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CONFERENCE & EXPO
AMERICAS

Fouling resistance test on Ceramic Coated Tubes via Dimethyl Ether degradation

Sanjay Lodha, Global Business Director – Tubacoat S.L.

Agenda

- Fouling in Refining & Petrochemical applications
- Tubacoat Solutions
- Fouling Resistance Tests
- Conclusions
- Case Study

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Fouling in Refining & Petrochemical applications

Fouling has been described as the major unresolved problem in heat transfer equipment. Operators spend trillions of dollars worldwide on annual basis servicing and replacing heat transfer equipment where different types of fouling are present

Fouling-related costs can be broken down into four main areas:

- Higher capital expenditures for oversized plants which includes excess surface area (10-50%), costs for extra space, increased transport and installation costs.
- Energy losses due to the decrease in thermal efficiency and increase in the pressure drop.
- Production losses during planned and unplanned plant shutdowns for fouling cleaning.
- Maintenance & cleaning of heat transfer equipment and use of antifoulants

Fouling in Refining & Petrochemical applications

Fouling can be classified as:

- Sedimentation or particulate fouling
- Crystallization or Precipitation fouling
- Chemical reaction fouling
- Corrosion fouling
- Biological fouling
- Solidification or freezing fouling

Examples of different types of Fouling on Heat Transfer Equipment

Agenda

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- **Tubacoat Solutions**
- Fouling Resistance Tests
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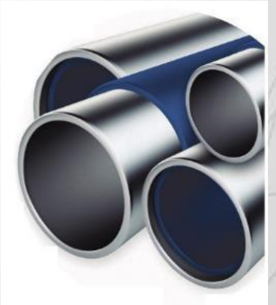
- Case Study

Tubacoat Solutions

Tubacoat is a Silica-Based Ceramic Coating for High Temperature conditions (up to 1,400°F/ 750°C) applied to tubular products to improve fouling, corrosion and erosion problems. Our coatings can be applied via Spray, Dipping, Waterfall glazing, Electropolishing Deposition (EPD) methods depending the application.

Ceramic Coating Properties:



- Anti-Adherent and Anti-Fouling
- Chemical Inertness
- Low Roughness ~ 0.3 µm
- High Hardness ~ 64 HRC
- High Abrasion resistance
- High Corrosion resistance
- Good Thermal Shock resistance
- Avg. Thickness 0.15 mm

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Tubacoat Solutions

Ceramic coatings can be applied to different substrates such as Carbon Steel, Low Chromes, Austenitic Stainless Steels and Nickel Alloys on the Outside Diameter (external surface) or to the Internal Diameter (internal surface) of tubular products (tubes and fittings) ranging from ¾" to 10" OD for different applications.

External surface

Internal surface

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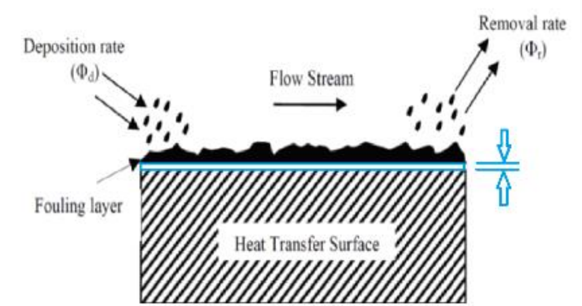
Tubacoat Solutions

The ceramic glass-finished layer will protect the inner or outer surface of the tubes of any heat transfer equipment

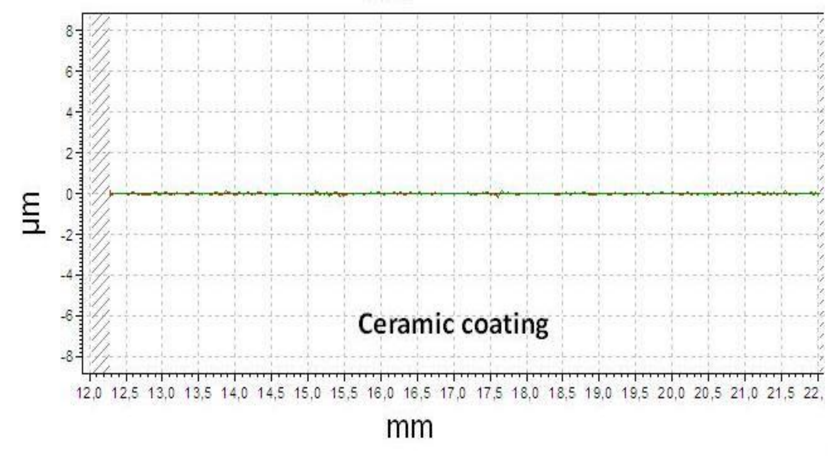


- ⬇ Deposition Rate will decrease due to its chemical inertness
- ⬆ Removal Rate will increase due to its anti-adhearence properties
- ⬇ Heat Transfer loss will improve due to lower fouling layer
- ⬆ Fluid Flow will maintain/increase the stream

Tubacoat Solutions

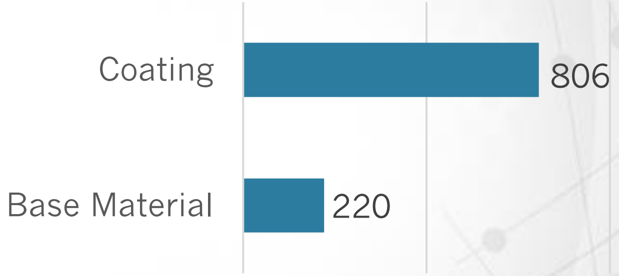
Performance Values

Roughness



Ra < 0.04 µm and Rz ≈ 0.3 µm

Hardness [HV]



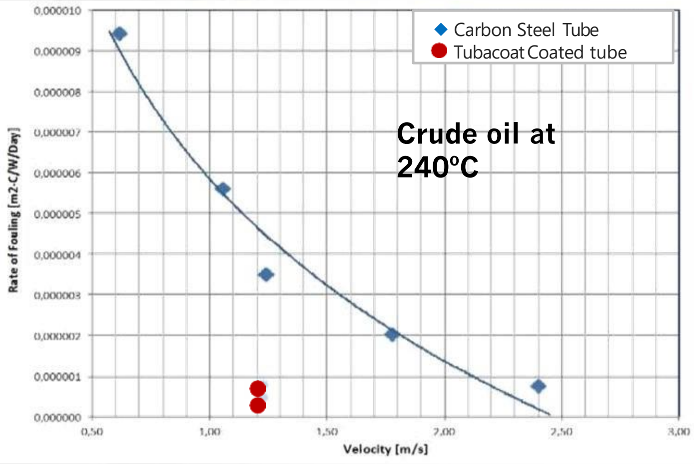
4 times harder tan base material

According to ASTM C 1327-03

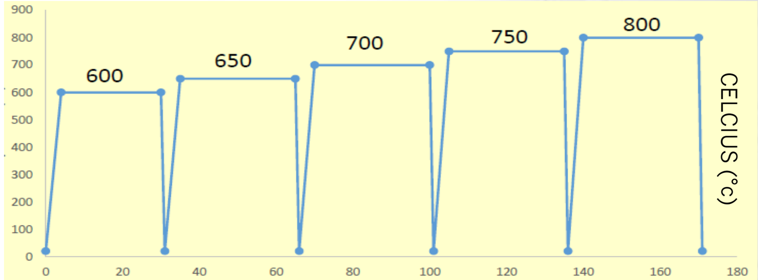
Tubacoat Solutions

Performance Values

Fouling Resistance



Thermal cycling Resistance



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

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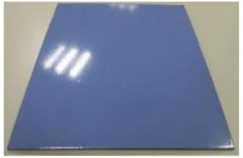
Tubacoat Solutions

Performance Values

Acid corrosion at boiling temperature

Conditions:

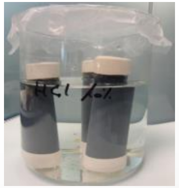
- Solution: boiling H_2SO_4 (30%)
- 18 h (UNE-EN ISO 28706-2)

Acid corrosion at boiling T	
Liquid Contact	
Vapour Contact	

Acid corrosion test HCL

Conditions:

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



Acid Corrosion Test	
0 h	
1000 h	
2000 h	

Tubacoat Solutions

TUBACOAT coating is vitrified above 800ºC (1500ºF) 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

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

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Fouling Resistance Test

Universidad del País Vasco / Euskal Herriko Unibertsitatea

Dimethyl ether (DME) at 700ºC has been used as reaction to generate carbon deposits over tube inner surfaces and compare the behavior between non-coated and coated specimens.

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

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)

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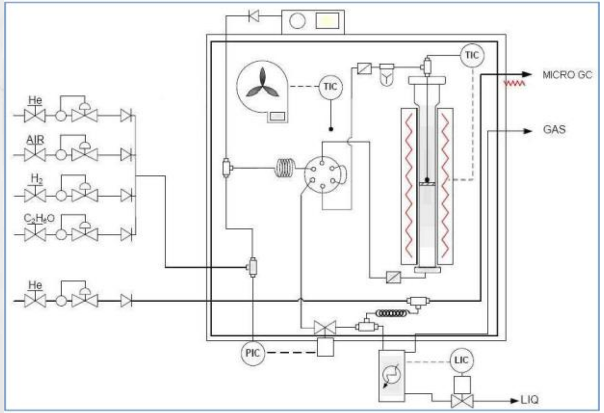
Fouling Resistance Test

- The testing rig was equipped with a tube sample located in a heated chamber and connected on-line to a gas chromatograph



Samples:

- 347H SS tubes
- 21mm ID
- 400mm length

- Feed Stream:
  - DME (Air Liquide, 99.99%) as reactive gas;
  - N2 (Air Liquide, 99.99%) as inert gas, and;
  - Purified air (Carburos M, 99.99%) as comburent.

Fouling Resistance Test

RESULTS

DME Degradation step

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

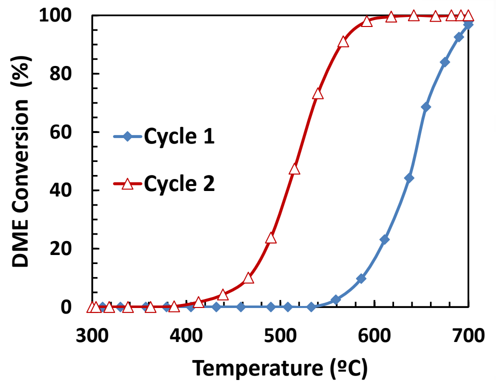
Cracking Study (Cycle 1)

- Temperature = 700ºC
- Residence time = 60s
- Time on stream: 20 h

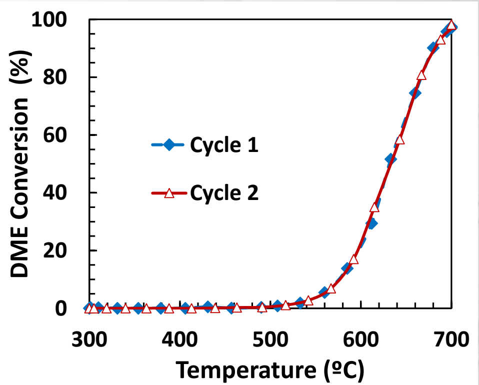
High H_2 + presence of (CO_2+H_2O) in the non coated tube

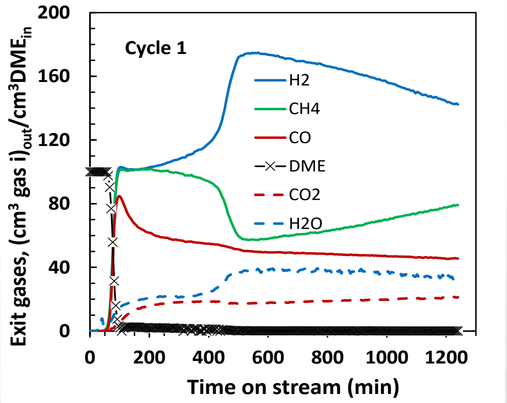
high solid carbon formation on non coated tube

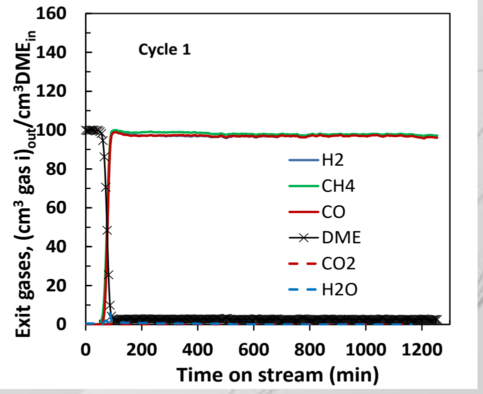
Without coating



With coating







Fouling Resistance Test

RESULTS

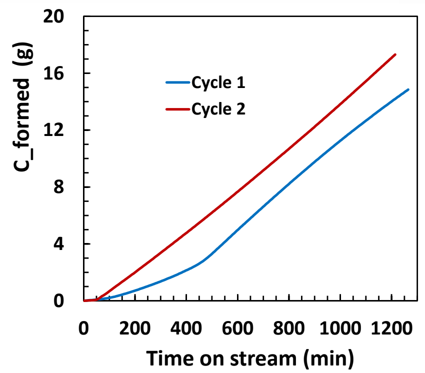
DME Degradation step

Study of carbon formation

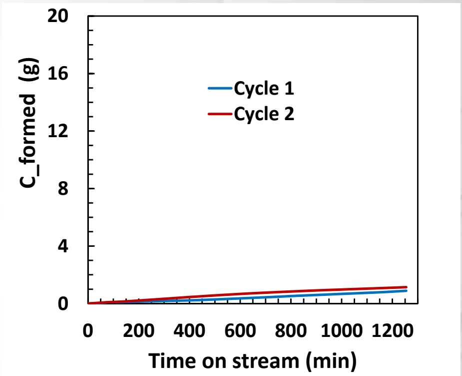
Calculation of carbon formed

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

Without coating



With coating



Study of carbon deposition

Air combustion (Cycle 1)

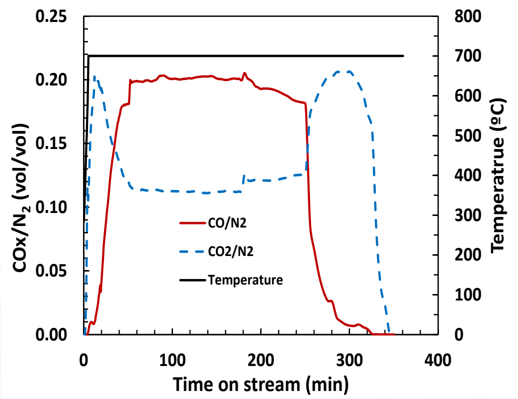
Combustion conditions:

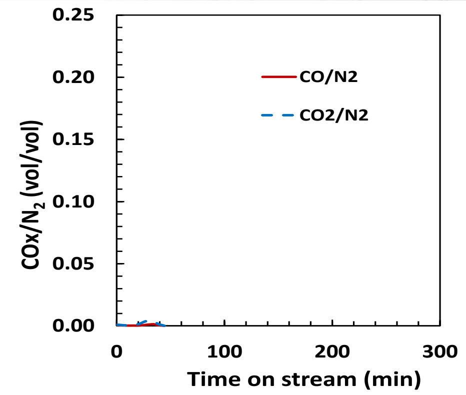
- Temperature= 300-700ºC
- Residence time = 6 s
- Time on stream(700ºC): CO2<0.1%

Carbon deposited

Integration of $(CO+CO_2)$ curves

high carbon deposition on non-coated tube





Fouling Resistance Test

Summary of Fouling Resistance tests on ceramic coated tubes via Dimethyl Ether degradation.

		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
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

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Conclusions

Fouling Resistance Test

- 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

Carbon deposition is an undesired side product, significantly inhibiting heat transfer as well as leading to performance degradation

Conclusions

Applying TUBACOAT to ID/OD Tubular products 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
  - Coating layer of 0.20 mm is applied on high quality base material steel grade

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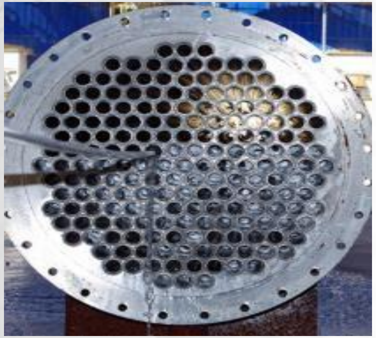
Case Study

CDU and VDU preheat exchangers



Fouling has been described as the major unresolved problem in heat transfer.

It is especially critical in preheat trains of CDU and VDU units:

- **Reduced heat transfer** efficiency
- **Frequent cleaning** required
- **High pressure drop**
- **Tube deformation** due to hotspots

PROBLEM DESCRIPTION

Case Study

CDU and VDU preheat exchangers

TUBACOAT anti-fouling inner coating

TUBACOAT SOLUTION

- Increased fouling resistance
- Increased heat transfer and reduced pressure drop
- Avoids frequent cleaning
- Avoids hotspots

Case Study

CDU and VDU preheat exchangers

RESULTS

Estsimated economic savings for 200,000 barrel/day CDU: **2 million USD/year**

- **Fouling factor decreased more than 3 times**
- Higher heat transfer efficiency
- Lower cleaning frequency
- Reduced maintenance costs

Case Study

Condenser corrosion

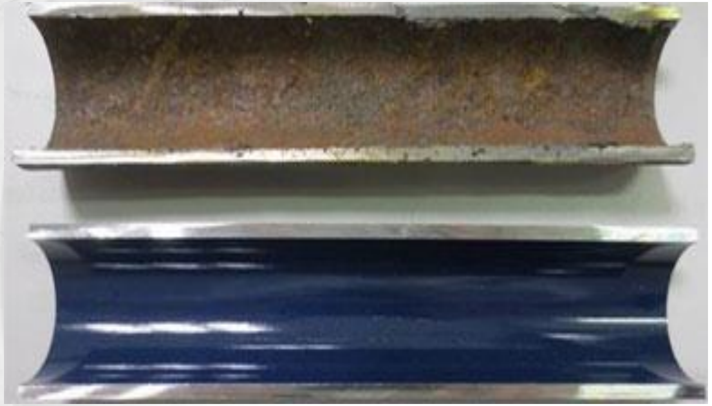
Corrosion in condensers is one of the most common problems in refineries and chemical plants, causing:

- **Unplanned shutdowns**
- **Frequent tube replacement**
- High maintenance and inspection costs
- Safety issues

Condensers are critical equipment subject to corrosion in many applications such as Sulfur recovery units, CDU, Hydrotreating or chemical plants

Case Study

Condenser corrosion



Condenser tube

Condenser tube with Tubacoat internal coating

Tubacoat can be applied on the inner or outer surface of condenser tubes to avoid corrosion caused by many different corrosive media such as nitric acid or sulfuric acid.

Corrosion in condensers many times starts under deposits. In these cases, Tubacoat anti-fouling properties further enhance corrosion resistance.

Case Study

Condenser corrosion

RESULTS

Tubacoat has been applied in different type of condensers **increasing tube life**:

- Sulfur condenser in SRU
- Nitric acid cooler condenser
- CDU overhead condenser
- Flue gas condenser

THANK YOU!

TUBACOAT PLANT IN CANTABRIA, SPAIN

Sanjay Lodha, Global Business Director
slodha@tubacex.com
+91996021500