TUBACOAT

ANTI-COKING SOLUTION FOR FIRED HEATERS
IN DELAYED COKER, VISBREAKER & VACUUM DISTILLATION UNITS

RefComm 2020
September 16, 2020

Sanjay Lodha
Global Business Director

- Tubacex Group
- Tubacoat concept
- Product characterization
- Coke deposition in fired heater tubes
- Chemical Inertness and Coking Resistance Study
- Field applications/Case Studies- Fired Heaters and others
- Anti Corrosion Commercial Application
- Conclusion

Global Presence

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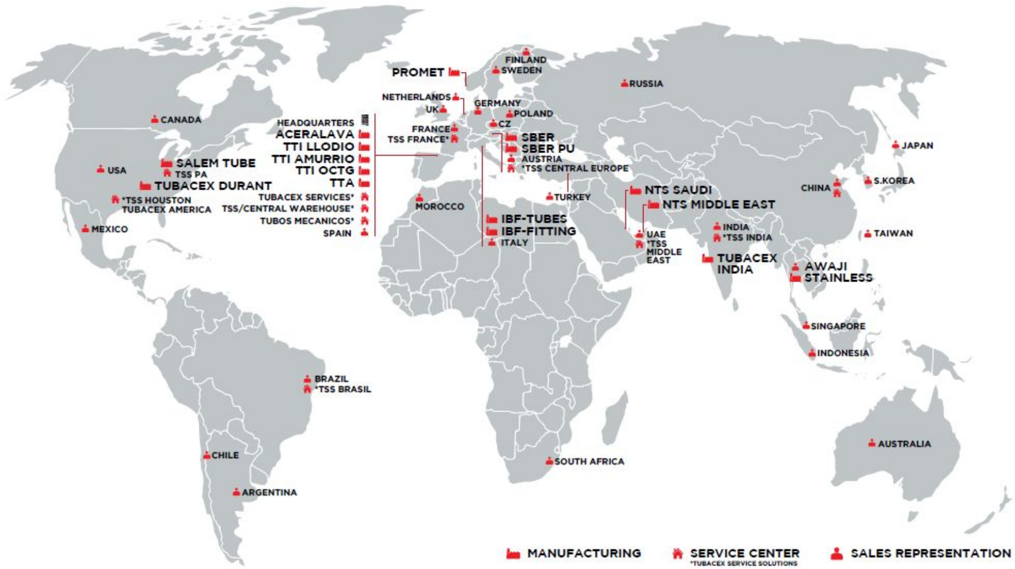

KEY FACTS

- **Sales: 700 million euros**
- **2600 professionals**
- **Full Range of Seamless Stainless tubular Products**

- **15 mills** in Spain, USA, Austria, Italy, India, Thailand, Norway, UAE & Saudi
- **Commercial presence** in over 30 countries
- A **Service Solutions Company,** providing services and master distribution

Steel billets & bars ▶ Extrusion ▶ Cold finishing ▶ Pipes & tubes fittings ▶ Master distribution ▶ Commercial network

Introduction

- ✔ Technology-based company
- ✔ 100% subsidiary of TUBACEX
- ✔ Engineering, industrial development and commercialization of tubular solutions based on advanced innovative coatings

Value-added products with…

- Outstanding corrosion resistance in different media and thermal conditions
- High abrasion resistance (64HRC hardness)
- Anti-adherent and anti-fouling properties
- Chemical inertness

Specifically developed to…

- Provide **long term reliable & competitive solutions** to industrial applications under severe working conditions and extreme environments

Potential applications

> Oil & Gas

> Fertilizers

> Chemical & petrochemical

> Industrial processes

> Powergen

- Furnaces
- Heat exchangers
- Condensers
- Boilers
- Reactors

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Key Properties

MORPHOLOGICAL

- **Roughness**
  Ra and Rz decrease ≈ 97% minimizing particle adhesion
- **Continuous coating layer**
  Thickness control based on suspension parameters & rheological properties
- **Chemical bonding**
  between metal substrate and ceramic coating

MECHANICAL

- **Hardness & Elasticity**
  Coating is harder than substrate but less elastic
- **Abrasion resistance**
  ≈94% decrease in mass loss

CHEMICAL

- **High corrosion resistance** compared to base material under different conditions and standard tests
- **Chemical inertness**
  of the coated tube surface avoids reactions

THERMAL

- **Thermal resistance**
  Good performance under thermal cycling. No delamination & No cracks
- **Thermal conductivity**
  f(T) Average (reference) 6 W/mK

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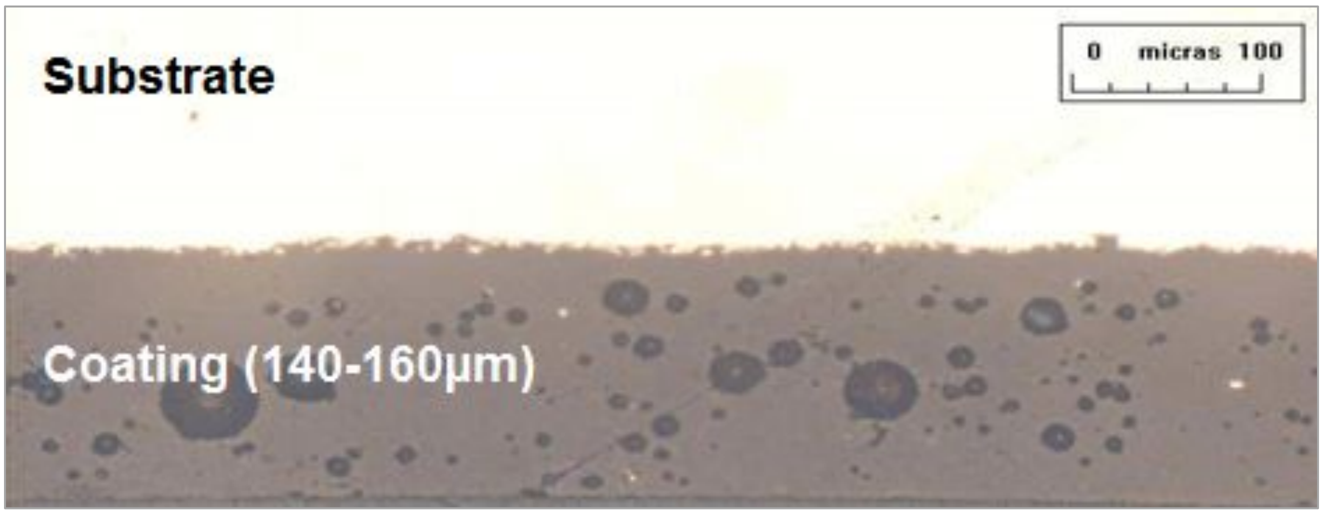
Morphological

Continuous **coating layer**
Thickness control based on suspension parameters & rheological properties



Typical coating thickness range: **100-150 µm**

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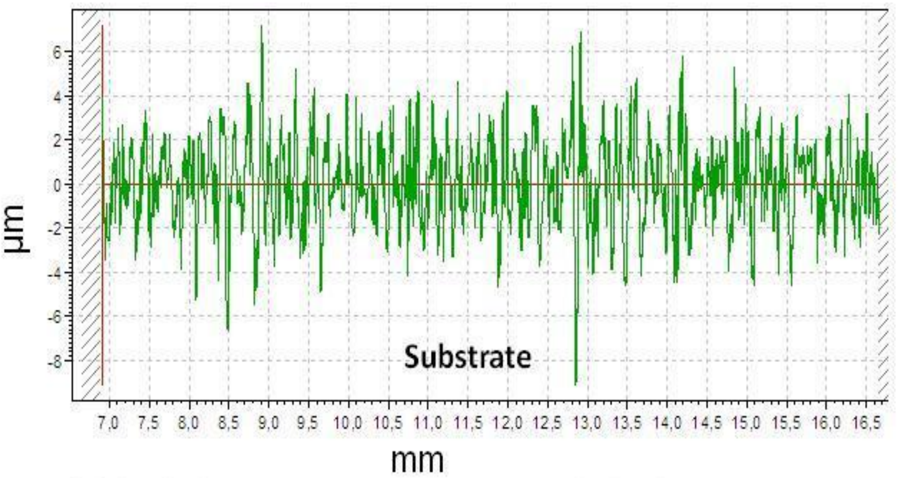
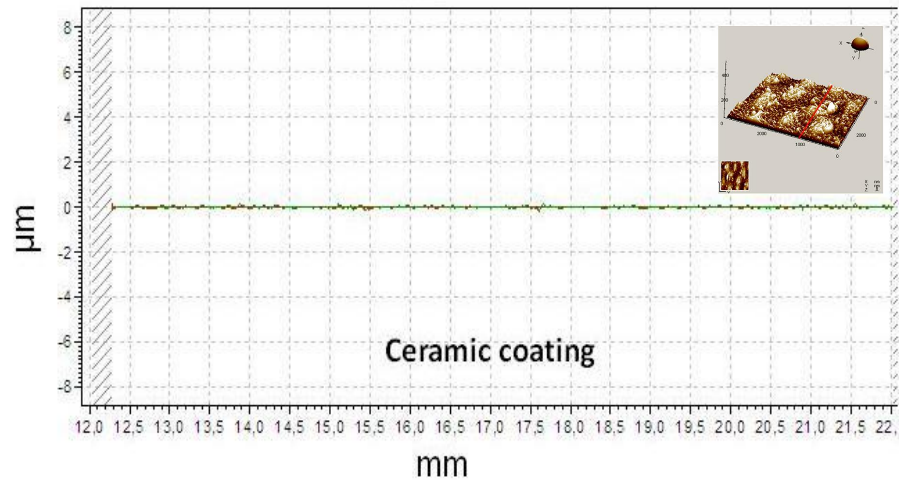
Anti-adherence

Roughness. Ra and Rz decrease ≈ 97% minimizing particle adhesion





Substrate

Ra ≈ 1,5 µm and Rz ≈ 7,8 µm

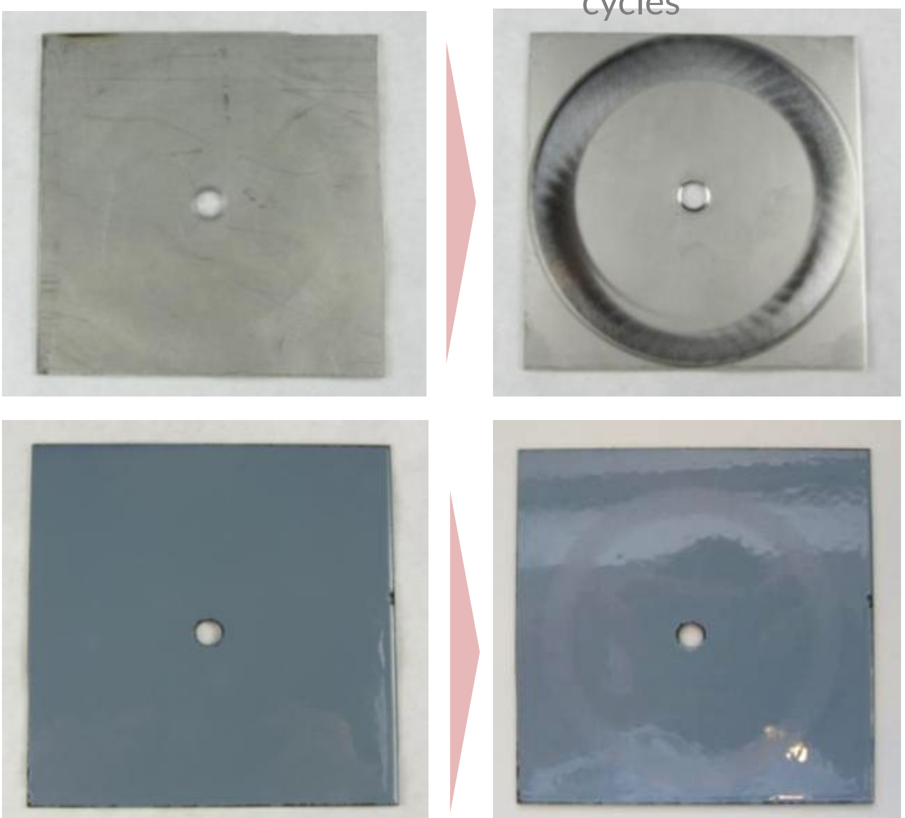
Ceramic coating

Ra < 0,04 µm and Rz ≈ 0,2 µm

Mechanical

Abrasion resistance
≈ 94% decrease in mass loss

0 cycles | 10.000 cycles



Mass loss for 10.000 cycles

$$\Delta w_n = \langle w_0 \rangle - \langle w_n \rangle$$

- Substrate

$$\Delta w_{10000} = 94.783 - 94.725$$
$$\Delta w_{10000} = 58\ mg$$

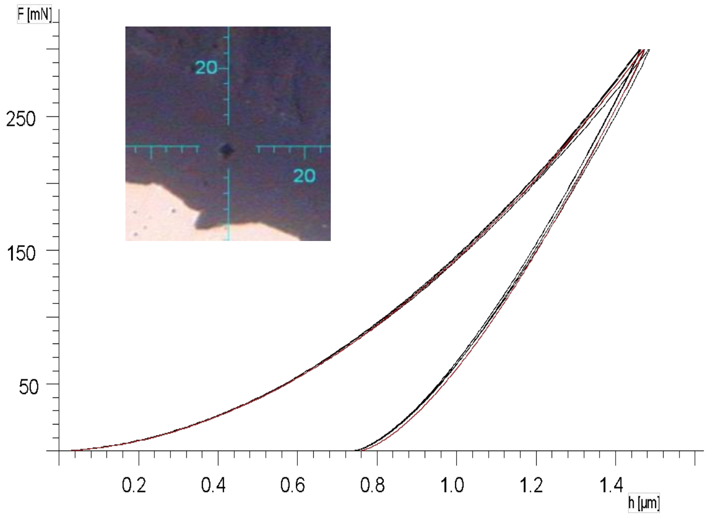
- Ceramic coating (T153)

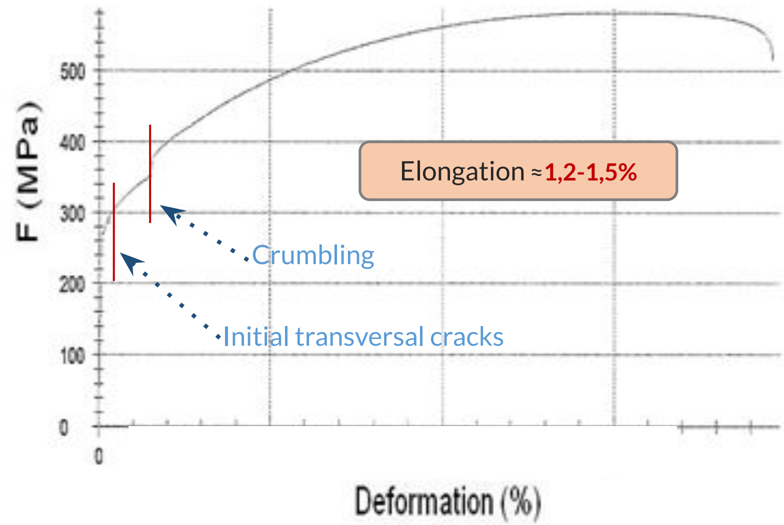
$$\Delta w_{10000} = 119.377 - 119.373$$
$$\Delta w_{10000} = 4\ mg$$

Mechanical

Hardness & Elasticity

Coating is harder than substrate but less elastic





	Base Material	Ceramic coating
Hardness (HV)	220	840
Elastic Modulus EIT (GPa)	140	87

Tensile results			
$R_{p0.2}$ MPa	R_{p1} MPa	$R_{p0.5}$ MPa	R_m MPa
288	323	301	582

Hardness and elasticity properties can be improved by modifying structure and composition of ceramic compounds and process conditions

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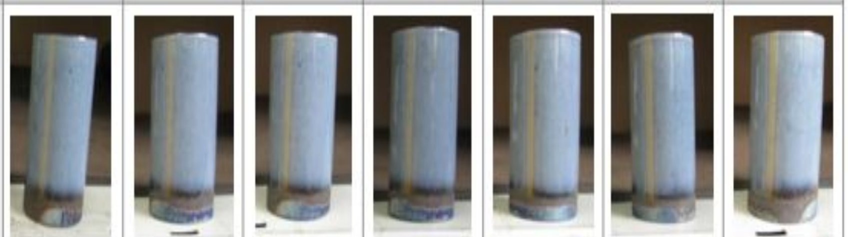
Thermal Resistance

Good performance under **thermal cycling**
No delamination – No crack

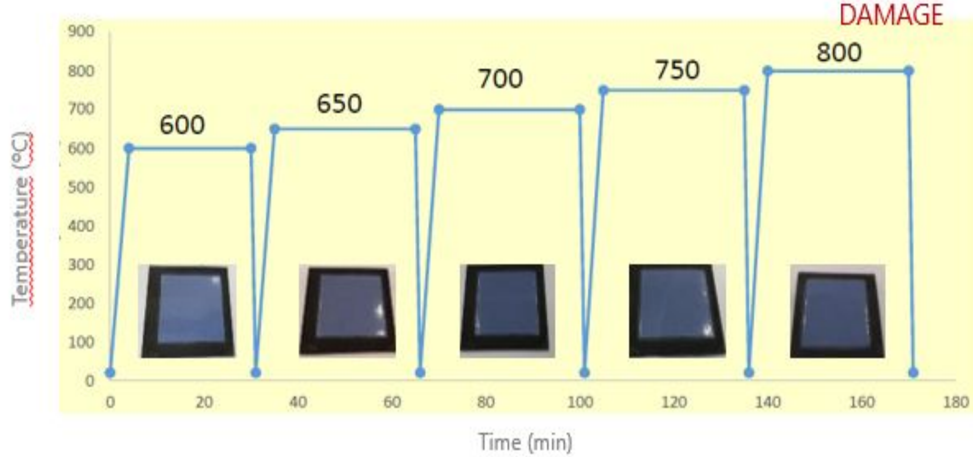
Thermal cycling (450ºC / 10min) + Rapid water cooling (15ºC)

n Cycles	0	1	2	3	4	5	6
Water cooled							

Different working temperature and thermal cycling resistance can be achieved by modifying structure and composition of ceramic compounds

Thermal cycling (30min) + Rapid water cooling (20ºC)

NO DAMAGE



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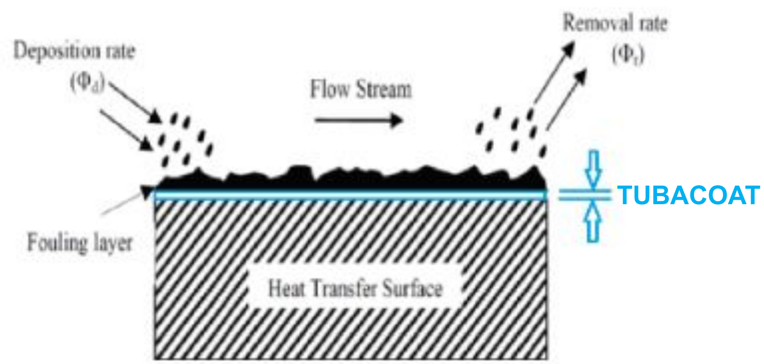
Characteristics

Tubacoat glass-finished layer will protect the inner or outer surface of the tubes.



Deposition Rate will decrease due to its chemical inertness and smoothness of surface

Removal Rate will increase due to its anti-adherence properties

Heat Transfer loss will reduce due to lower fouling layer

Fluid Flow will maintain/increase the stream

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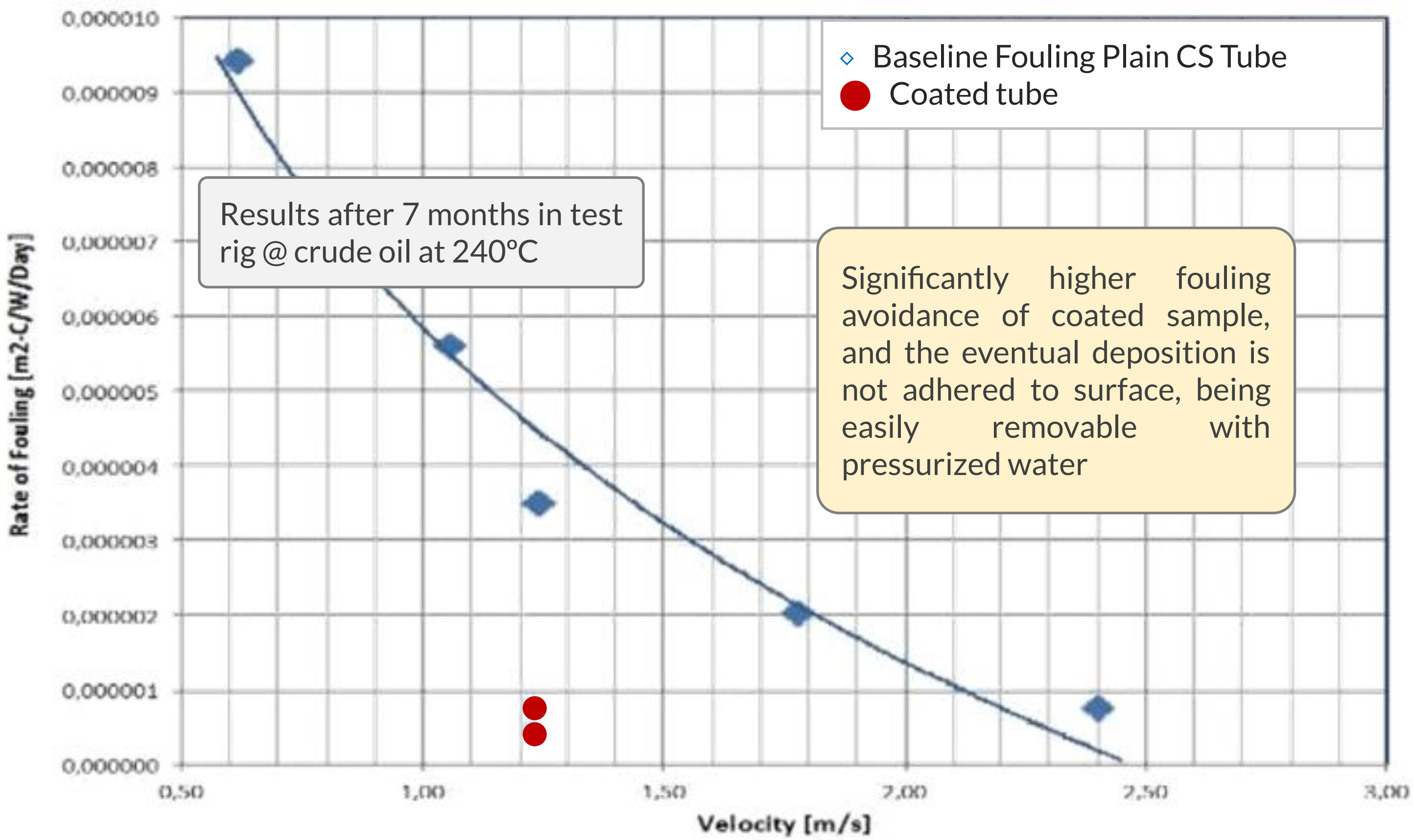
Rate of fouling

High fouling avoidance & low adherence
of coated tube compared to bare material



Chemical

High corrosion resistance
compared to base material

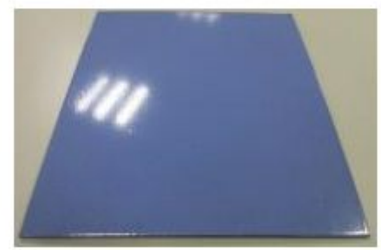
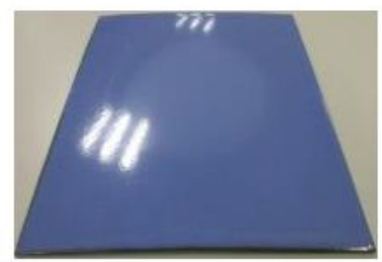
Acid corrosion test

- *Conditions:*
  - Solution: 10% HCl at 22°C
  - Visual inspection

Acid Corrosion Test	
0 h	
1000 h	
2000 h	

Acid corrosion at boiling temperature

- *Conditions:*
  - Solution: boiling H_2SO_4 (30%)
  - 18 h (UNE-EN ISO 28706-2)

Acid corrosion at boiling T	
Liquid Contact	
Vapour Contact	

Unique Ceramic Coating Technology

TUBACOAT	Property	In-situ coatings
↑ Low roughness	**Fouling/Coking resistance**	↓ High roughness
↑ Chemical bonding	**Corrosion resistance**	↓ Lack of bonding
↑ high hardness	**Abrasion resistance**	↓ low hardness
↑ Chemical bonding	**High temperature resistance**	↓ Lack of bonding
↔ In factory & local weld coating	**On-site application**	↑ Direct application

The coating is vitrified above **800°C/1470°F** which provides **chemical bonding** and "glass" properties, enhancing adherence between coating and substrate and **increasing resistance to fouling, corrosion and abrasion at high temperature** compared to in-situ coatings

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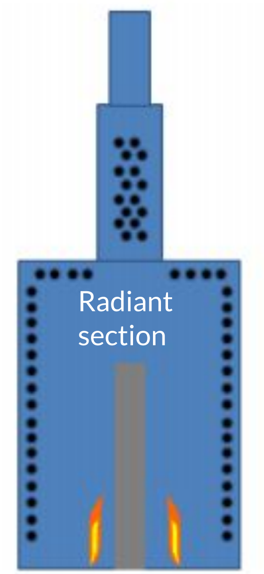
Delayed coker, Visbreaker & VDU fired heaters

DCU / VB / VDU



Example fired heater cell

Coke deposition

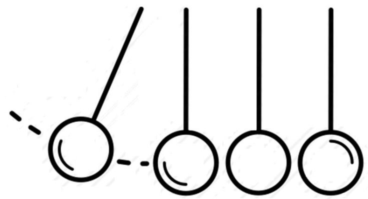
High value products

Low value feedstock

Coke deposition problems

As coke layer grows….

- ↓ Heat transfer & ↑ Tube skin temp
- ↓ Effective area & ↑ Pressure drop



Efficiency loss

NEED FOR FREQUENT DECOKING

Production loss

Higher OPEX

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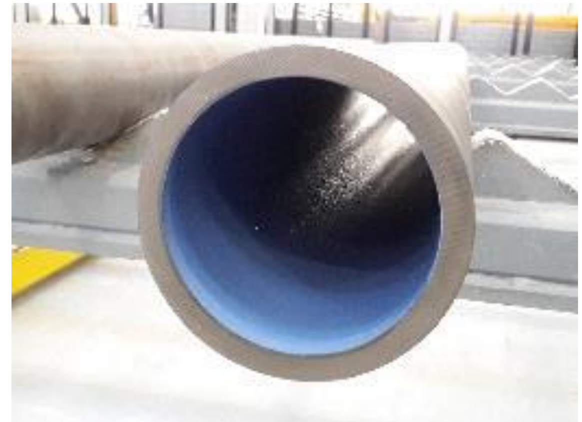
Anti-coking Solution For Fired Heaters

When the coating is applied to the inner surface of heater tubes:

- Minimizes coke formation (chemical inertness)
- Minimizes coke deposition (anti-fouling)



Fired heater with coating applied will obtain:

- Longer run lengths
- Lower fuel consumption
- Increased safety and reliability

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Coking Resistance Study

- DME cracks towards the equimolecular CO, H_2 and CH_4 (Eq. (1)- depends on T)

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- Parallel reactions of the gaseous products occur (Eqs. 2-4) depending on T and on the characteristics of the contact surface (*active sites on the surface*)

DME cracking:	$\mathbf{CH_3OCH_3} \xrightarrow{\Delta} CH_4 + CO + H_2$	(1)	→	Thermal route
Boudouard reaction:	$\mathbf{2CO} \Leftrightarrow CO_2 + C\downarrow$	(2)		
Methane decomposition:	$CH_4 \Leftrightarrow H_2 + C\downarrow$	(3)	→	Active sites (Eqs. 2-4)
Reverse-Water Gas Shift:	$CO_2 + H_2 \Leftrightarrow CO + H_2O$	(4)		

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Chemical inertia and reproducibility

- Temperature = 300-700°C/572-1290°F
- Residence time = 60s
- Time on stream: 80 min

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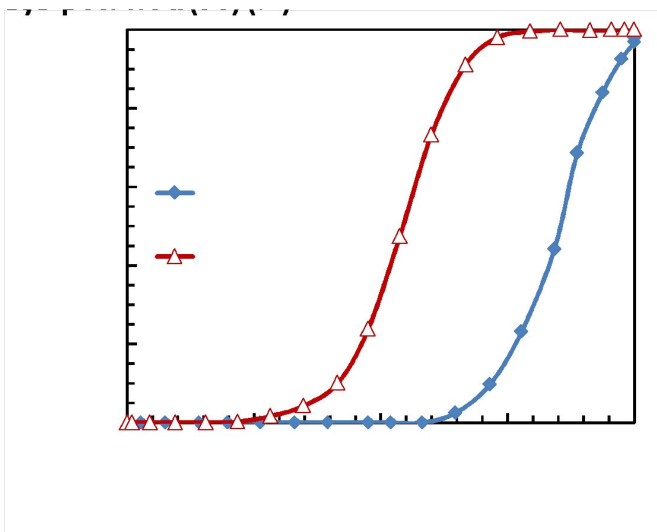
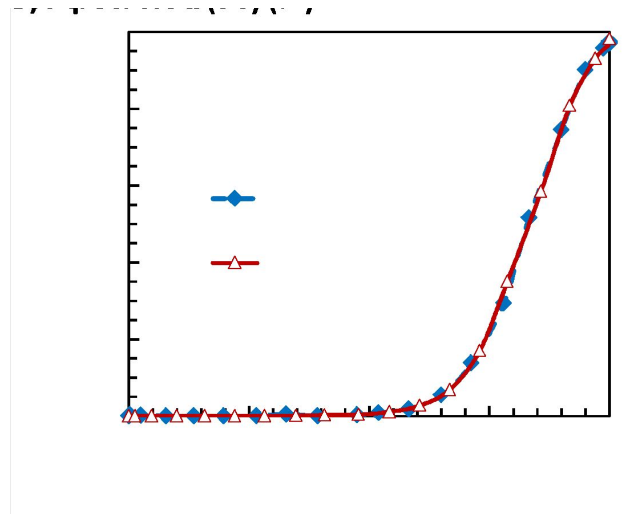
Degradation Temperatures

	NON COATED		COATED	
Cycle	1	2	1	2
T10 (°C)	587	465	574	571
T50 (°C)	641	518	631	632
T90 (°C)	685	565	680	682

Without coating



With coating



- **COATED TUBES ARE CHEMICALLY INERT PREVENTING COKE FORMING REACTIONS**

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Study of carbon formation

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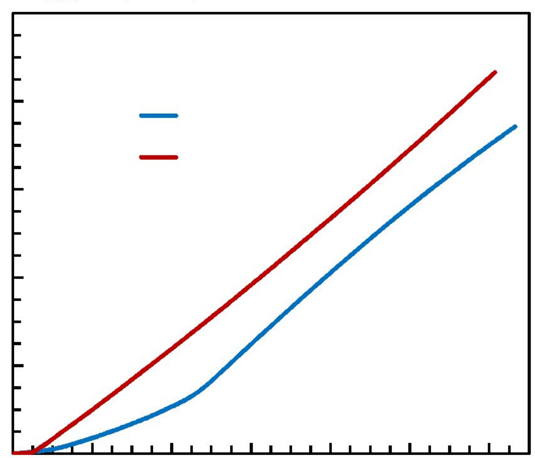
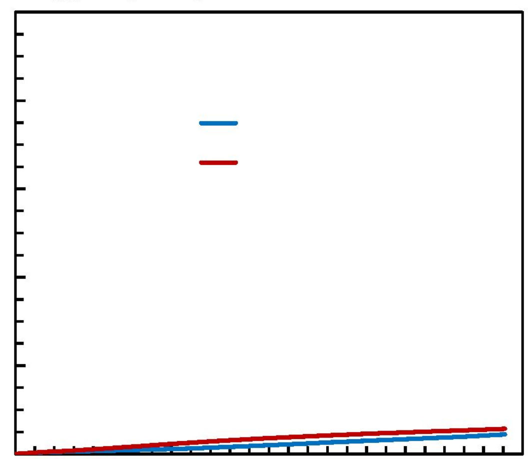
Calculation of carbon formed

$$(DME)_{in} - (DME+CO+CO2+CH_4)_{out}$$

Without coating



With coating



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Study of carbon deposition

Combustion conditions:

- Temperature= 300-700°C/572-1290°F
- Residence time = 6 s
- Time on stream(700°C/1290°F): CO2<0.1%

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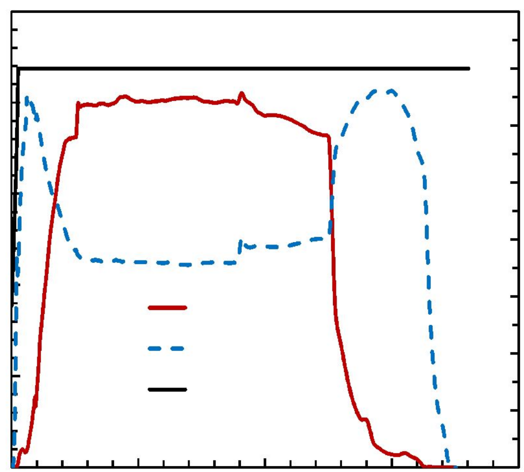
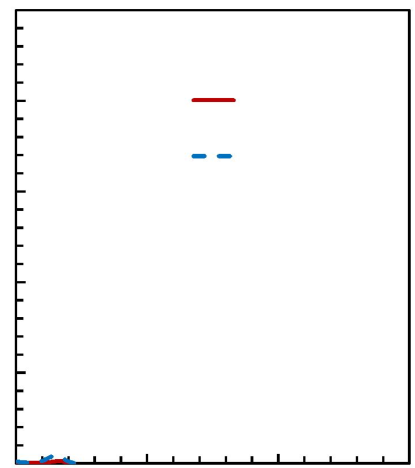
Carbon deposited

Integration of $(CO+CO_2)$ curves

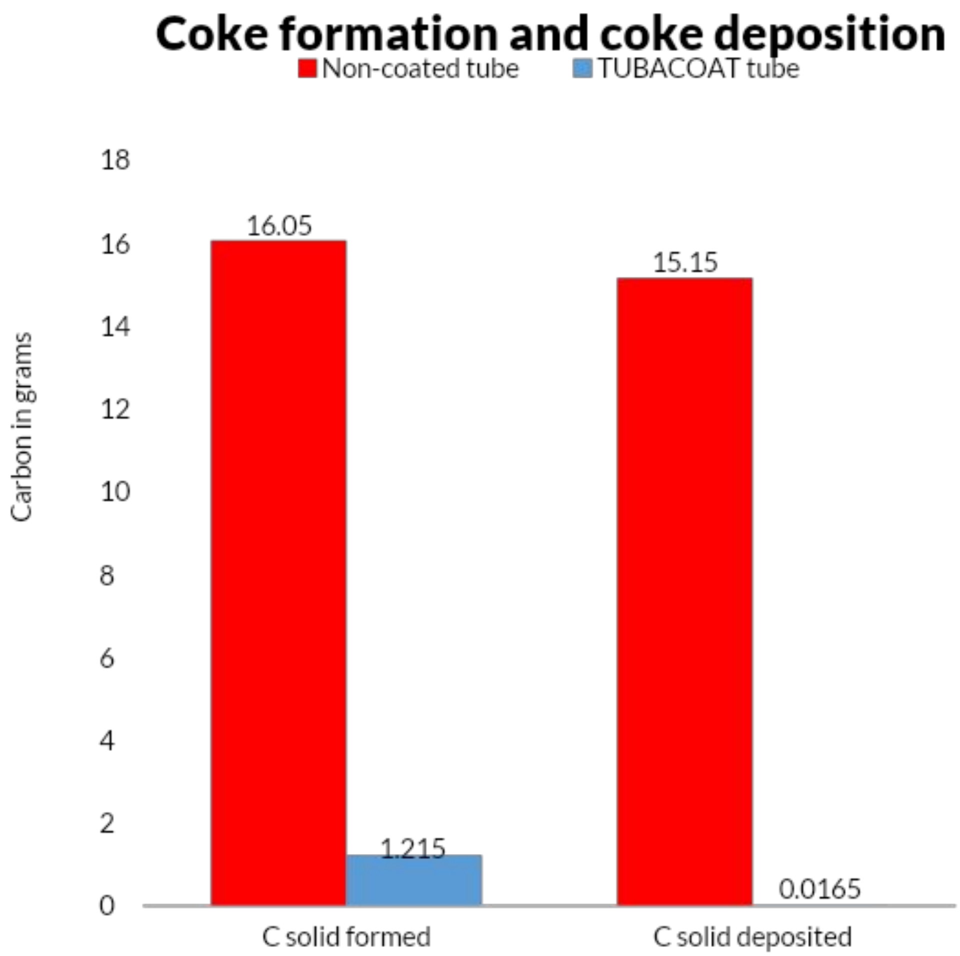
Without coating



With coating



Chemical Inertness and Coking Resistance Study



Conclusions

- **Chemical inertness** of coated tube surface **avoids coking reactions** occurring in the active sites of non-coated tubes
- **Carbon formed** is **10 times lower** in coated tube vs non-coated tube
- **Carbon deposited** is **100 times lower** in coated tube vs non-coated tube

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Visbreaker Unit

PROBLEM DESCRIPTION

Coke deposition inside the tubes causing:

- **Fired heaters** frequent shutdown for pigging
  □ **Huge loss of production cost**

- **Preheat exchangers** constantly taken out of service due to coke accumulation
  □ **Tube deformation related to hot spots**

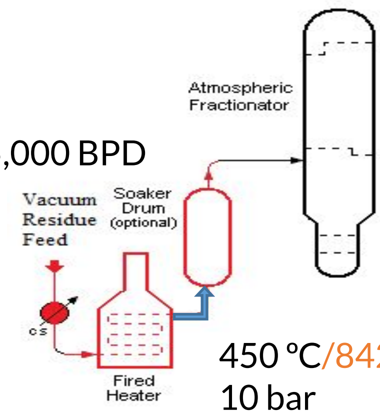
- Poor **Heat transfer efficiency** due to coke layer □ **High fuel consumption in the furnace**

TUBACOAT TRIAL

ID coated tubes, bends and flanges installed at the furnace outlet line to prove anti-fouling properties.

Dimensions: OD 4", Sch. 80 - 317L SS

15,000 BPD



450 °C/842 °F,
10 bar

Visbreaker Unit

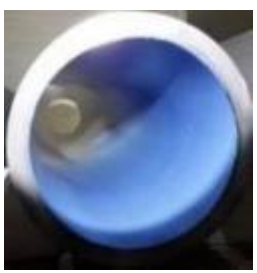
TRIAL RESULTS (after 9 months)

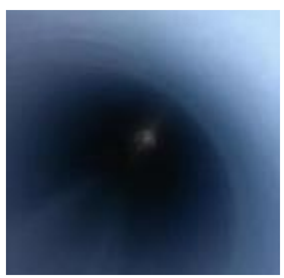
Coke deposition inside the tubes causing:

- **Very thin coke layer** - not detected by Radiographic test - 75% reduction in coke deposition.

- **Coke was much easier to remove** - 3 times lower water pressure than before was enough to remove all the coke.

- **Decoking services** - may use softer pigs and cleaning will be less frequent





CONCLUSIONS

- **Run lengths without decoking**/online spalling can be **increased between 3 and 4 times**
- **Savings** by Customer **1.5 Million USD per year**
  - 1.1 M$ higher throughput (reduced shutdown time 7days/yr)
  - 0.15 M$ furnace online spalling/pigging,
  - 0.15 M$ fuel consumption,
  - 0.10 M$ Heat Exchanger cleaning

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Delayed Coker Furnace

- Refinery operates 1 Delayed Coker, with normal capacity 124,000 barrel/day.
- Delayed Coker has 3 furnaces. Each furnace 6 passes. Each pass 30 radiant tubes
- Heater tube material: P9

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Decoking Problem

- Frequent decoking is required due to coke layer build up leading to:
  - High pressure drop
  - Increase in tube metal skin temperature
- Each furnace requires pigging every 3 months and online spalling every 30-45 days in 2 passes/furnace
- During pigging, one full furnace is out of service for 3-4 days unit running at 70% capacity. During Online Spalling, reduced capacity to 93% for one day/pass.

Every time one furnace is taken out of service for pigging, the cost due to reduced throughput is approximately 3.6 MM USD/furnace

Every time online spalling is performed in 2 passes of 1 furnace, the cost due to reduced throughput is approximately 125 KUSD/furnace

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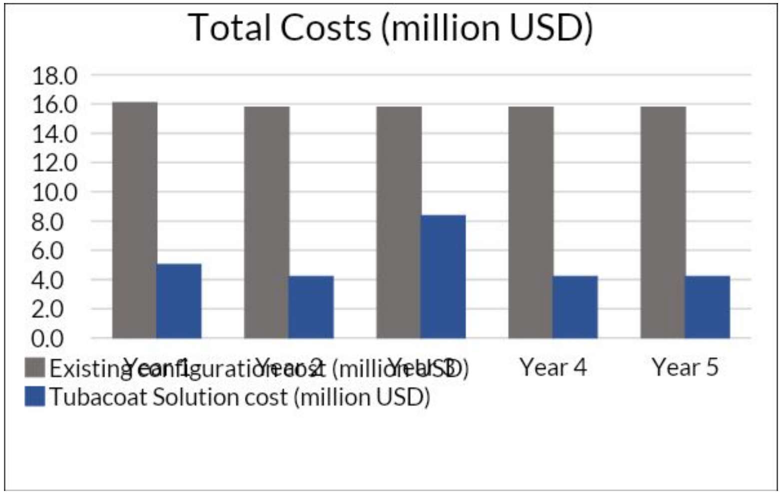
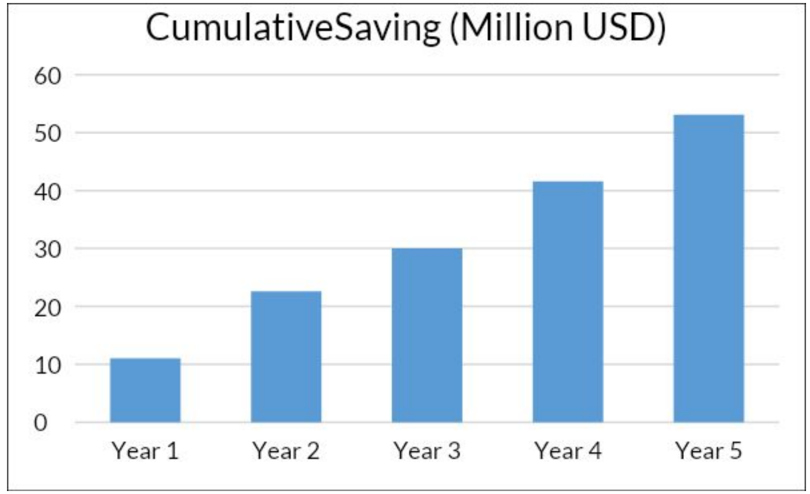
Tubacoat solution





Cost: Tube cost (year 1) + cost due to reduced throughput during decoking + cost due to higher fuel consumption

By extending Run Length without decoking by 3 times, estimated incremental benefit of 10 million USD/year.

Anti-coking solution – Coating during spalling/pigging

Online spalling:

- Coating designed to withstand online spalling (high temperature and thermal shock).

Mechanical pigging :

- Pigs of 64 Rockwell C (RHC) can be used without damage to coating.

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Delayed Coker Furnace

PROBLEM DESCRIPTION

- Heater tube material: 9 Cr 1 Mo
- Currently, their heaters requires online spalling every 50 days when wall temperature is 630°C/1166°F
  - 7 spalls per year
- During spalling operation, 1 of 6 passes needs to be out of service, so overall throughput to the unit is reduced to 85%.
- Spalling time takes approximately 1 day per pass
  - 6 days per spall

CONCLUSIONS

- Due to coke deposition, every year throughput is reduced to 85% for 42 days.
- Estimated potential savings by End user around 3 million USD per year based on large size of their DCU.


Example of Delayed coker unit

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Delayed Coker Furnace

Example of Delayed coker furnace

Problem description

- Heater tube material: 347H
- Heater requires online spalling every 2-3 months and also mechanical pigging once per year 4 spalls per year and 1 mechanical pigging
- During spalling, one pass needs to be out of service, so overall throughput to the unit is reduced to 75%. Spalling time takes approximately 1 day per pass 4 days per spall.
- Pigging requires full unit shutdown for 6 days

Conclusion

- Due to coke deposition, every year the unit is shutdown for 6 days and throughput is reduced to 75% for 16 days
- Estimated potential savings by End user around 2.5 million USD per year

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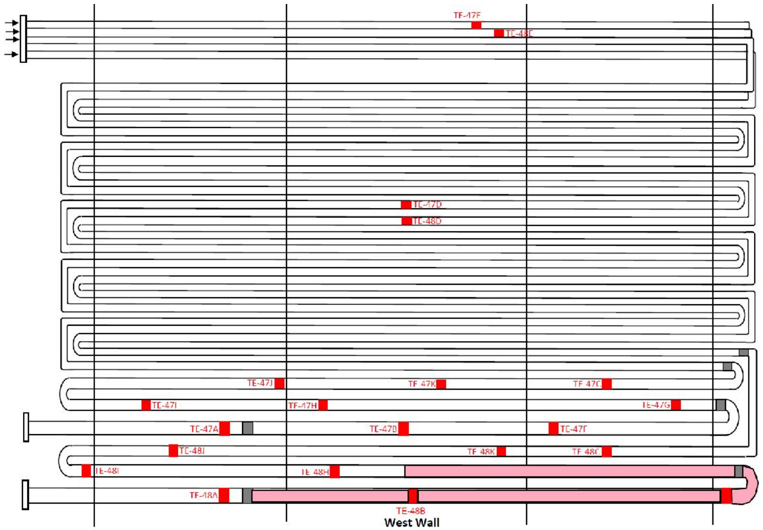
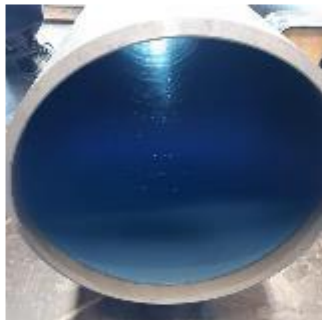
Vacuum Distillation Furnace



Problem Description

Furnace outlet line with severe coke fouling causing:

- **Outlet line replacement (8”,10” and 12” OD Tubes)** every year
- Frequent **decoking operations by mechanical pigging**
- Traces of **Polythionic acid stress corrosion cracking**



Tubacoat Solution

Tubacoat inner coated tubes, bends and reducers installed at the furnace outlet line

Base material: 317L SS @ Dimensions: OD 8” and 10” OD Lines

- **ROI expected in 1.5 Years**

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Vacuum Distillation Furnace (Canada)

Description:

- End User processing heavy hydrocarbons from oil sands (API gravity @ 15C: 22.3)
- VD Unit comprises 2 furnace with 4 passes each with 16 lines on 6” OD Line and 8”, 10” and 12” Outlet line
- Refiner agreed to test TC Anti-fouling properties where the highest coke formation occurs
- The Refiner recently upgraded the metallurgy to 317L SS but severe coke formation and traces of PASCC are still present
- After testing TC Anti-coking solution, refiner will include ID coated Lines for all passes and furnace
- ROI expected in 1.5 Years

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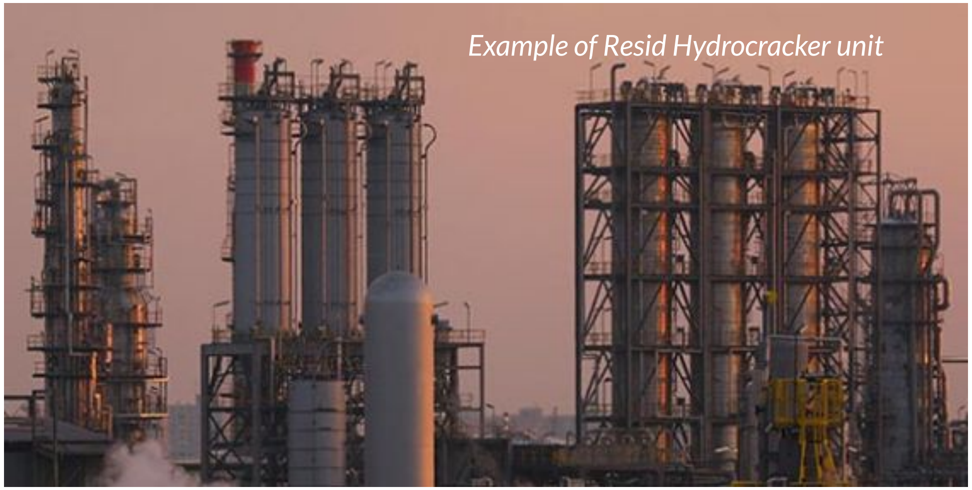
Hydrocracker (RHC)

PROBLEM DESCRIPTION

- Each of their 8 Resid Hydrocracker reactors has more than 800 risers that are crucial for proper feed distribution in the reactor
- Reactors operate at more than 400°C/752°F and more than 130 bar.
- Severe fouling occurs at the bottom section of all Resid Hydrocracker Risers
- This leads to maldistribution of process stream and reduced conversion rate

CONCLUSIONS

- With coating, fouling will be minimized leading to improved conversion of resid feed to clean fuels.
- High economic benefits under evaluation.


Example of Resid Hydrocracker unit

Vacuum Vistillation Unit (Europe)

Tubes installed in VDU furnace

Inner surface view

Tubacoat Solution

Tubacoat inner coated tubes

Base material: 317 SS @ Dimensions: OD 5", Sch. 40

Trial **in progress**

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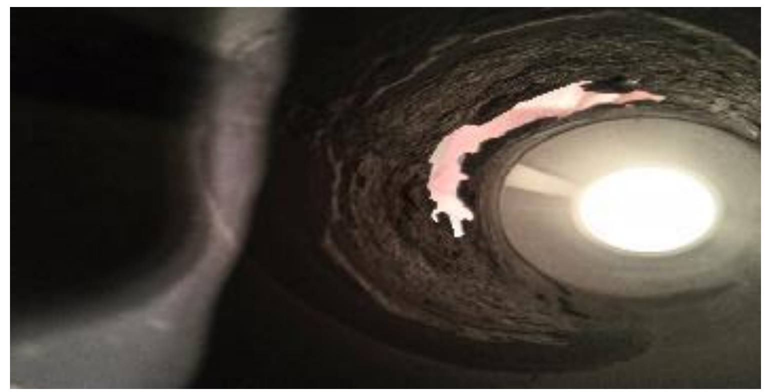
Coke Calciner

- **Working Conditions**
  - Oil fumes rich in vanadates at 850ºC
  - Metal surface 570ºC
  - Low pressure (welded tube)

Substrate Material TP310 (bare)



Chemical corrosion

Efficiency loss

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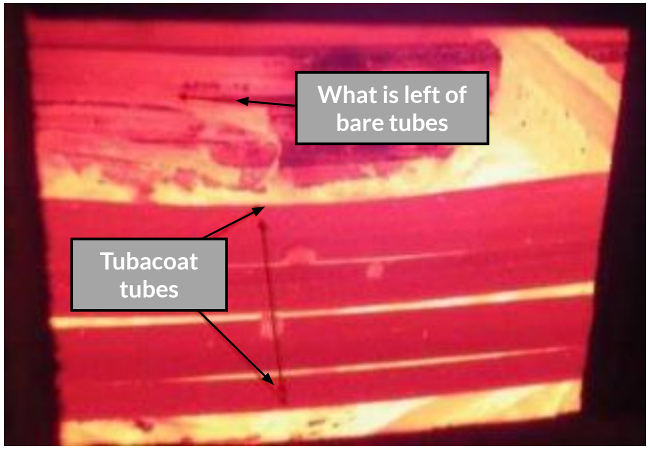
Coke calciner



(Image @ 10 months working)

TUBACOAT SOLUTION

- 9 TP310 (OD63.5;WT2.41) outer coated prototypes were placed in the upper row (the hottest) of the calciner recuperator in May 2015
- Only the 9 coated tubes were remaining in the area, even suffering overheating during last weeks of operation prior to planned plant shutdown
- The rest of tubes were broken and blinded

TUBACOAT
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Coke calciner

TUBACOAT SOLUTION

≈ 800 tubes (TP310 grade, OD63.5/WT2.41, outer coating), delivered to customer in Jan'2017 and installed in coke calciner in April 2017.

Status: facility in full operation (& continuous performance monitoring)

TUBACOAT
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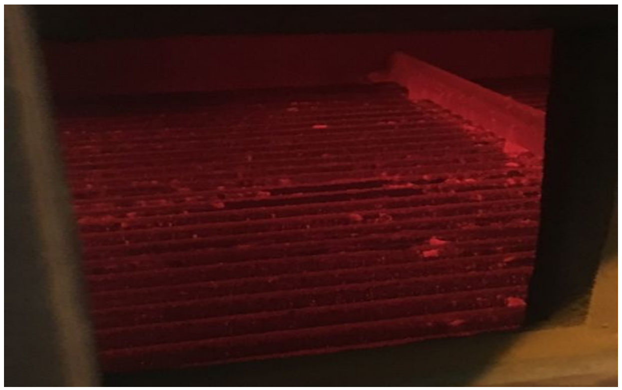
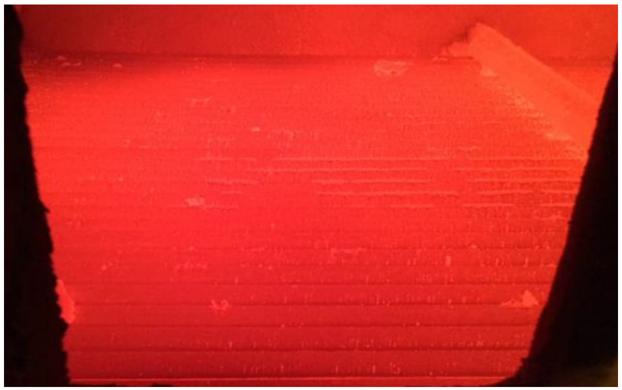
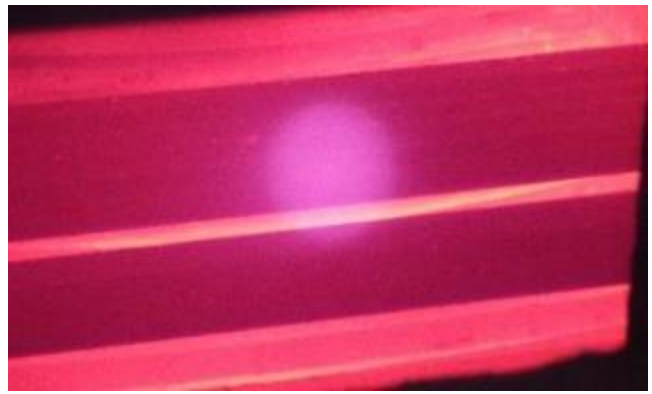
Coke calciner

TUBACOAT SOLUTION:

Operator received 3 times cycle length, savings of US $2 million/yr.

Real pictures of coated tubes in coke calciner recuperator after 15 **months** running in full operation

- Tubacex Group
- Tubacoat concept
- Product characterization
- Coke deposition in fired heater tubes
- Chemical Inertness and Coking Resistance Study
- Field applications/Case Studies- Fired Heaters and others
- Anti Corrosion Commercial Application
- Conclusion

Conclusion –Tubacoat Anti-coking Solutions – Value to customers

Applying inner coating in DCU/ VU/VDU/RHC tubes is:

✔ PROFITABLE

- **Longer run lengths** improving overall throughput
- Easier and much **less frequent cleaning** operations

✔ SAFE

- **Increased safety** by reducing the number of shutdowns and start-up operations and avoidance of hotspots

✔ CLEAN

- **Reduced fuel consumption** due to increased heat transfer efficiency and **CO_2 reduction**

✔ RELIABLE

- **Ad-hoc Formula** designed for specific applications
- Ceramic Coating applied to **Carbon Steel, Stainless Steel and Nickel Alloy Materials**

Commercial Applications and Trials

Refinery & Petrochemical

- Reliance Industries Limited
- OMV
- NAYARA ENERGY
- bp
- DOLPHIN ENERGY دولفين للطاقة
- REPSOL
- ExxonMobil
- Chevron

Powergen & Others

- ENIM INNOVATE AND ACT
- KOBELCO
- ANDRITZ
- wood.
- ence ENERGÍA & CELULOSA
- zabalgarbi

THANK YOU!

TUBACOAT PLANT IN CANTABRIA, SPAIN

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