standard SOR ethane conversion—67%
- Run length pressure limited or temperature limited
- Average decoke time—two days
- Percentage of coke deposition reduction with pretreatment.

The economics for several case studies are detailed in Table 2. Case 2 shows the impact of pretreatment on the run length for standard cracking conditions. Case 3 gives the impact of pretreatment associated with a 10% ethane throughput increase. Case 4 simulates the impact of pretreatment associated with a conversion increase. This case would be representative of a back-end limited plant.

According to the simulation, significant increase of ethylene production can be obtained, particularly for Case 3. This of course would contribute to increased margins for the production unit.

Overview. The new pretreatment with sulfur and silicon is a simple procedure directly done onsite and has been tested on ethane furnaces. The recommended procedure for optimized ethane steam-cracking units involves treating the cracking tubes after they have been decoked followed by continuous DMDS injection from the start of ethylene production. Coke reduction observed on industrial tests using the pretreatment has great potential to positively impact economics of ethylene production. ■

NOMENCLATURE

Cr	Chromium
Fe	Iron
Ni	Nickel
Si	Silicon
S	Sulfur

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Harry Woerde is currently working as senior process engineer in the Ethylene Technology group of Technip Benelux B.V., Zoetermeer, The Netherlands. He joined Kinetics Technology International (KT) in 1983, which was acquired by TECHNIP in 1999, where he has held various positions. Mr. Woerde has been actively involved in the development of the CLX technology. He holds a master's degree in chemical engineering from Delft University and a master's degree in catalysis from Leiden University. He can be reached at e-mail: hwoerde@technip-coflexip.com.

Simon Barendregt is the Vice President of Ethylene with Technip Benelux and is responsible for the ethylene business and technology development. Mr. Barendregt has been responsible for the SPYRO development and commercialization since 1978.



He holds an MSc degree in chemical engineering at the Technical University of Delft. He joined Technip Zoetermeer (formerly KTI The Netherlands) in 1973 and has been active in ethylene plant, furnace, syngas design and engineering, product development and in senior management positions. Before joining KTI, Mr. Barendregt was previously employed with Gulf Oil, Rotterdam, and was involved in the ethylene and styrene unit operations.



Francis Humblot is currently working on the CLX project, a new technology developed by ATOFINA and Technip to reduce coke formation in steamcracker furnaces. Born in 1968, he received his PhD from the University of Lyon in 1995, where he concentrated on

the preparation of supported platinum-tin catalysts used for light alkane dehydrogenation, working in conjunction with Institut Français du Pétrole (IFP). Dr. Humblot did postdoctoral work with Rhodia on the synthesis of asymmetric phosphorous ligands and joined ATOFINA in 1997 where he specializes in the sulfur chemical field. Dr. Humblot is currently in charge of new applications of sulfur compounds in refining and petrochemistry.

Claude Brun is the ATOFINA Technical Manager and R&D coordinator for organosulfur compounds, dedicated to the energy market. He earned his doctorate at the University of Strasbourg. He joined the Elf group in 1974 and held several positions in research. Dr. Brun was responsible for projects on high-pressure polyethylene and on Ziegler Natta catalysts for propylene and ethylene polymerization. Before joining the Elf group, he worked on scientific database for Hoffman La Roche Basel.



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