TUBACOAT – An Efficient and Cost Effective Advanced Coating Solution for Tubular Products in Extreme Refinery and Petrochemical Applications

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REFCOMM® MUMBAI 11–14 November 2019

TUBACOAT

TUBACEX GROUP

Agenda

- *Introduction*
- *Tubacoat concept*
- *Product characterization*
- *Chemical Inertness and Coking Resistance Study*
- *Field applications*
- *Conclusions*

Introduction

- Reduction of overall maintenance costs in critical equipments has been the need of the hour at many refineries and petrochemical plants.
- Use of advanced stainless steel and CRA's is the next logical solution to increase the service life of critical components and minimizing operation and maintenance costs.
- The selection is always driven by Cost optimization Vs Corrosion resistance.
- Ceramic coated tube concept offers a cost efficient and environmental friendly solution to protect valuable assets from corrosion, abrasion and other forms of structural degradation.
- The solution has been well accepted for various extreme conditions and with in-house developed industrial process the thin tailor made ceramic coating when used tubular applications for steel tubes have resulted in outstanding corrosion resistance in different media and thermal conditions.

Tubacoat Concept

Solutions

Value-added products with…

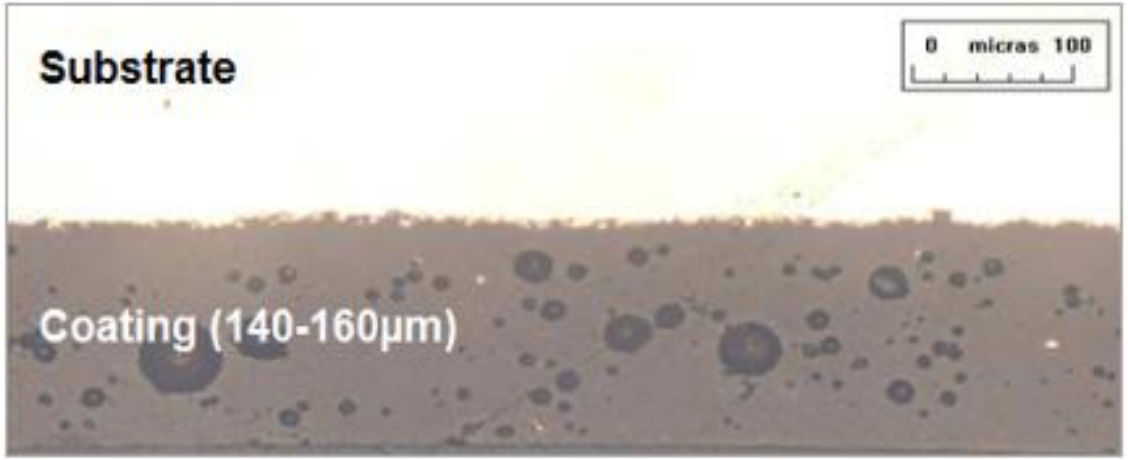
Specifically developed to…

- ✓ Outstanding corrosion resistance in different media and thermal conditions
- ✓ High abrasion resistance (64HRC hardness)
- ✓ Anti-adherent and anti-fouling properties
- ✓ Chemical inertness
- ✓ Provide long term reliable & competitive solutions to industrial applications under severe working conditions and extreme environments

Product Characterization

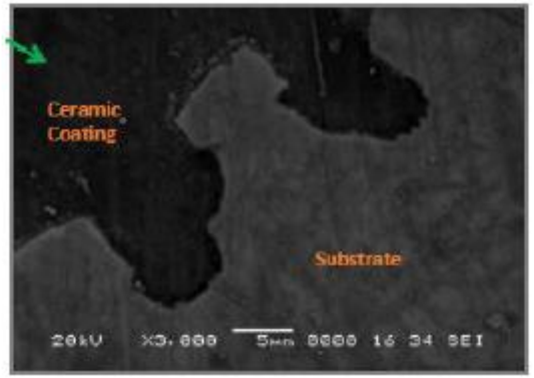
Morphological

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

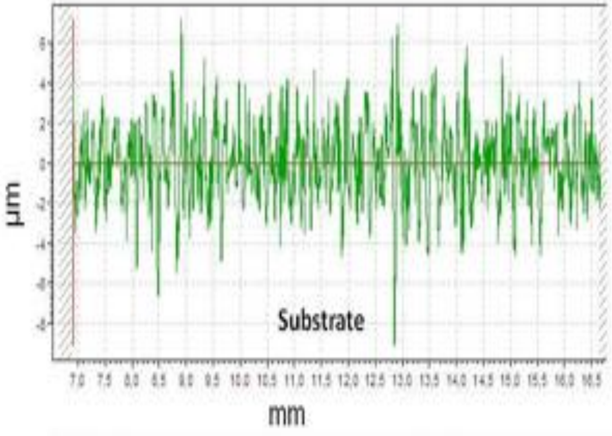


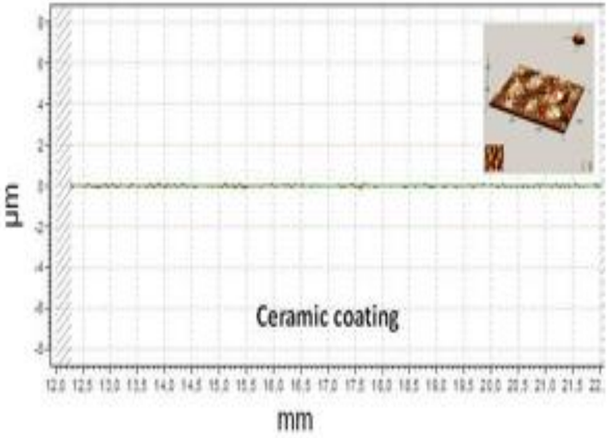
Typical coating thickness range: 100-150 µm

After coating process, coating thickness is measured in every tube with **ultrasonic thickness gauge**



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





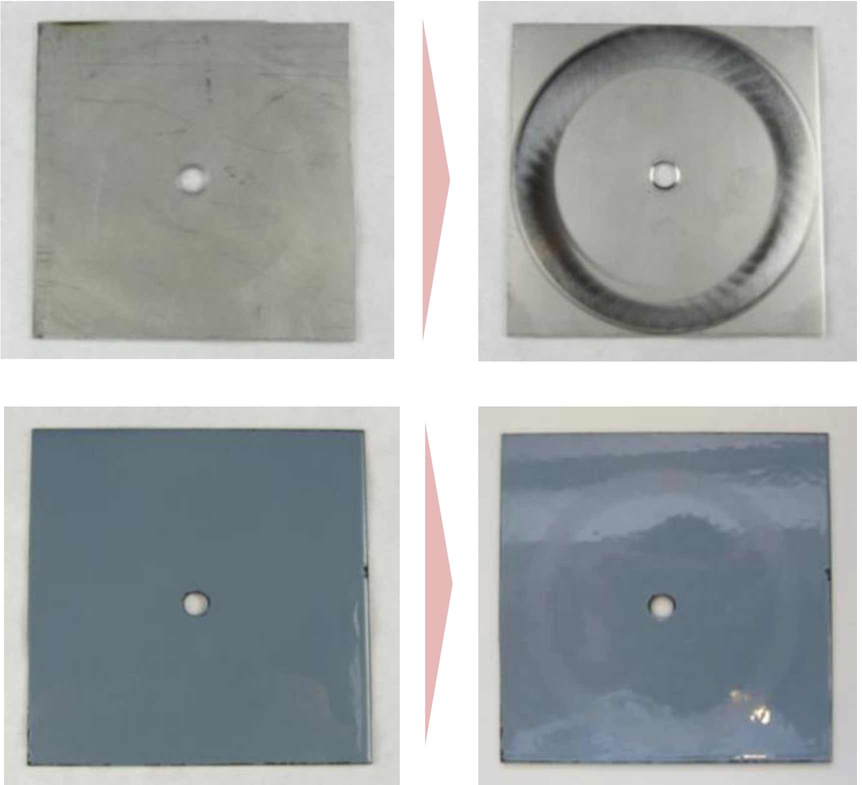
Substrate	Ceramic coating
Ra ≈ 1,5 µm and Rz ≈ 7,8 µm	Ra < 0,04 µm and Rz ≈ 0,2 µm

Product Characterization

Mechanical

Abrasion resistance
≈ 94% decrease in mass loss

0 cycles | 10.000 cycles



Mass loss for 10.000 cycles

$$\Delta w_n = < w_0 > - < w_n >$$

- Substrate

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

$$\Delta w_{10000} = 58\ mg$$

- Ceramic coating (T153)

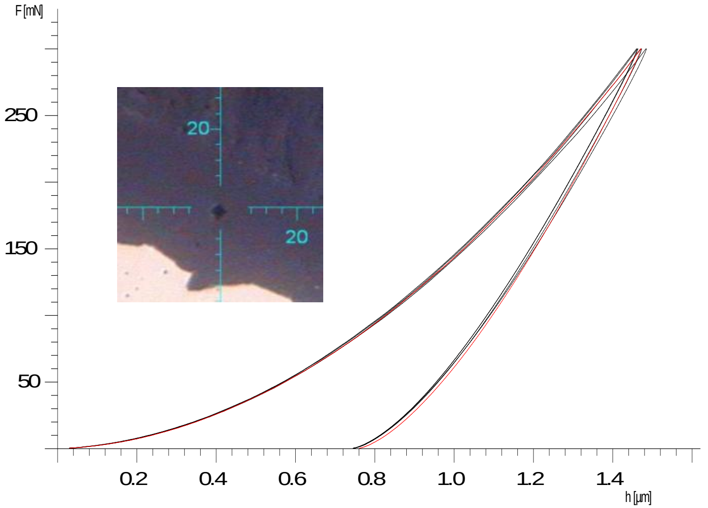
$$\Delta w_{10000} = 119.377 - 119.373$$

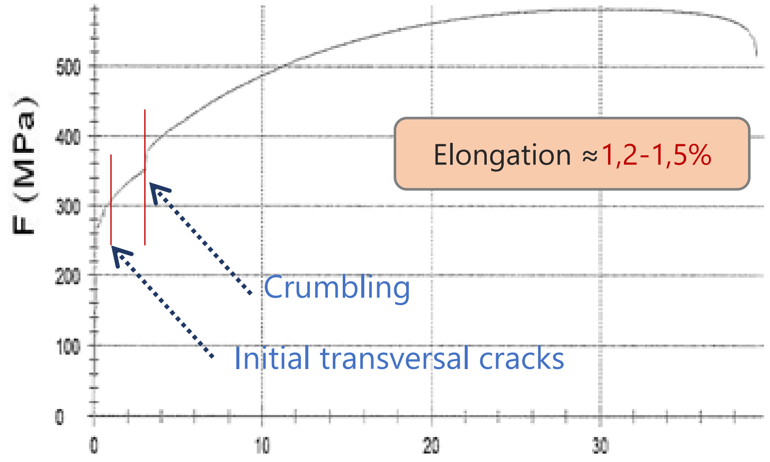
$$\Delta w_{10000} = 4\ mg$$

Product characterization

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

Product Characterization

Thermal Resistance

Good performance under thermal cycling
No delamination – No cracks

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

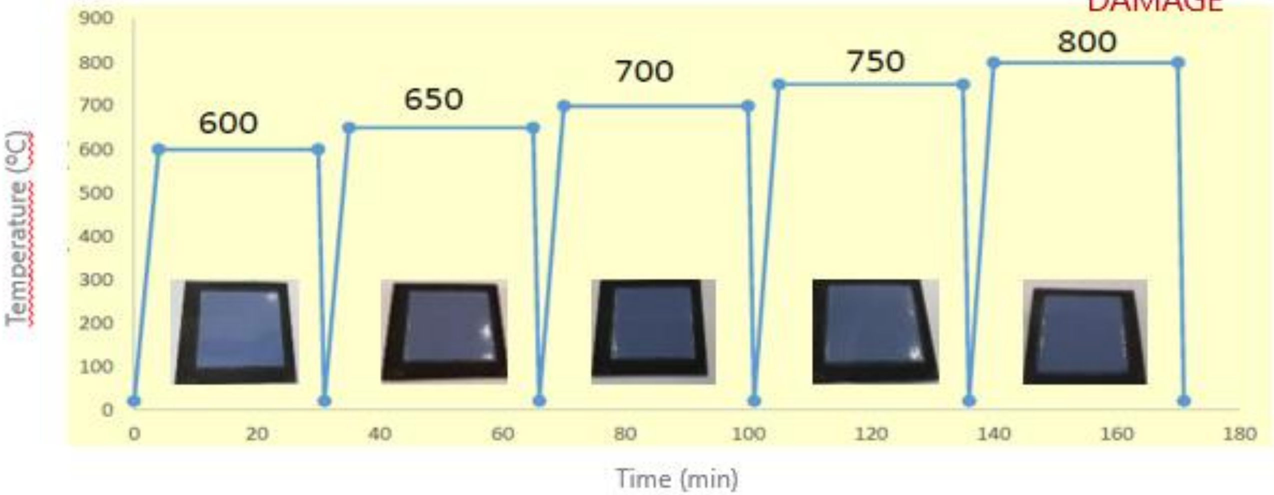
n Cycles	0	1	2	3	4	5	6
Water cooled							

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

Good performance under thermal cycling
No delamination – No cracks

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

NO DAMAGE



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Product characterization

Emissivity

Emissivity values >0.80
Reference ≈ 0,83 (@ 550ºC)

Coating	VP15	VP15 + 25% SiO2	VP15 + 25% SiO2 + 25% PIG (Cr-Cu-Fe)
Substrate	Inox 310	Inox 310	Inox 310
ROUGHNESS(Ra)	0,03	0,08	0,11
THICKNESS (µm)	132	108	112
			
AVG EMISIVITY AT 20ºC	0,892	0,889	0,889
AVG EMISIVITY AT 550ºC	0,834	0,838	0,832

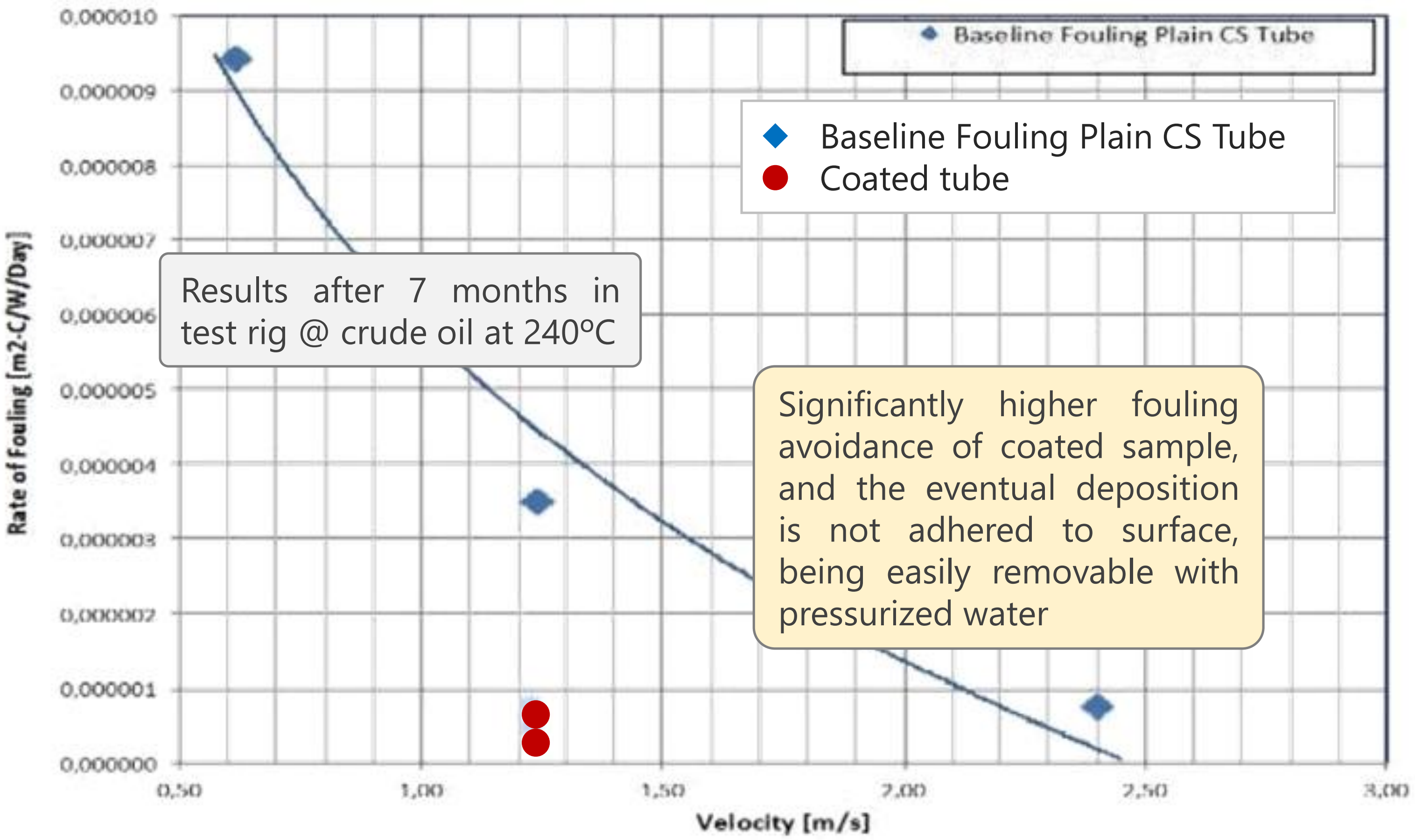
MEASURING CONDITIONS

Measurement method	SNEHT	**Measurement method**	SNHRRT/V1-MIR
Temperature (T)	550°C	**Temperature (T)**	25°C
Polar angle (θ)	0°	**Polar angle (θ)**	12°
Spectral range	1.8 to 26 µm	**Azimuth angle (φ)**	0°, 45°, 90°, 135°
		Spectral range	2 to 20 µm

Product Characterization

Rate of fouling

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



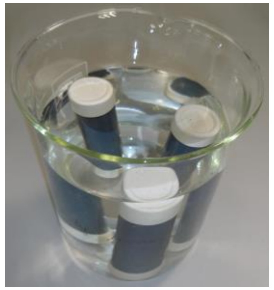
Product Characterization

Chemical

High corrosion resistance
compared to base material

Seawater corrosion test

- *Conditions:*
  - Solution: 3,5% NaCl at 22°C
  - Visual inspection



Seawater Corrosion Test	
0 h	
1.000 h	
16.000 h	

High corrosion resistance for offshore applications

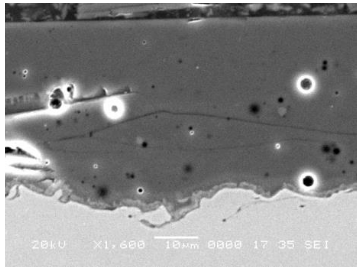
Product Characterization

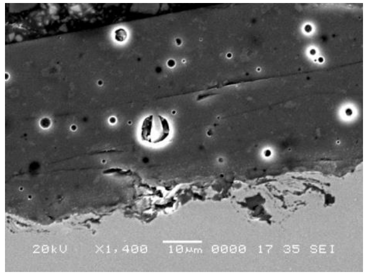
Chemical

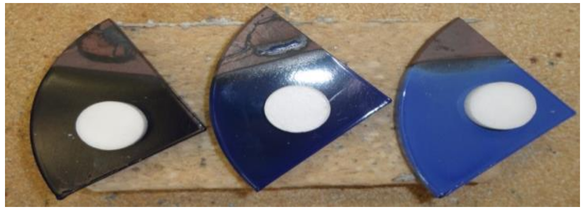
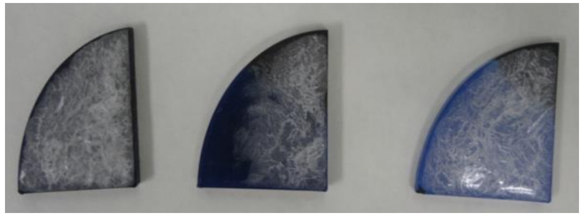
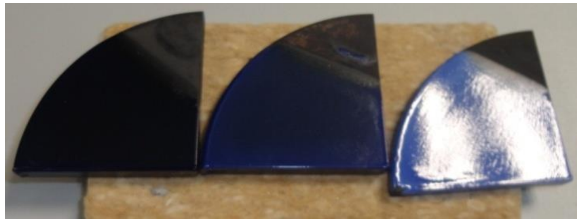
High corrosion resistance
compared to base material

Molten salt corrosion test

- *Conditions:*
  - Molten salt composition: NaNO3 + KNO3 (60/40)
  - Blocks of molten salts positioned over ceramic coating
  - 46 cycles HEATING (8 h at 400ºC)/cooling (air)
  - Visual and optical microscopy inspection





Molten salt Corrosion Test	
Initial (t0)	
46 cycles (before cleaning)	
46 cycles (after cleaning)	

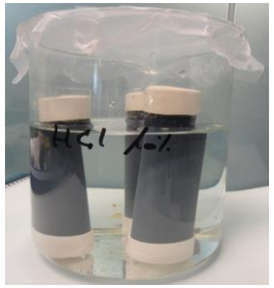
Product Characterization

Chemical

High corrosion resistance
compared to base material

Acid corrosion test

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



Loss of brightness during timing test, but ceramic coating continues to protect the metal substrate

Acid Corrosion Test	
0 h	
1000 h	
2000 h	

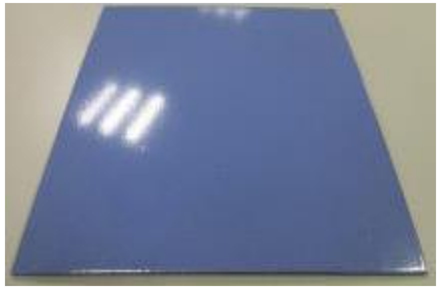
Product Characterization

Chemical

High corrosion resistance
compared to base material

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	

Product characterization

General

MORPHOLOGICAL

- Continuous coating layer
  Thickness control based on suspension parameters & rheological properties
- Roughness. Ra and Rz decrease ≈ 97% minimizing particle adhesion
- Good 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
- Good adherence. Impact test: No coating detachments at medium loads

CHEMICAL

- High corrosion resistance compared to base material under different conditions and standard tests
- Chemical inertness

THERMAL

Thermal resistance

- Good performance under thermal cycling
- No delamination – No cracks

Thermal conductivity

- Thermal conductivity range ≈ 5-8 W/mK = f(T) Average (reference) 6 W/mK

Product Characterization

Comparison with in-situ ceramic coatings

TUBACOAT	*Property*	In-situ ceramic coatings
↑ Chemical bonding/Low porosity	**Corrosion resistance**	↓ Lack of bonding/High porosity
↑ Low roughness	**Clogging resistance**	↓ High roughness
↑ High hardness (64 HRC)	**Abrasion resistance**	↓ Low hardness
↔ Under development (*)	**Radiation absorbance**	↑ High roughness

(*) Ad-hoc development according to Tubacoat integrated solution approach

TUBACOAT coating is vitrified above 800ºC which provides chemical bonding and "glass" properties, enhancing adherence, corrosion and erosion resistance compared to in-situ coatings

Product Characterization

Comparison with in-situ ceramic coatings

TUBACOAT	*Property*	In-situ ceramic coatings
↑ Chemical bonding (*)	**Thermal cycling resistance**	↓ Lack of bonding
↑ Low roughness	**Ash fouling resistance**	↓ High roughness
↑ Chemical bonding	**Mechanical resistance**	↓ Low adherence
↔ In factory & local weld coating	**On-site application**	↑ Direct application

(*) Ad-hoc engineering to match thermal expansion coefficient of substrate and coating in whole temp range

TUBACOAT coating is vitrified above 800ºC which provides chemical bonding and "glass" properties, enhancing adherence, corrosion and erosion resistance compared to in-situ coatings

Product Characterization

Chemical inertness & coking resistance

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Universidad del País Vasco Euskal Herriko Unibertsitatea

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

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

Product Characterization

Chemical inertness & coking resistance

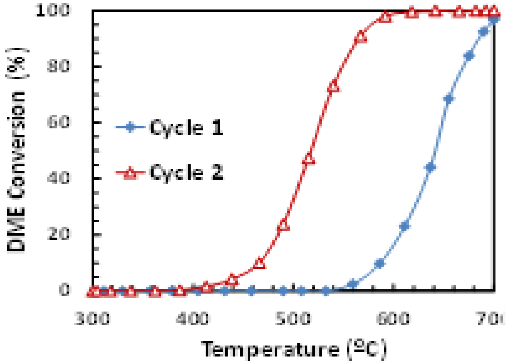
Chemical inertia and reproducibility

- Temperature = 300-700ºC
- Residence time = 60s
- Time on stream: 80 min

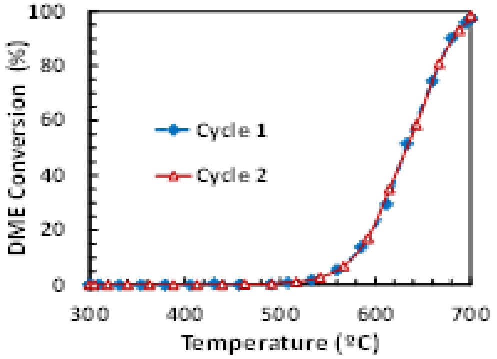
Degradation Temperatures

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

Without coating



With coating



Study of carbon deposition

Combustion conditions:

- Temperature= 300-700ºC
- Residence time = 6 s
- Time on stream(700ºC): CO2<0

Carbon deposited

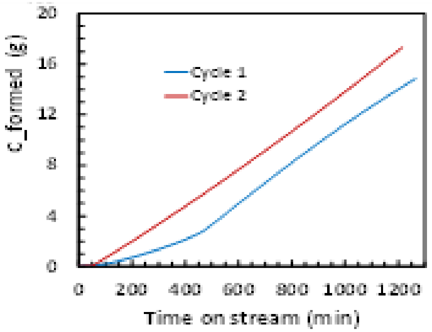
Integration of ($CO+CO_2$) curves

Study of carbon formation

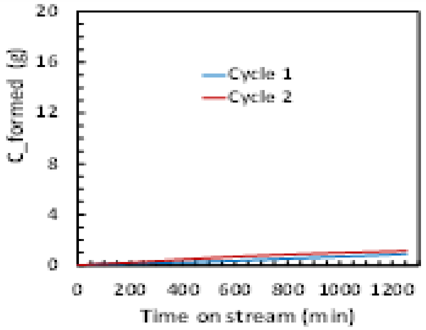
Calculation of carbon formed

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

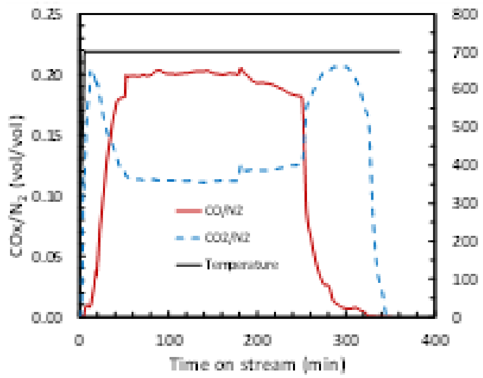
Without coating



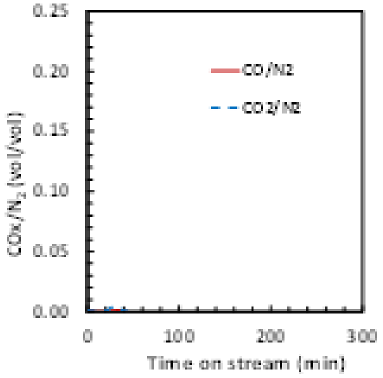
With coating



Without coating



With coating



Product Characterization

Chemical inertness & coking resistance

Summary of DME Degradation – Air Combustion Tests

Grade AISI 347		Non coated tube		Coated tube	
		Cycle 1	Cycle 2	Cycle 1	Cycle 2
DME Degradation	g DME Fed	97.5	94.7	96.9	97.5
	g DME degraded	91.2	90.9	88.9	89.6
	% DME degraded	93.6	96.0	91.7	92.0
	g C degraded	47.6	46.8	48.1	48.8
	g C gas ($CO+CH_4+CO_2$)	32.8	29.5	47.2	47.3
	g C solid formed	**14.8**	**17.3**	**0.89**	**1.54**
	% (gC solid formed/gC degraded)	**31.2**	**37.0**	**1.85**	**3.16**
Air Combustion	g C deposited	**14.6**	**15.7**	**0.016**	**0.017**
	%(gC deposited/gC formed)	98.2	90.8	1.79	1.13
	%(gC deposited/gC degraded)	**30.6**	**33.6**	**0.033**	**0.036**

Conclusions

- The chemical inertness of the coated tube surface avoids the parallel reactions occurring in the active sites present on the non-coated tube
- The carbon deposition-removal cycles (by DME degradation-air combustion) can be repeated without observing deterioration on the coated surface in contact with the gases
- The carbon formed is one order magnitude lower than on non-coated tubes due to the absence of parallel reactions forming soot (Boudouard reaction and CH_4 decomposition)
- The amount of carbon deposited is two order magnitude lower than on the non coated tube, and its percentage referred to carbon degraded is three order magnitude lower than on the non-coated tube

Field applications & Experience CASE 1

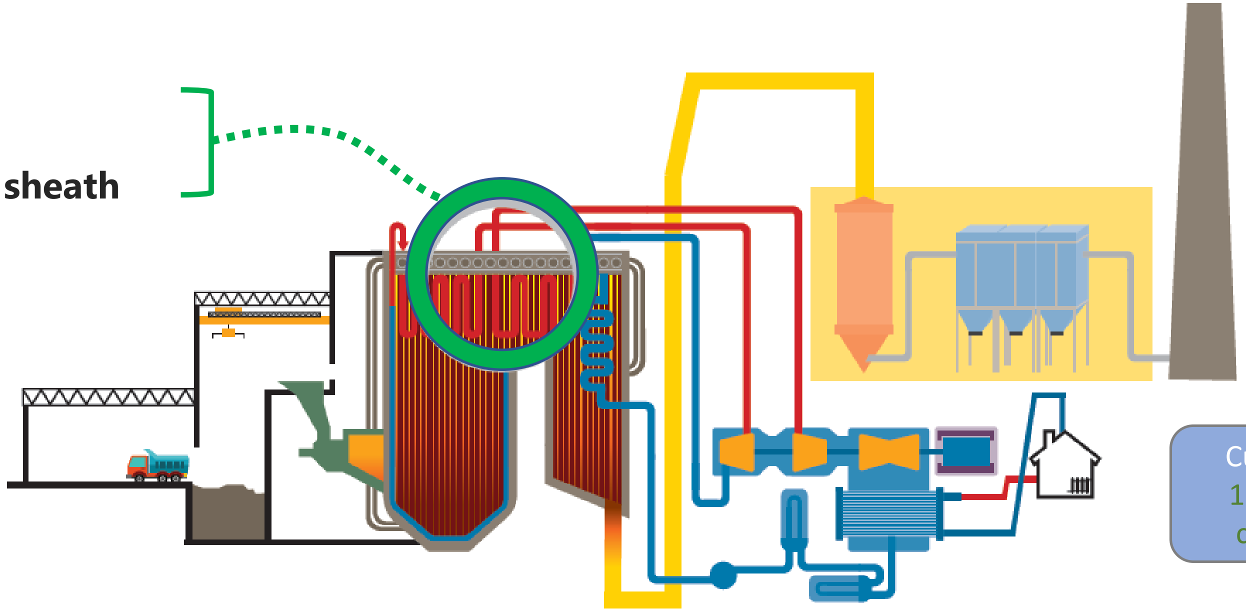
Steam reheater & Thermocouple sheath

Working conditions

Steam temperature	Pressure	Fumes temperature	Inner fluid media	Outter fluid media	Others
300 ºC	170 bar	850 ºC	Steam	W to E fumes	Alkaline ashes

Applications

- Steam reheater
- **Thermocouple sheath**



Current solution
16Mo3+Inconel cladding 4 mm

Chemical corrosion | Efficiency loss | High OPEX

Field applications & Experience CASE 1

Steam reheater

TP310H outer coated tubes
vs *16Mo3 + Inconel overlay*

TUBACOAT SOLUTION

First prototypes installed in 2014

Field applications & Experience CASE 1

Steam reheater

TP310H outer coated tube before boiler cleaning [plant stoppage]
(after 1 year service)

TP310H outer coated tube before boiler cleaning [plant stoppage]
(after 2 year service)

TP310H outer coated tube before boiler cleaning [plant stoppage]
(after 2 year service)

(a) 1st year tube cleaned

(b) 2nd year tube cleaned

Field applications & Experience CASE 1

Steam reheater

Results

- Low ash adherence
- Glossy surface after 4 years in operation
- Negligible loss of mass

PATENTED

Conclusions

- Excellent corrosion resistance
- Excellent coat bonding under thermal stress
- Homogeneous performance
- No ash adherence to outer surface

Major Improvements

- Longer tube life expectation
- Reduced cleaning and maintenance
- Improved thermal efficiency
- Possibility to increase thermal cycle temperature

Field applications & Experience CASE 2

Coke calciner

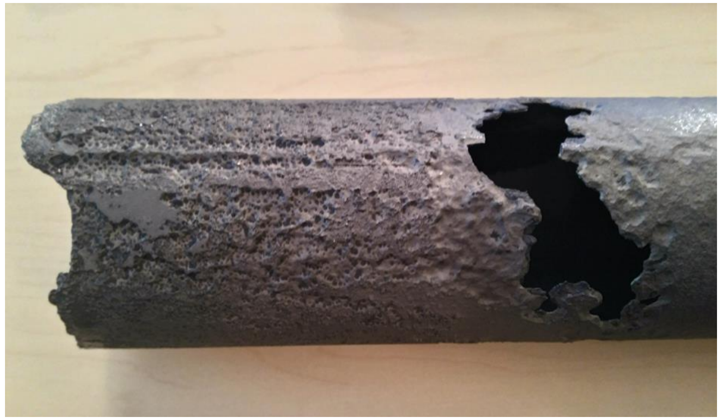
Application

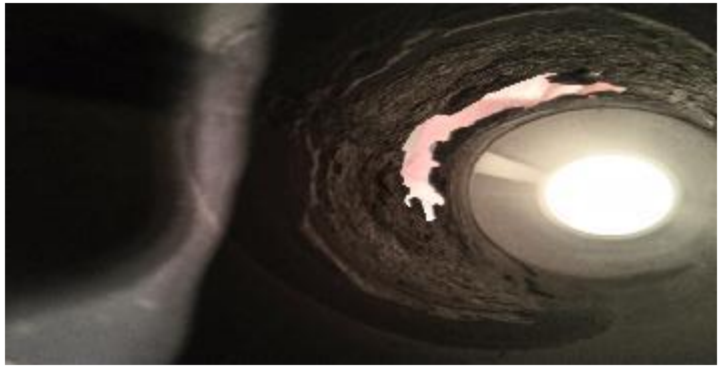
- Coke Calciner Recuperator

Working Conditions

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

Current solution
TP310 (bare)



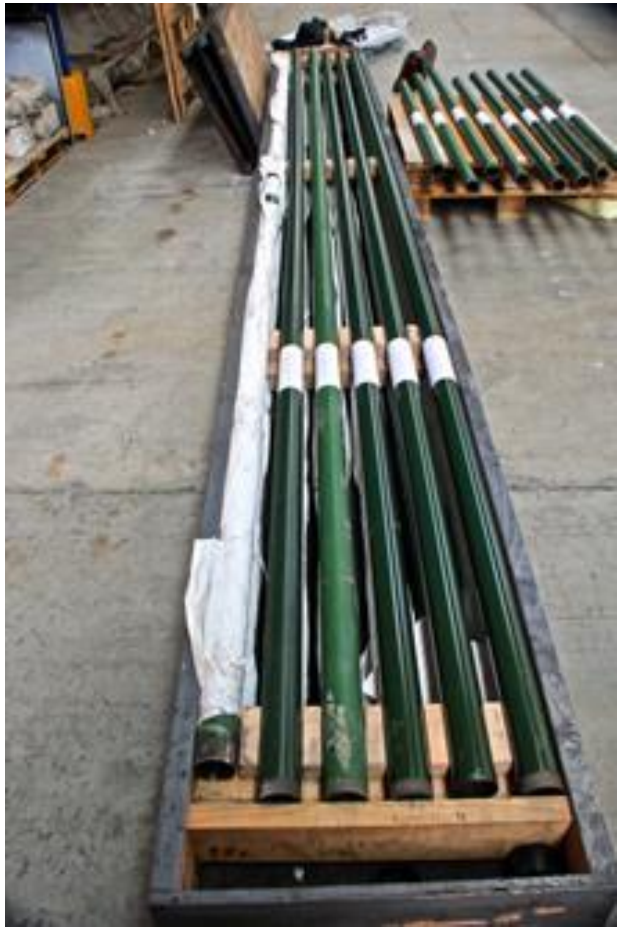


Chemical corrosion

Efficiency loss

Field applications & Experience CASE 2

Coke calciner



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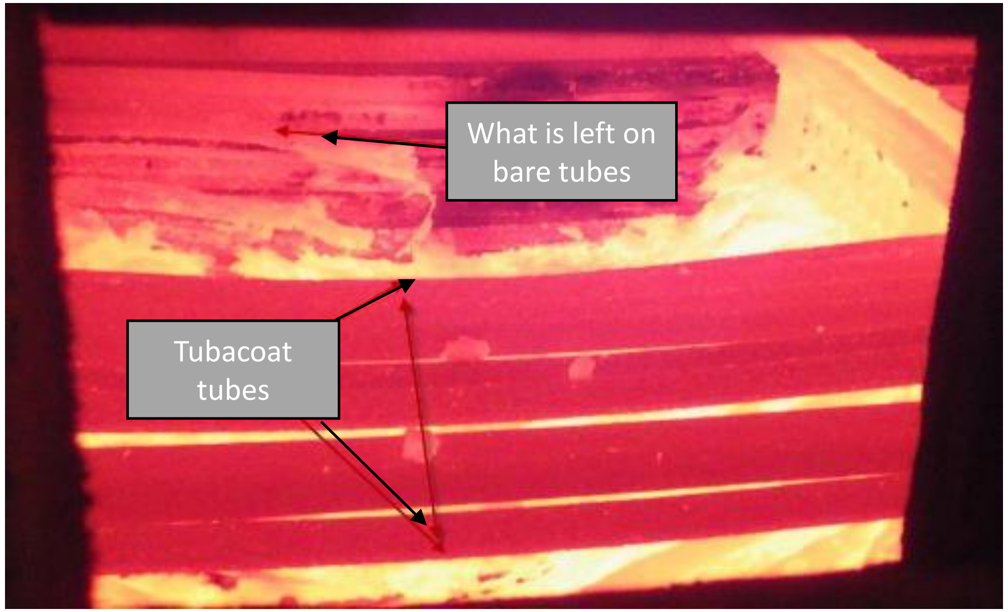
9 TP310 (OD63.5;WT2.41) outer coated prototypes were placed in the upper row (the hottest) of the calciner recuperator in May 2015

Field applications & Experience CASE 2

Coke calciner

TUBACOAT SOLUTION



(Image @ 10 months working)

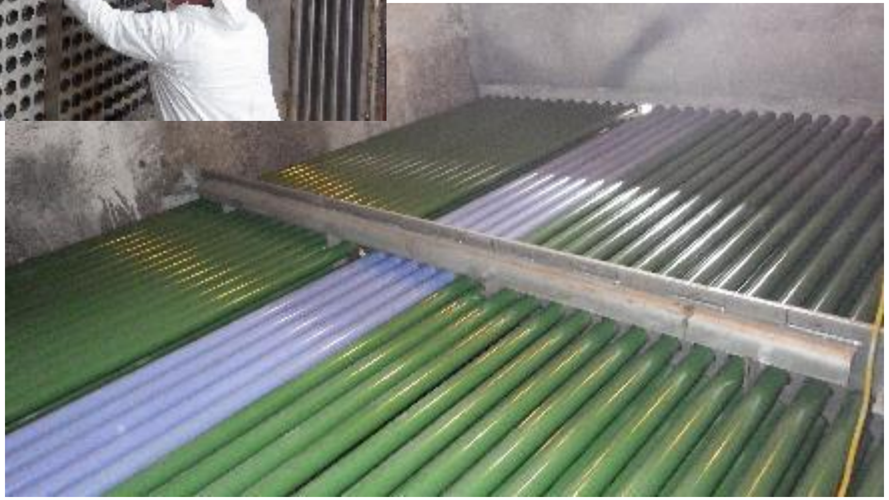
Only the 9 coated tubes were remaining in the area, even suffering overheating during last weeks of operation prior to planned plant shutdown

The rest of tubes were broken and blinded

Field applications & Experience CASE 2

Coke calciner

TUBACOAT SOLUTION

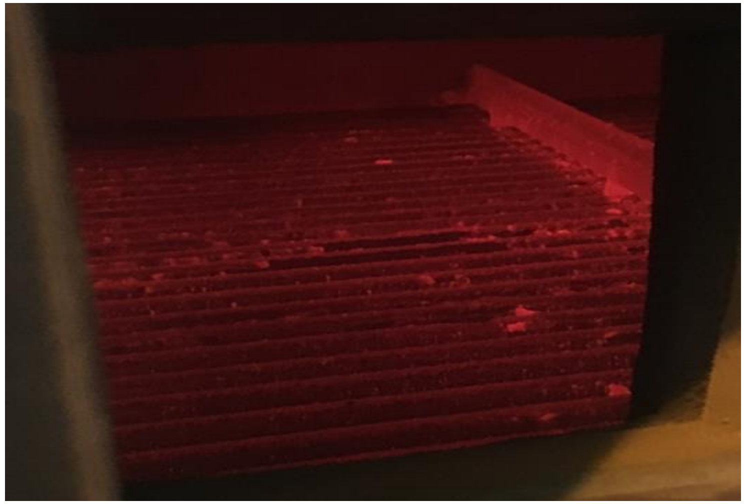


≈ 800 tubes (TP310 grade, OD63.5/WT2.41, outer coating), delivered to customer in Jan’2017 and installed in coke calciner in April 2017.

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

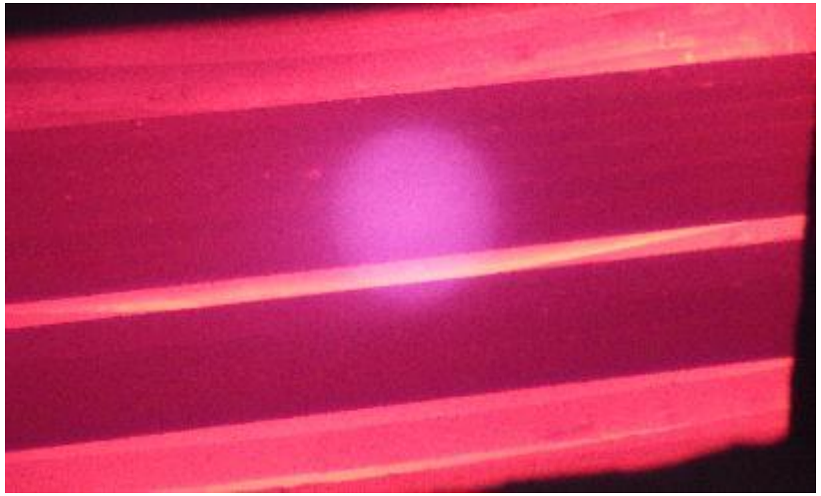
Field applications & Experience CASE 2

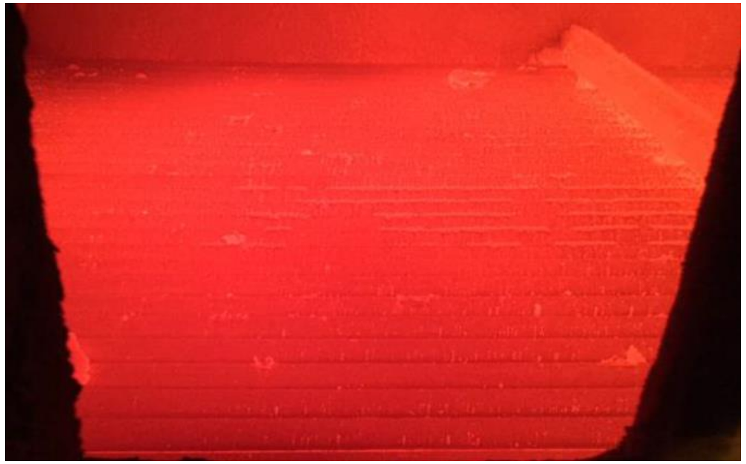
Coke calciner



TUBACOAT SOLUTION

Real pictures of coated tubes in coke calciner recuperator after 8 months running in full operation





Refinery

Anti-clogging

TUBACOAT ANTI-CLOGGING PROPOSAL

(Coker / Visbreaker / Crude distillation / IGCC downstream lines)

Commercial trial run in real application

- Vacuum Distillation Unit
- 317 Grade
- OD 141, WT 6.5, 5500 mm

Refinery

Corrosion/erosion

TUBACOAT CORROSION/EROSION RESISTANCE PROPOSAL

Overhead condenser

Commercial trial run in real application

- Crude Distillation Unit
- P235GH
- OD 30, WT 2.5, 5000 mm

Field Applications

On Site Welding Solution

On-site weld coating

Coated welds

Field Applications

Trials

Refinery & Petrochemical

BP
SHELL
CHEVRON
OMV
REPSOL
SILURIA
RELIANCE

Powergen & Others

CNIM
WOOD
KOBELCO
ANDRITZ
ZABALGARBI
ENCE
UT TEM
ST BIOMASS

Conclusion

TUBACOAT VALUE PROPOSAL & POTENTIAL APPLICATIONS

↑ ENERGY EFFICIENCY

↑ AVAILABILITY

- ❑ Coker (clogging)
- ❑ Visbreaker (clogging)
- ❑ Crude distillation (clogging)
- ❑ Desulphurization (corrosion)
- ❑ Process lines (corrosion/erosion)
- ❑ Heat exchanger (corrosion)
- ❑ Heat exchanger (clogging)

THANK YOU!

TUBACOAT PLANT IN CANTABRIA, SPAIN

WWW.TUBACEX.COM