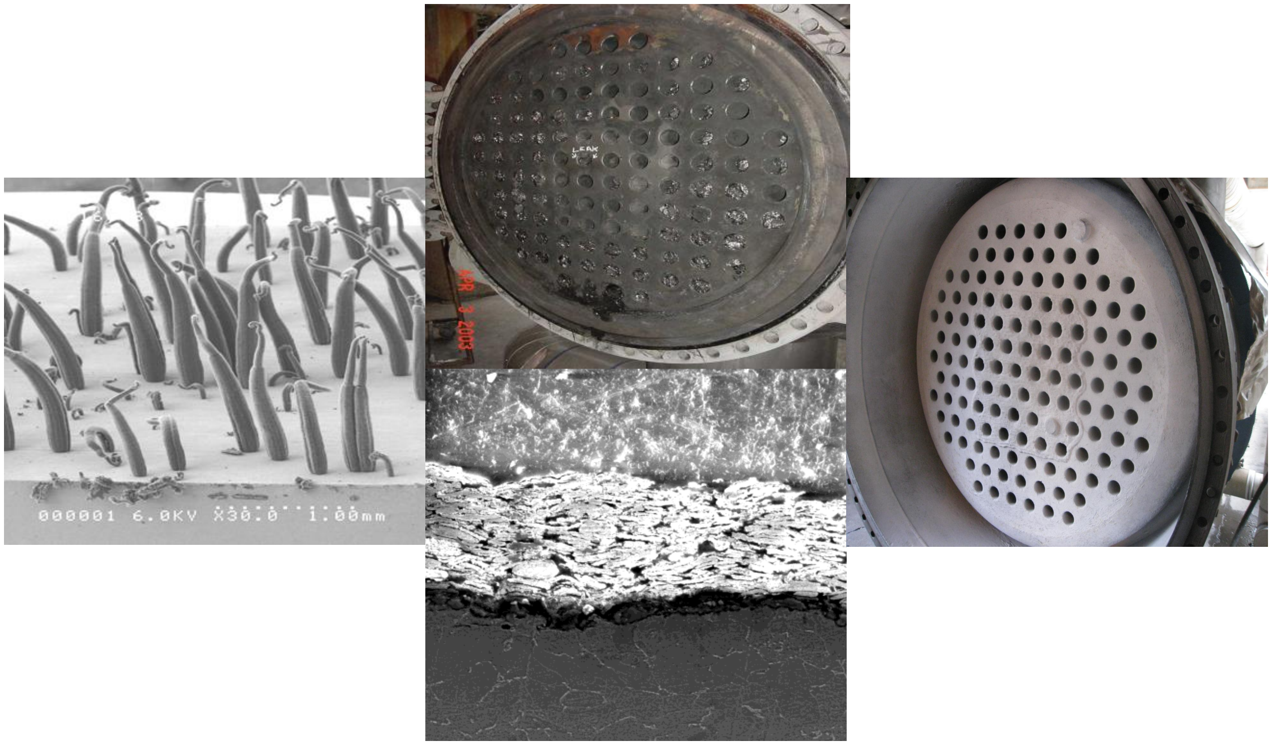
KnightHawk Industries EZ De-COKE



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Typical Operation of TLE

- Coke formation and collection in the TLE typically results in poorer heat transfer, which in turn results in decreased production of high-pressure steam, slower heat removal from the process gasses & a larger pressure drop across the TLE.
- The typical operating cycle for TLEs is to operate a period of time cooling the product stream from the pyrolysis furnace during which, coke forms.
- When the pressure drop becomes too high, the TLE will be hot cleaned (on line de-coking cycle) using steam & air injected into the inlet cone to remove coke.
- This is only partially effective & after two to four cycles of operation and on line de-coke, the TLE inlet cone must be opened so coke can be removed through more aggressive methods (usually mechanical).
- This Mechanical De-Coke process usually damages the inlet cone refractory and TLE tubesheet.
- Damage must be repaired or replaced at significant cost.

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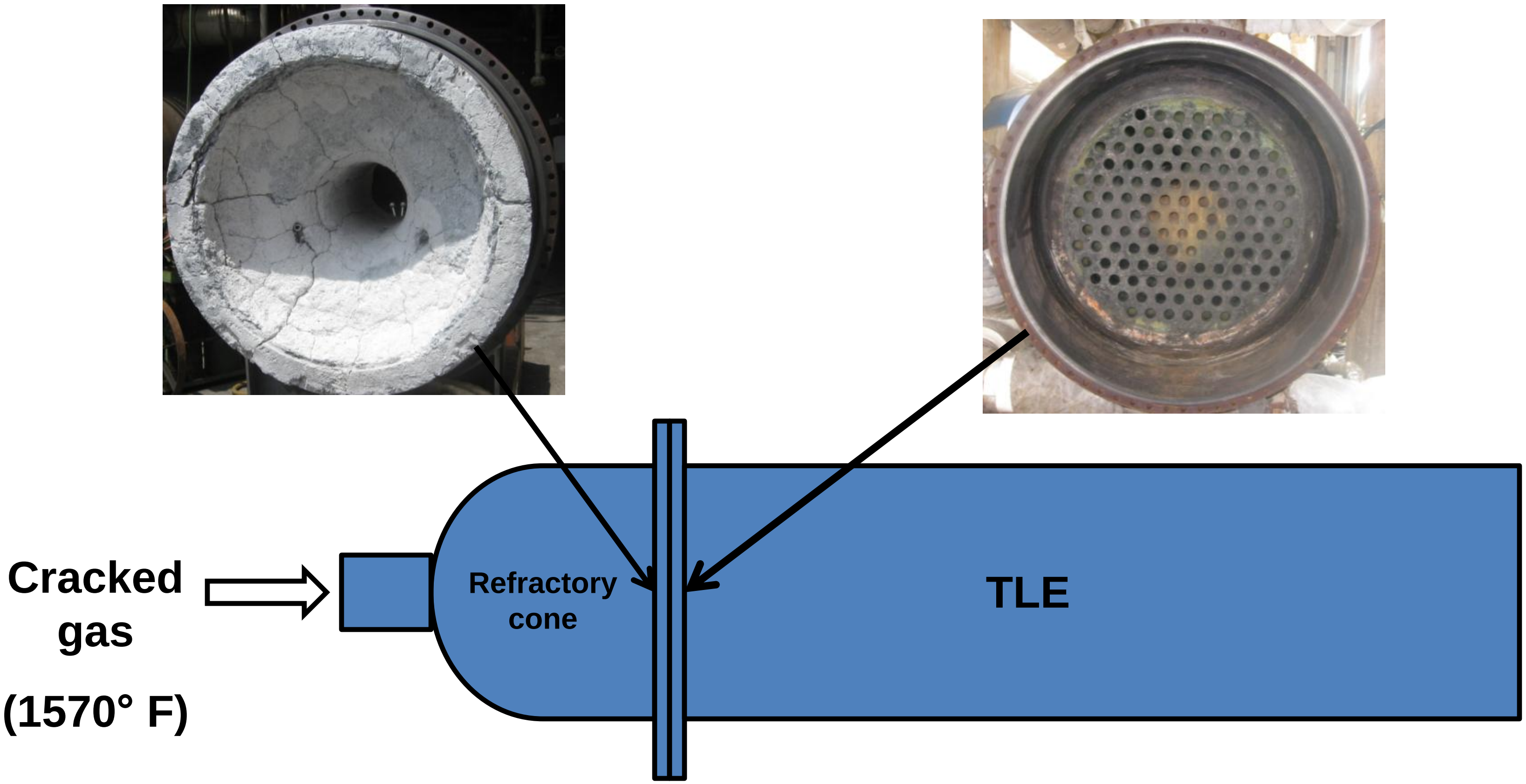
Pyrolysis of Ethane/Propane to Produce Ethylene



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Coke Formation in Ethylene Plants

- Coke is classified into two types: Catalytic coke and Pyrolytic coke.
- Catalytic coke is formed by dehydrogenation of hydrocarbons with catalytic action of metal components on the surface.
  - Metal components, mostly Nickel and Iron, catalyze hydrocarbons to eliminate Hydrogen.
  - Coke formed this way is very hard, therefore, called hard coke and difficult to remove.
- Pyrolytic coke conveniently divided into gaseous and condensation coke, is rather soft and easier to remove than catalytic coke.
  - Gaseous coke is formed by dehydrogenation of such light olefinic hydrocarbon as acetylene.
  - Condensation coke is formed by condensation, polymerization, and dehydrogenation of heavy aromatic compounds.

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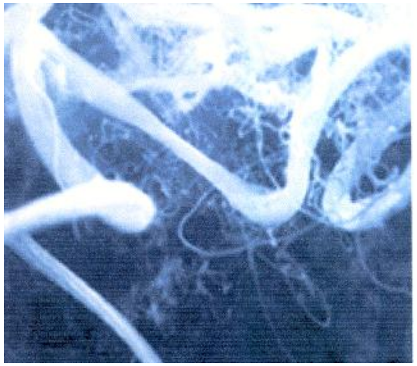
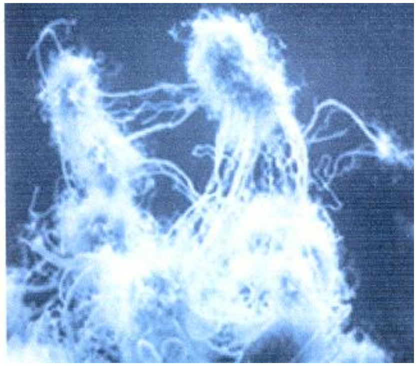
Catalytic Coke

- Catalytic coke is formed by a gas phase hydrocarbon reaction with catalytic action of surface metals at 350° - 1050°C (662° -1922°F).
- Metal components presenting catalytic activities are generally on the order of Ni>>>>Fe>>Cr, NiO>Ni, FeO>Fe>Fe_2O_3.
- These metals and oxides catalyze the reaction to form filament and coil type coke by successive dehydrogenation.





- The picture on the left shows filamentous coke by metal-hydrocarbon reaction and on the right shows coil type coke by Fe-acetylene reaction.
- Catalytic coke is important in the initial coke forming stage and may act as a trap for pyrolytic coke.

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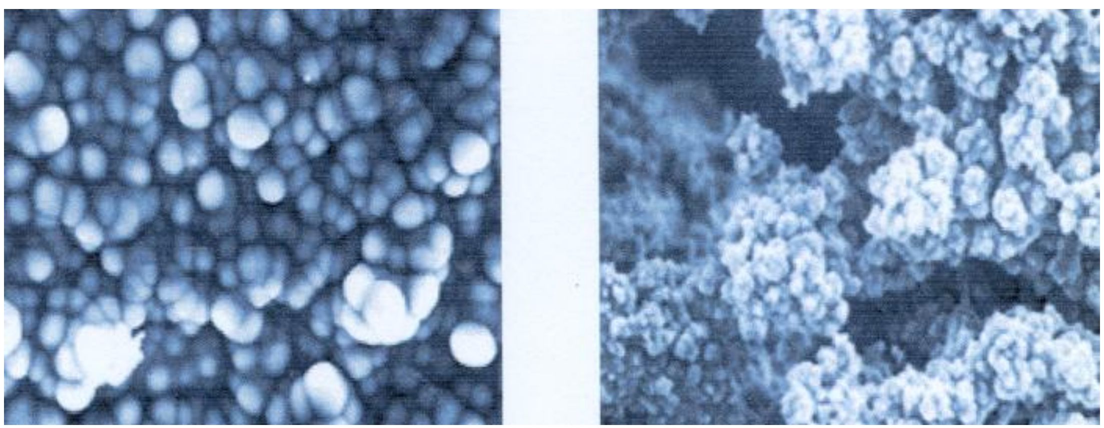
Pyrolytic Coke

- Pyrolytic coke is classified into either gaseous or condensation coke depending on which hydrocarbon is the precursor and it is difficult to predict its exact structural shape.
- It could be classified as globular, black mirror, fluffy or amorphous types according to morphology.
- The pictures below shows typical pyrolytic coke.



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Coke Precursor

- Typical coke precursors are heavy aromatic like tar droplets or micro-species whose molecular weight is less than 100 combined with lighter components such as acetylene, ethylene and butadiene etc, and free radicals such as methyl, ethyl, propyl and benzyl etc.
- These precursors affect the type of coke that forms and the rate of coke accumulation.
- Heavy aromatic droplets spread out on surfaces and form featureless coke or spherical coke.
- Micro-species, especially from acetylene types form not only filamentous coke by catalytic action but also spherical coke by aromatization and dehydrogenation.
- In addition, micro-species promote growth of filamentous coke as well as spherical coke because of low molecular weight and high diffusivity.
- Free radicals form coke and promote the coking rate by condensing in the gas phase or reacting with other coke radicals.

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Potential Mechanism of Coke Formation

Coke Formation Can Be Summarized as:

- Hydrocarbons react by catalyst action of metal components on metal surfaces and forms filamentous coke, which grows and provides deposit sites for various types of coke.
- Free radical coking causes coke filaments to thicken and, as catalytic coke filaments grow, carbon starts to block the metal surfaces.
- Tar formed by condensation collects in the filaments.
- Filaments formed by catalytic coking stop growing when metal particles become covered with carbon
- At this point radical and condensation coking become dominant.

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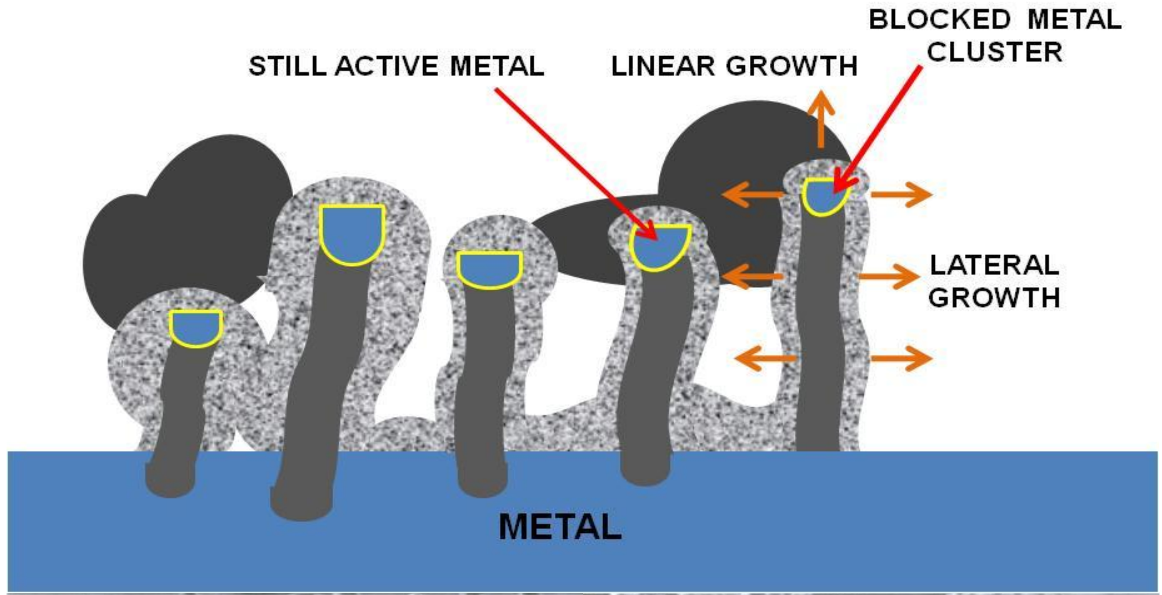
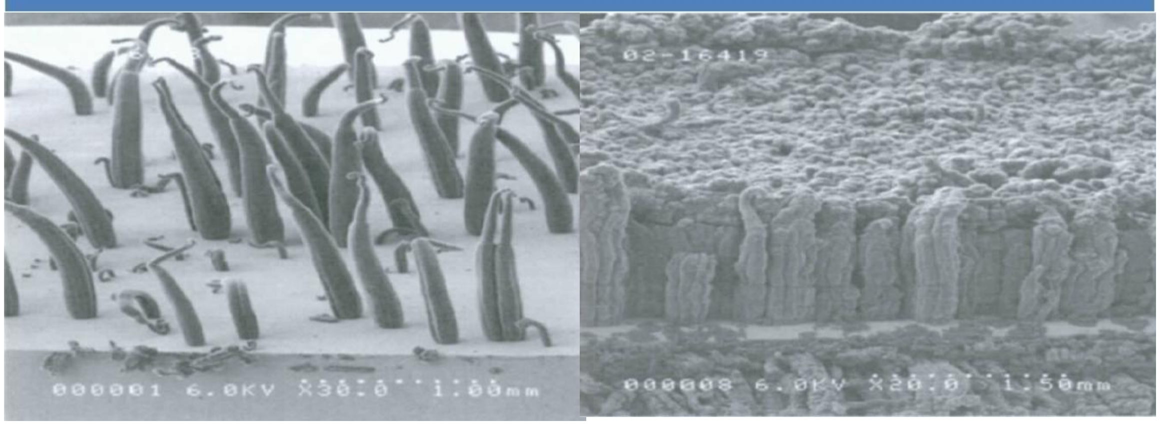
Coking Process





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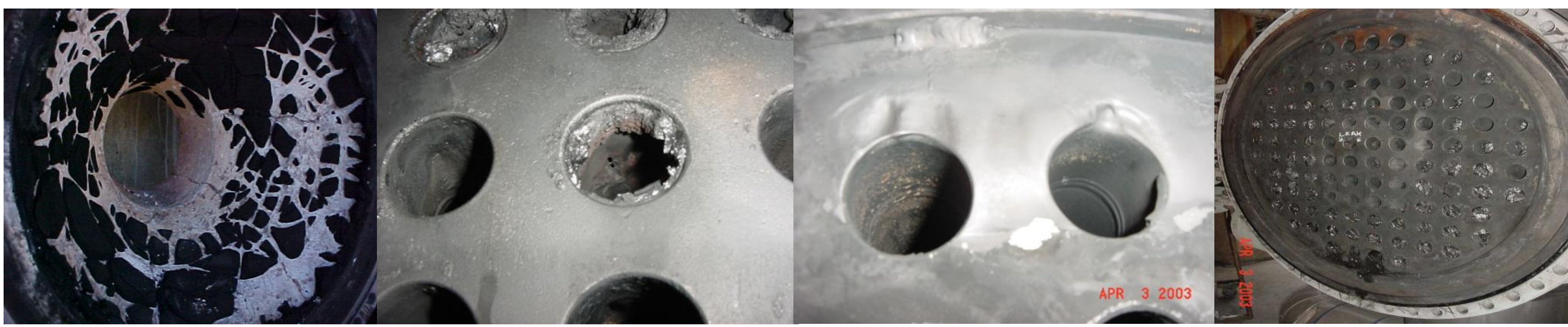
Coking in Transfer Line Exchangers

- Gas from the cracking furnace fraught with coke precursors is quenched to stop the reaction in the TLE before the main fractioner .
- Coke formation is common on the refractory of the inlet cone wall, inside the TLE tubing and on the tubesheet surface.
- This coking causes two problems, namely a larger pressure drop and spalling either of which can lead to reduced product and operational outages for decoking.



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KHI Intra-body Flow Distributor (IFD) Patented

- KHI's IFD is patented & designed according to your operating conditions, to distribute the gas flow into the TLE in a uniform turbulent configuration to help alleviate recirculation and dead zones that lead to coking, erosion, corrosion and film boiling thereby extending run times and reducing equipment damage.
- KHI's IFD is fabricated of high temperature alloy cast to survive the environment in the inlet cone.

Patent Pending

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Coke Inhibitor – Anti-Coke Surface Coating

- Significant efforts have been made over the past twenty years in developing coke inhibiting methods.
- Coke inhibitors, i.e., chemical additives, or special coatings of metal surfaces which suppress coke formation.
- Coke inhibitors/surface coating are applied to work by passivation of catalytically active metal sites through chemical bonding interactions, and/or forming a thin layer to physically isolate metal sites from coke precursors in the process stream, and/or interfering with those free radical reactions leading to coke formation by blocking active sites on surfaces
- KHI's approach is to apply a surface coating that passivates catalytically active metal sites in a form of a thin film to physically isolate metal sites, block them and potentially provide a non-stick surface to reduce coke accumulation and for easy removal

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Anti-Coke Coating - Desirable Characteristics

- Resistant to high temperature (1600°F or higher).
- Easy to apply to existing installations (retrofit ability).
- Adheres well to metal and/or refractory surfaces.
- Effective as a thin film and/or layer.
- Water based (rather than organic solvent based) material that can be readily sprayed onto surfaces at room temperature.
- Good adhesion and/or bonding to metal and/or refractory surfaces.
- **KHI's solution is EZ De-Coke Coating.** (Patent Pending)

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Physical Properties of EZ De-Coke

- EZ De-Coke coating is thermally stable to 850°C (1562°F) in an oxidizing atmosphere, even up to 1000°C (1832°F) in a reducing atmosphere with a negligible rate of reaction and can be used in a vacuum/inert atmosphere at temperatures of 2000°C (3632°F).
- High thermal conductivity.
- Low thermal expansion.
- High thermal shock resistance.

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Physical Properties of EZ De-Coke

(Continued)

- Chemically inert and high resistance to chemical attack (corrosion resistant).
- Unaffected by molten metals, slag and dross when contacted.
- Provides excellent parting plane.
- Reduces sticking in glass forming applications.

Patent Pending

Questions That Had To Be Answered

- How effectively does the lubricious and good parting property of EZ De-Coke work to provide an anti-coking surface?
- How effective would EZ De-Coke be in isolating and blocking catalytically active metal sites for coke formation?
- What is the optimum coating thickness?
- What is the optimum concentration and viscosity for application?
- How well would EZ De-Coke adhere to the surface to prevent or alleviate coke formation?

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Plant Test

- KHI worked with a major US ethylene producer to prove the effectiveness of EZ De-Coke as an anti-coking film (barrier) on existing TLE installations.
- Plant testing was an overwhelming success.
- KHI EZ De-Coke Coating is born!

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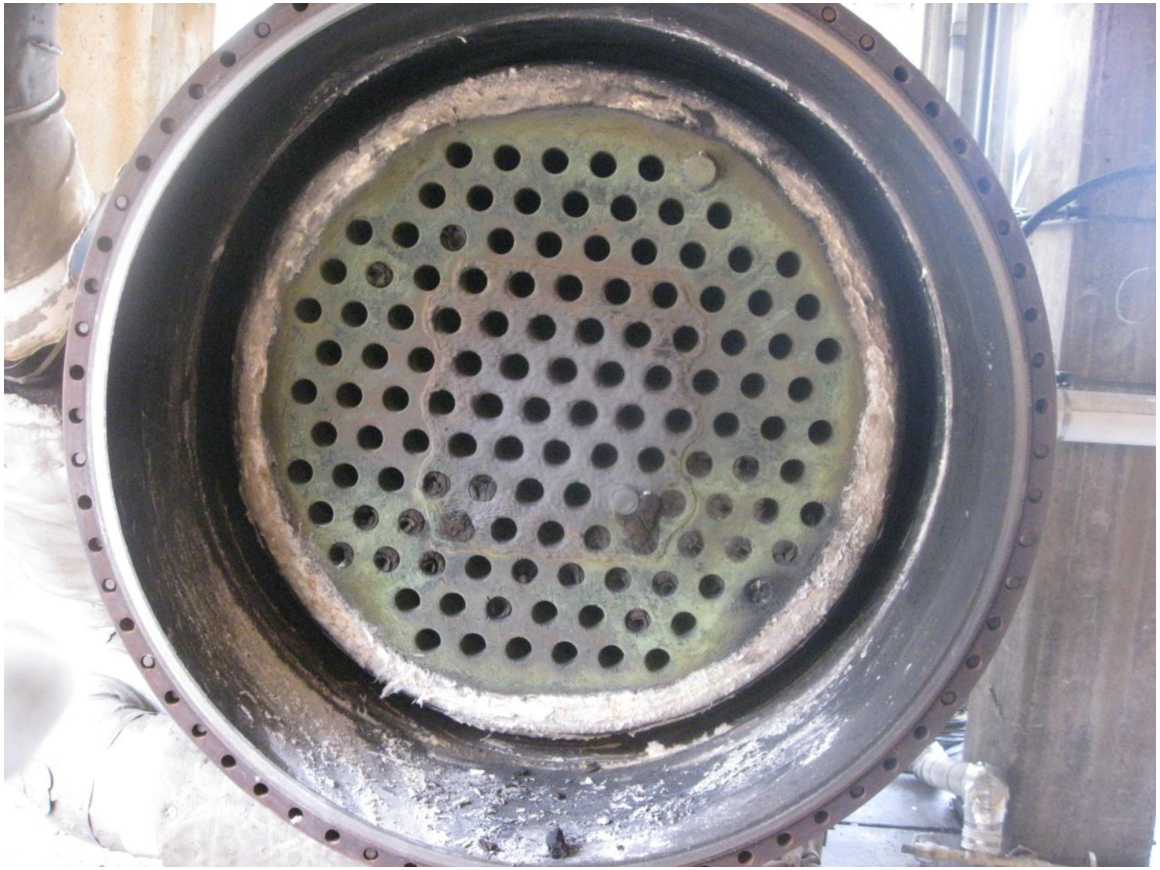
TLE Inlet Tubesheet Surface



Ran 3 cycles with EZ De-Coke, decoked on-line and opened for cleaning and re-coating

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Surface Preparation Before Recoating

Hydro-blast cleaning of TLE inlet tubesheet surface. No Chiseling.

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Tubesheet Surface Ready for Re-Coating

Hydro-blasted, dried and hand-brushed TLE inlet tubesheet surface ready for re-coating.

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Applying First Coat of EZ De-Coke

Application (spraying) of first coat of EZ De-Coke to TLE inlet tubesheet surface.

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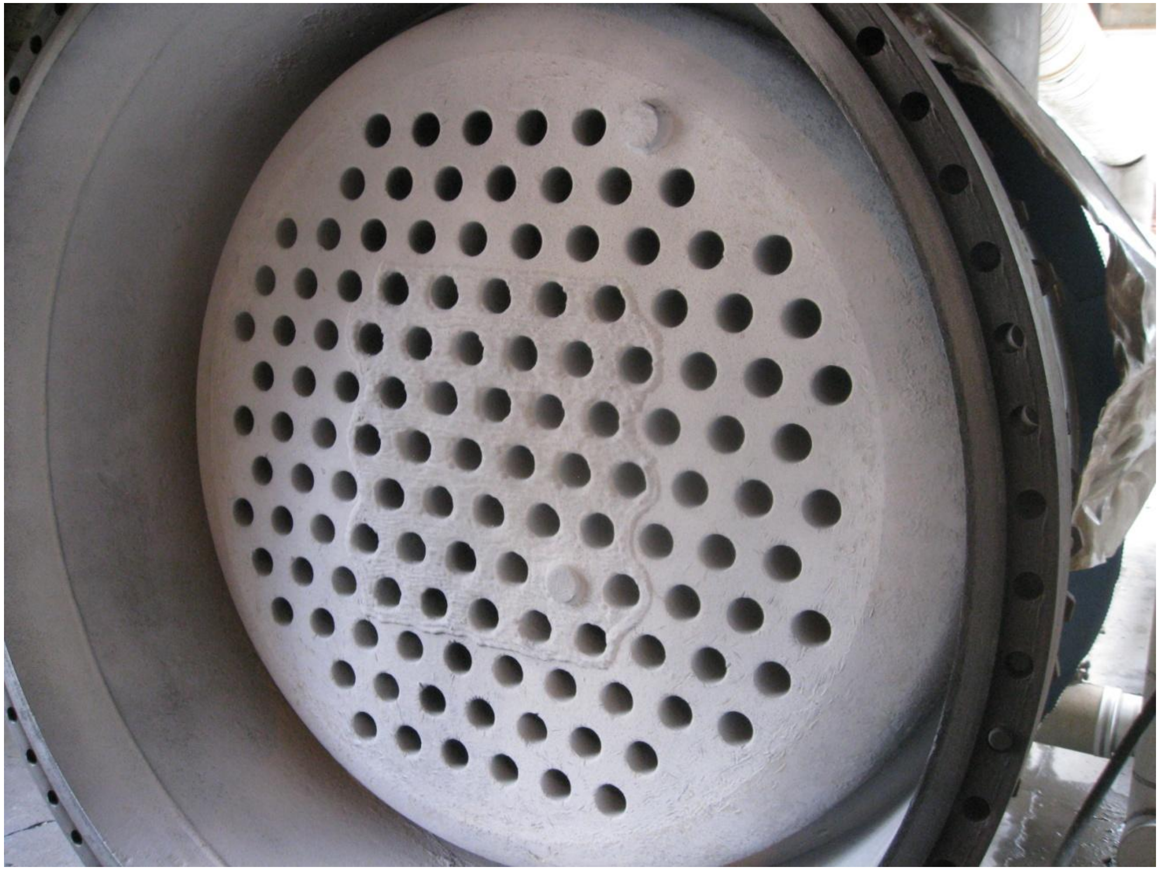
First Coat Sprayed and Dried



First coat dried at room temperature and ready for second coat.

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Test Result - Success

- EZ De-Coke provided easier & more effective on-line TLE decoking in shorter time as it isolates and blocks catalytic sites for coke formation and presents non or less coke sticking surface.
- EZ De-Coke increased the number of run cycles (run time) with on-line decoking before opening up TLE for mechanical decoking,
- Mechanical decoking was much easier with EZ De-Coke, it was completed in a shorter time and with less damage to the TLE components than previous cleaning without EZ De-Coke .
- EZ De-Coke can be applied to new as well as to existing TLE installations (retrofit) to afford the same effect and benefits.

Patent Pending

Bottom Line

- EZ De-Coke Slowed the buildup of coke.
- EZ De-Coke increased the number of TLE run cycles (run time) with on-line decoking before opening up the unit for mechanical decoking.
- EZ De-Coke made Mechanical Decoking much easier & faster; reducing outage time and no damage to the tube sheet or refractory.
- EZ De-Coke can be applied to new as well as to existing TLE installations (retrofit) to afford same effect and benefit.

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