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

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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...

✓ 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

Specifically developed to...
Product Characterization

Morphological

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

Substrate
Coating (140-160 μm)

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

Ra ≈ 1.5 μm and Rz ≈ 7.8 μm

Ceramic coating

Ra < 0.04 μm and Rz < 0.2 μm
Product Characterization

Mechanical

Abrasion resistance
≈ 94% decrease in mass loss

Mass loss for 10,000 cycles

\[ \Delta w_n = <w_0> - <w_n> \]

- Substrate
  \[ \Delta w_{10000} = 94.783 - 94.725 \]
  \[ \Delta w_{10000} = 58 \text{ mg} \]

- Ceramic coating (T153)
  \[ \Delta w_{10000} = 119.377 - 119.373 \]
  \[ \Delta w_{10000} = 4 \text{ mg} \]
Product characterization

Mechanical

Hardness & Elasticity
Coating is harder than substrate but less elastic

<table>
<thead>
<tr>
<th>Base Material</th>
<th>Ceramic coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HV)</td>
<td>220</td>
</tr>
<tr>
<td>Elastic Modulus EIT (GPa)</td>
<td>140</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Tensile results</th>
<th>$R_{p0.2}$ (MPa)</th>
<th>$R_{p1}$ (MPa)</th>
<th>$R_{p0.5}$ (MPa)</th>
<th>$R_m$ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288</td>
<td>323</td>
<td>301</td>
<td>582</td>
</tr>
</tbody>
</table>

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 (450°C / 10min) + Rapid water cooling (15°C)

<table>
<thead>
<tr>
<th>n Cycles</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
</table>

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 (20°C)

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MUMBAI
11–14 November 2019

TUBACOAT
TUBACEX GROUP
Product characterization

Emissivity

Emissivity values >0.80
Reference ≈ 0.83 (@ 550°C)

<table>
<thead>
<tr>
<th>Coating</th>
<th>VP15</th>
<th>VP15 + 25% SiO2</th>
<th>VP15 + 25% SiO2 + 25% PIG (Cr-Cu-Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>Inox 310</td>
<td>Inox 310</td>
<td>Inox 310</td>
</tr>
<tr>
<td>ROUGHNESS (Ra)</td>
<td>0.03</td>
<td>0.08</td>
<td>0.11</td>
</tr>
<tr>
<td>THICKNESS (µm)</td>
<td>112</td>
<td>108</td>
<td>112</td>
</tr>
</tbody>
</table>

AVG EMISIVITY AT 20°C 0.892 0.889 0.889
AVG EMISIVITY AT 550°C 0.834 0.838 0.832

MEASURING CONDITIONS

<table>
<thead>
<tr>
<th>Measurement method</th>
<th>SNEHT</th>
<th>Measurement method</th>
<th>SNHRRT/V1-MIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (T)</td>
<td>550°C</td>
<td>Temperature (T)</td>
<td>25°C</td>
</tr>
<tr>
<td>Polar angle (θ)</td>
<td>0°</td>
<td>Polar angle (θ)</td>
<td>12°</td>
</tr>
<tr>
<td>Spectral range</td>
<td>1.8 to 26 µm</td>
<td>Azimuth angle (φ)</td>
<td>0°, 45°, 90°, 135°</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Spectral range</td>
<td>2 to 20 µm</td>
</tr>
</tbody>
</table>
Rate of fouling

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

Baseline Fouling Plain CS Tube
Coated tube

Results after 7 months in test rig @ crude oil at 240°C

Significantly higher fouling avoidance of coated sample, and the eventual deposition is not adhered to surface, being easily removable with pressurized water.
High corrosion resistance compared to base material

Seawater corrosion test

- **Conditions:**
  - Solution: 3.5% NaCl at 22°C
  - Visual inspection

*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

<table>
<thead>
<tr>
<th>Molten salt Corrosion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Initial (t0)</strong></td>
</tr>
<tr>
<td><img src="image1" alt="Initial" /></td>
</tr>
<tr>
<td><strong>46 cycles (before cleaning)</strong></td>
</tr>
<tr>
<td><img src="image2" alt="46 cycles before cleaning" /></td>
</tr>
<tr>
<td><strong>46 cycles (after cleaning)</strong></td>
</tr>
<tr>
<td><img src="image3" alt="46 cycles after cleaning" /></td>
</tr>
</tbody>
</table>
Product Characterization

Chemical

High corrosion resistance compared to base material

Acid corrosion test

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

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

<table>
<thead>
<tr>
<th>Acid Corrosion Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 h</td>
</tr>
<tr>
<td>1000 h</td>
</tr>
<tr>
<td>2000 h</td>
</tr>
</tbody>
</table>

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Acid corrosion at boiling temperature

- **Conditions:**
  - Solution: boiling H2SO4 (30%)
  - 18 h (UNE-EN ISO 28706-2)
Product characterization

General

MORPHOLOGICAL
- Continuous coating layer
  Thickness control based on suspension parameters & rheological properties
- Roughness. \( Ra \) and \( R_z \) decrease \( \approx 97\% \) 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. \( \approx 94\% \) 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 \( \approx 5-8 \text{ W/mK} = f(T) \)
  - Average (reference) \( 6 \text{ W/mK} \)
## Product Characterization

### Comparison with in-situ ceramic coatings

<table>
<thead>
<tr>
<th>TUBACOAT</th>
<th>Property</th>
<th>In-situ ceramic coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Chemical bonding/Low porosity</td>
<td>Corrosion resistance</td>
</tr>
<tr>
<td></td>
<td>Low roughness</td>
<td>Clogging resistance</td>
</tr>
<tr>
<td></td>
<td>High hardness (64 HRC)</td>
<td>Abrasion resistance</td>
</tr>
<tr>
<td></td>
<td>Under development (*)</td>
<td>Radiation absorbance</td>
</tr>
</tbody>
</table>

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

TUBACOAT coating is vitrified above 800°C 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

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<tr>
<th>TUBACOAT</th>
<th>Property</th>
<th>In-situ ceramic coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td>Chemical bonding (*)</td>
<td>↓</td>
</tr>
<tr>
<td>↑</td>
<td>Low roughness</td>
<td>↓</td>
</tr>
<tr>
<td>↑</td>
<td>Chemical bonding</td>
<td>↓</td>
</tr>
<tr>
<td>↔</td>
<td>In factory &amp; local weld coating</td>
<td>↑</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TUBACOAT</th>
<th>Property</th>
<th>In-situ ceramic coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑</td>
<td>Thermal cycling resistance</td>
<td>↓ Lack of bonding</td>
</tr>
<tr>
<td>↑</td>
<td>Ash fouling resistance</td>
<td>↓ High roughness</td>
</tr>
<tr>
<td>↑</td>
<td>Mechanical resistance</td>
<td>↓ Low adherence</td>
</tr>
<tr>
<td>↔</td>
<td>On-site application</td>
<td>↑ Direct application</td>
</tr>
</tbody>
</table>

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

TUBACOAT coating is vitrified above 800°C which provides chemical bonding and “glass” properties, enhancing adherence, corrosion and erosion resistance compared to in-situ coatings.
Product Characterization

Chemical inertness & coking resistance

- DME cracks towards the equimolecular CO, H₂ and CH₄ (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: \( \text{CH}_3\text{OCH}_3 \xrightarrow{\Delta} \text{CH}_4 + \text{CO} + \text{H}_2 \) (1)

Boudouard reaction: \( 2\text{CO} \Leftrightarrow \text{CO}_2 + \text{C} \downarrow \) (2)

Methane decomposition: \( \text{CH}_4 \Leftrightarrow \text{H}_2 + \text{C} \downarrow \) (3)

Reverse-Water Gas Shift: \( \text{CO}_2 + \text{H}_2 \Leftrightarrow \text{CO} + \text{H}_2\text{O} \) (4)
Product Characterization

Chemical inertness & coking resistance

Chemical inertia and reproducibility

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

Degradation Temperatures

<table>
<thead>
<tr>
<th>Cycle</th>
<th>NON COATED</th>
<th>COATED</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>587</td>
<td>466</td>
</tr>
<tr>
<td>TSO</td>
<td>641</td>
<td>518</td>
</tr>
<tr>
<td>TSO</td>
<td>663</td>
<td>632</td>
</tr>
<tr>
<td>TSO</td>
<td>482</td>
<td>546</td>
</tr>
<tr>
<td>TSO</td>
<td>580</td>
<td>682</td>
</tr>
</tbody>
</table>

Without coating

With coating

Study of carbon formation

Calculation of carbon formed

\[(DME)_{\text{in}} - (DME + CO + CO_2 + CH_4)_{\text{tot}}\]

Study of carbon deposition

Combustion conditions:
- Temperature = 300-700°C
- Residence time = 6 s
- Time on stream (700°C): CO2 < 0

Carbon deposited

Integration of \((CO + CO_2)\) curves
# Product Characterization

## Chemical inertness & coking resistance

### Summary of DME Degradation – Air Combustion Tests

<table>
<thead>
<tr>
<th>Grade AISI 347</th>
<th>Non coated tube</th>
<th>Coated tube</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cycle 1</td>
<td>Cycle 2</td>
</tr>
<tr>
<td>g DME Fed</td>
<td>97.5</td>
<td>94.7</td>
</tr>
<tr>
<td>g DME degraded</td>
<td>91.2</td>
<td>90.9</td>
</tr>
<tr>
<td>% DME degraded</td>
<td>93.6</td>
<td>96.0</td>
</tr>
<tr>
<td>g C degraded</td>
<td>47.6</td>
<td>46.8</td>
</tr>
<tr>
<td>g C gas (CO+CH₄+CO₂)</td>
<td>32.8</td>
<td>29.5</td>
</tr>
<tr>
<td>g C solid formed</td>
<td>14.8</td>
<td>17.3</td>
</tr>
<tr>
<td>% (gC solid formed/gC degraded)</td>
<td>31.2</td>
<td>37.0</td>
</tr>
<tr>
<td>g C deposited</td>
<td>14.6</td>
<td>15.7</td>
</tr>
<tr>
<td>% (gC deposited/gC formed)</td>
<td>98.2</td>
<td>90.8</td>
</tr>
<tr>
<td>% (gC deposited/gC degraded)</td>
<td>30.6</td>
<td>33.6</td>
</tr>
</tbody>
</table>

### 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 CH₄ 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: 300 °C
- Pressure: 170 bar
- Fumes temperature: 850 °C
- Inner fluid media: Steam
- Outer fluid media: W to E fumes
- Others: 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 re heater

TP310H outer coated tubes vs 16Mo3 + Inconel overlay

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)

Tubes untouched, without cleaning

(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

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

PATENTED
Field applications & Experience CASE 2

Coke calciner

**Application**
- Coke Calciner Recuperator

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

Current solution
TP310 (bare)

Chemical corrosion  Efficiency loss
Field applications & Experience CASE 2

Coke calciner

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.
Field applications & Experience CASE 2

Coke calciner

≈ 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

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

OUTER COATING

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**

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

↑ ENERGY EFFICIENCY

↑ AVAILABILITY
THANK YOU!

TUBACOAT PLANT IN CANTABRIA, SPAIN

WWW.TUBACEX.COM