Ethylene Middle East Technology Conference

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Emisshield®

Energy Enhancing Systems

Dr. John Olver PhD, P.E.

Impact on Process Tube Coking and Process Heat Transfer by High-Emissivity Coating Systems

Presentation: Two Step Process- Radiant Wall / Process Tubes

- Radiation in gas fired furnaces
- High Emissivity coating properties
- Furnace simulation with High Emissivity coating
- Process Tube Coking
- Process Tube performance with High Emissivity coatings

Thanks to REI and Dr. Brad Adams

Note: Phillips Petroleum installed the first HE Coating on refractory walls in 1997 and got a 6% production increase.

Furnace Radiative Heat Transfer

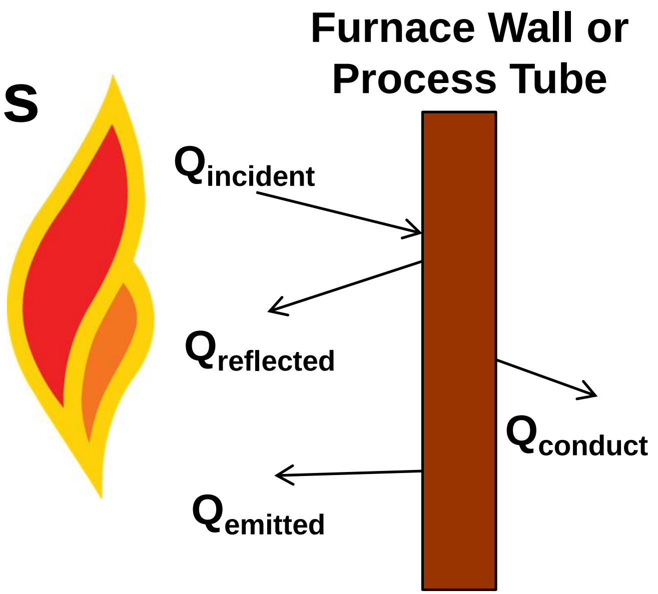
Flames / heat source radiate to furnace walls and process tubes

Surfaces absorb and reflect incoming radiation

- Absorbed radiation is either reemitted or conducted into surface
- Non-absorbed radiation is reflected back into gas

Better to reflect or reemit incident radiation?

- Reflection = low emissivity
- Absorption / emission = high emissivity
- Heat Flow - Hot to cold - $T_1 > T_2$

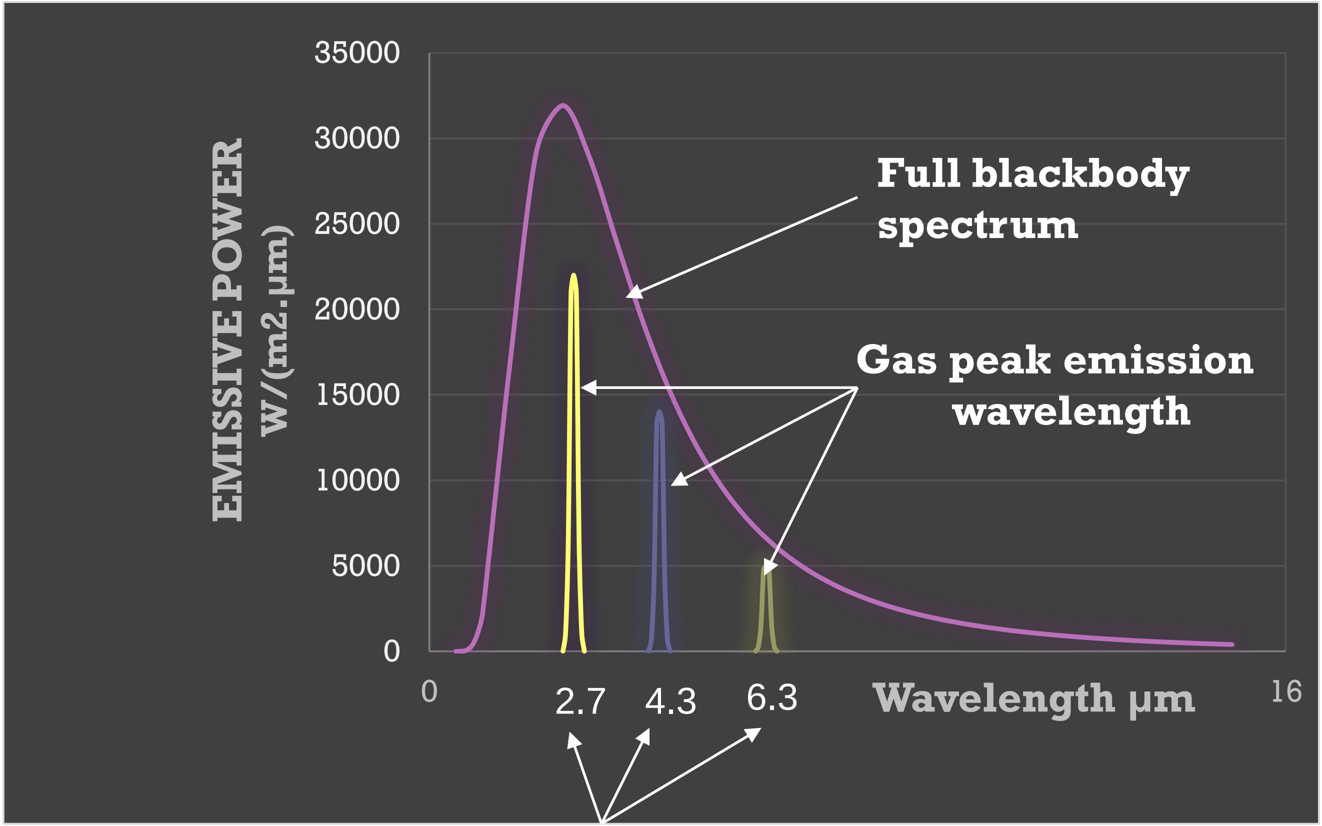


$$Q_{inc} = Q_{refl} + Q_{emit} + Q_{cond}$$

Natural Gas Absorption / Emission Bands

Natural Gas emits and absorbs radiation only at absorption band wavelengths; gas is transparent in between bands

Most surfaces emit radiation over full wavelength spectrum (similar to blackbody)

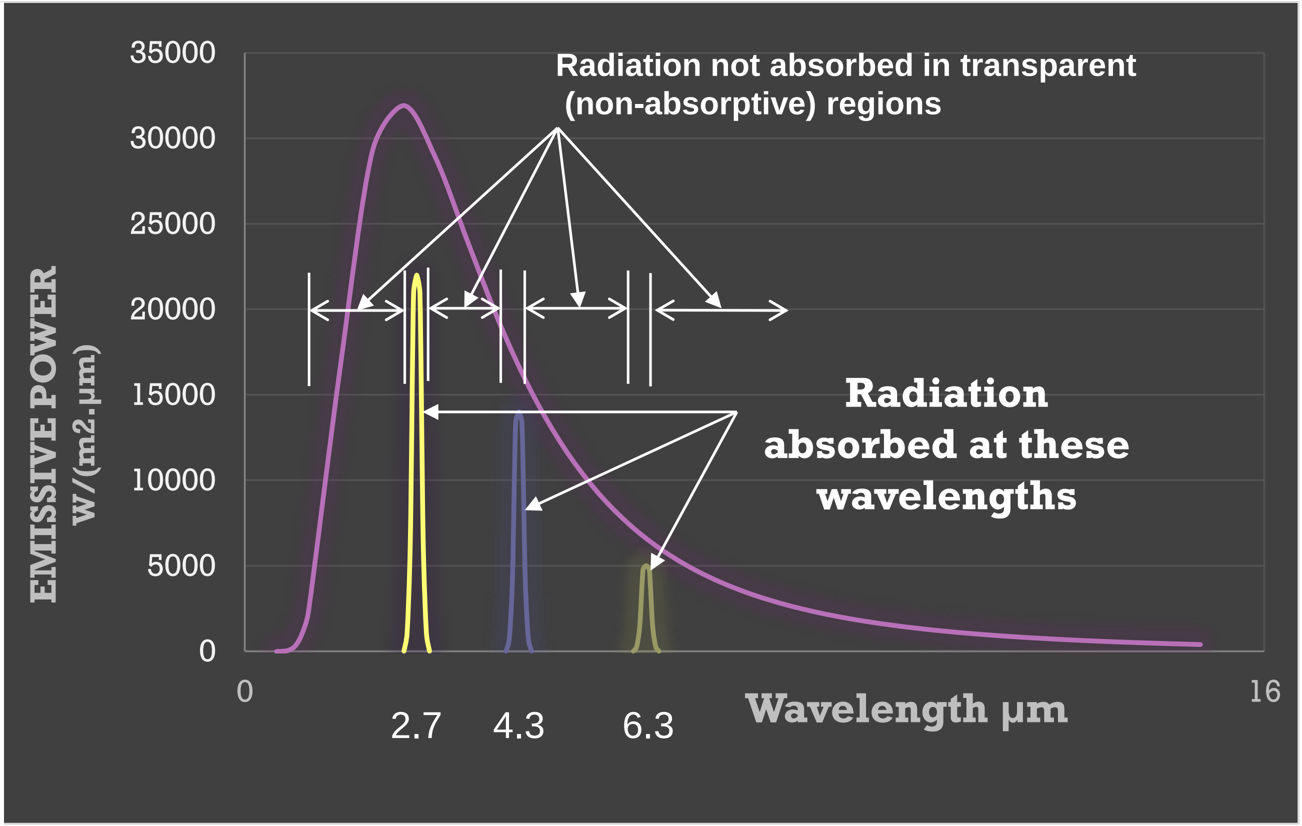


Main absorption wavelengths in combustion gases (H_2O, CO_2)

Reflection vs Emission

Radiation *reflected* by walls is partially reabsorbed by gas

Radiation *emitted* by walls is mostly transmitted through transparent bands

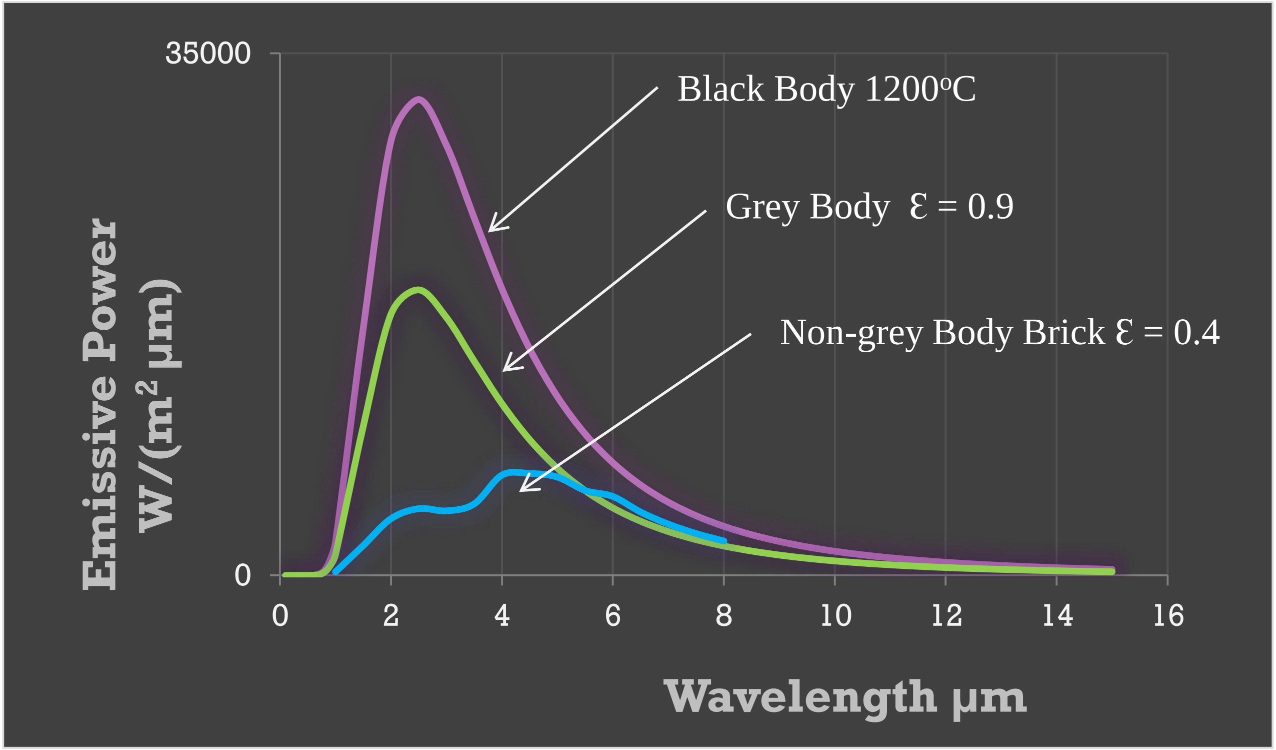


*** Reducing the amount of reflected radiation reduces the amount of radiant energy reabsorbed in the gas and increases furnace radiant efficiency.**

High Emissivity Coatings on Refractory Walls

Coating increases surface emissivity and absorptivity

- For Ɛ = 0.9, 90% of incident radiation is absorbed and reemitted
- More emitted radiation transmitted through transparent gas regions
- Less reflected radiation reabsorbed in gas
- Increases radiant efficiency



Emisshield® coating behaves nearly as a blackbody

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CFD Wall Simulation Summary

By Reaction Engineering International

Parameter	Case1	Case2
Wall Emissivity	0.4	0.9
Firing Rate (MW)	15.26	15.26
Flue Gas Exit Temperature (°C)	1,223	1,194
Tube Heat Absorption (MW)	5.95	6.18
Max Tube Temperature (°C)	1,352	1,356
Fluid Outlet Temperature (°C)	855	859
Casing Loss (% of firing rate)	1.6	1.6
Furnace Efficiency (%)	39.0	40.5

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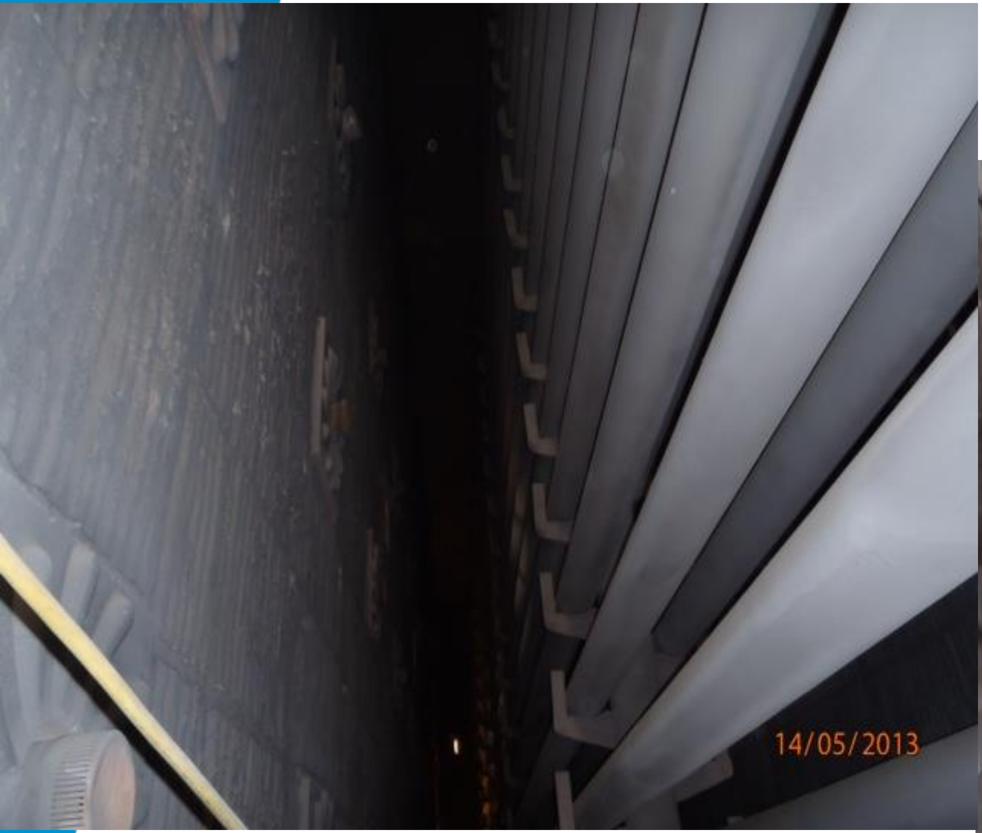
Furnace Radiant Wall CFD, HE Coating Summary

High emissivity coatings improve radiant efficiency by increased refractory absorption and reemission.

Application in cracking furnaces showed:

- **6% fuel savings with 9% reduction in steam production**
- **5% fuel savings with 6% increase in production output and doubling of time between de-coke cycles**
- **Must Re-optimize the furnace!**

Why and When To Coat Process Tubes?



Mechanisms For Coke Formation

- Heterogenous Catalytic
- Homogenous Droplets
- Heterogenous Free-Radical

TMT / Reaction rates / Tube Metallurgy

- *Munoz, Van Geem, Reyniers and Maren; "Industrial and Engineering Chemistry Research" 2014*

Reduction of Coking Technologies

- Three Dimensional Reactor Technologies
- Surface Technologies – Coatings and Oxide Formation from Metallurgy
- Feed Additive Technologies
- Ceramic Process Tubes

Process Tube Material Issues

Catalyst to Coking

Fe

Ni

Metallurgy Changes

High Ni/Cr

HP- Nb

Aluminum Enriched Alloys

Development of Cr, Al, Ni oxide layer on tube exterior

Hemispherical Emissivity Results

TPRL-ASTM C835-06

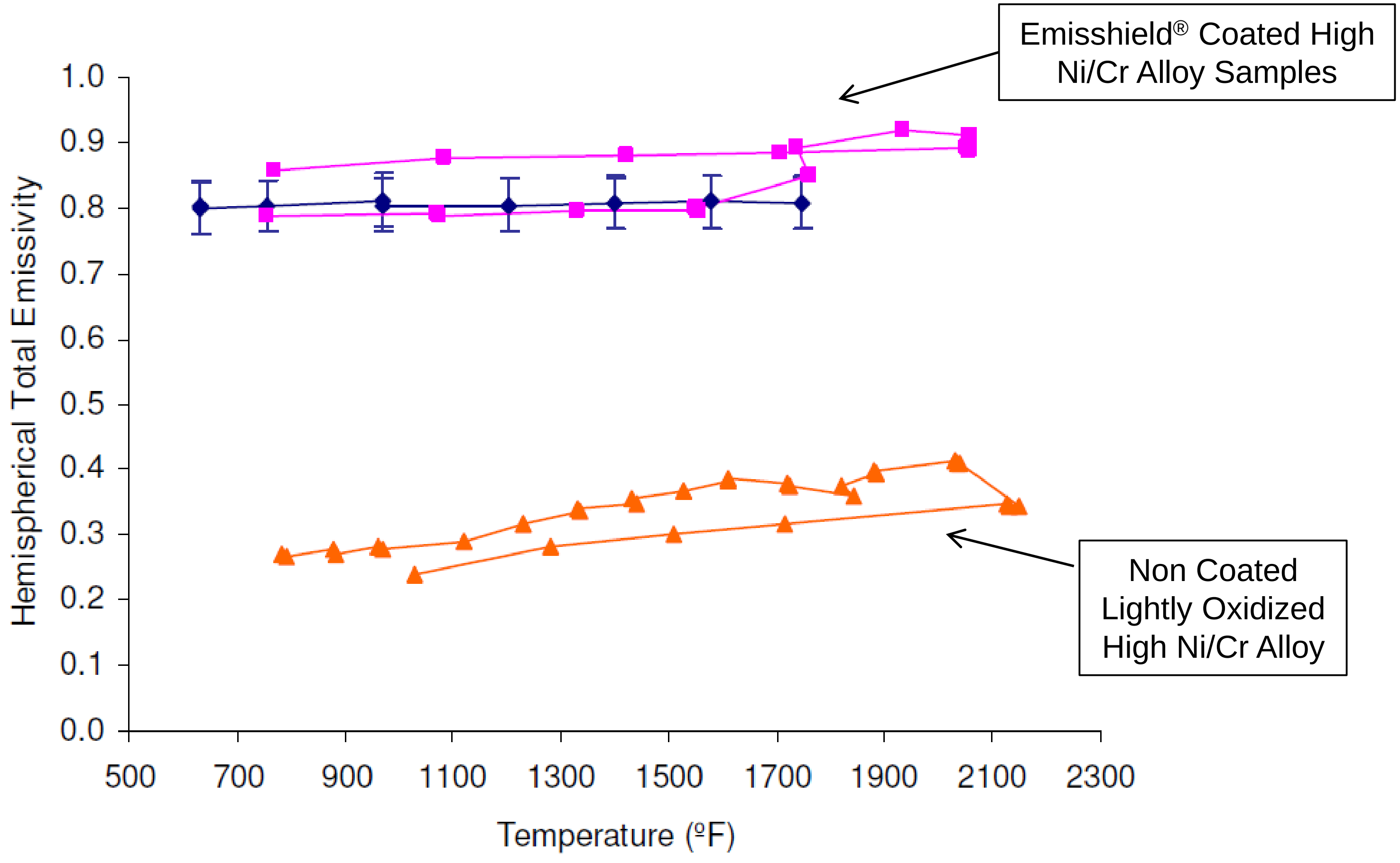


Figure 1. Hemispherical Total Emissivity

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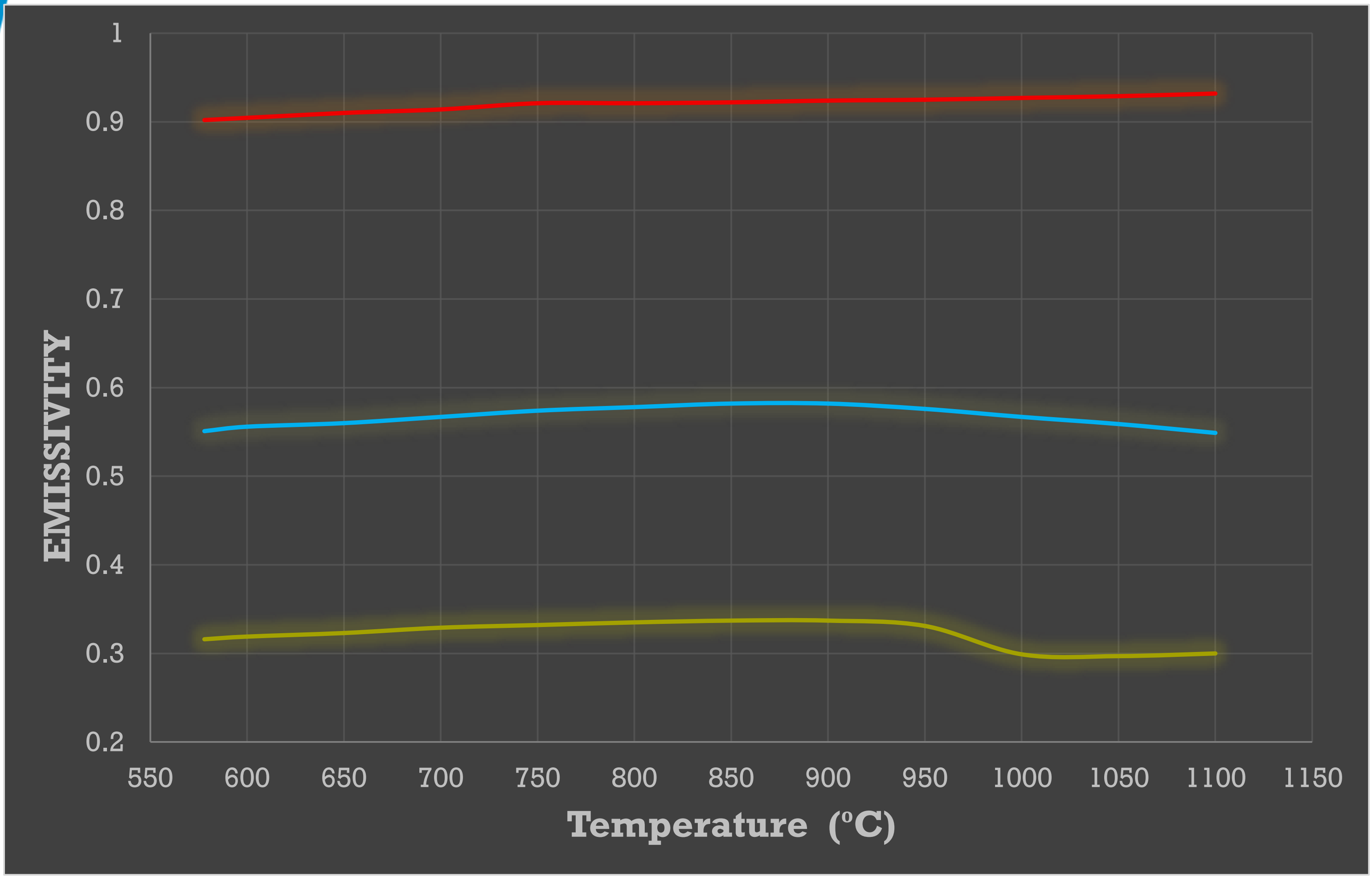
Hemispherical Emissivity of High Ni/Cr Petrochemical Process Tubes

Emisshield IP-113 Coated — Uncoated Grit Blasted & Thermal Oxidized — Uncoated Lightly Oxidized



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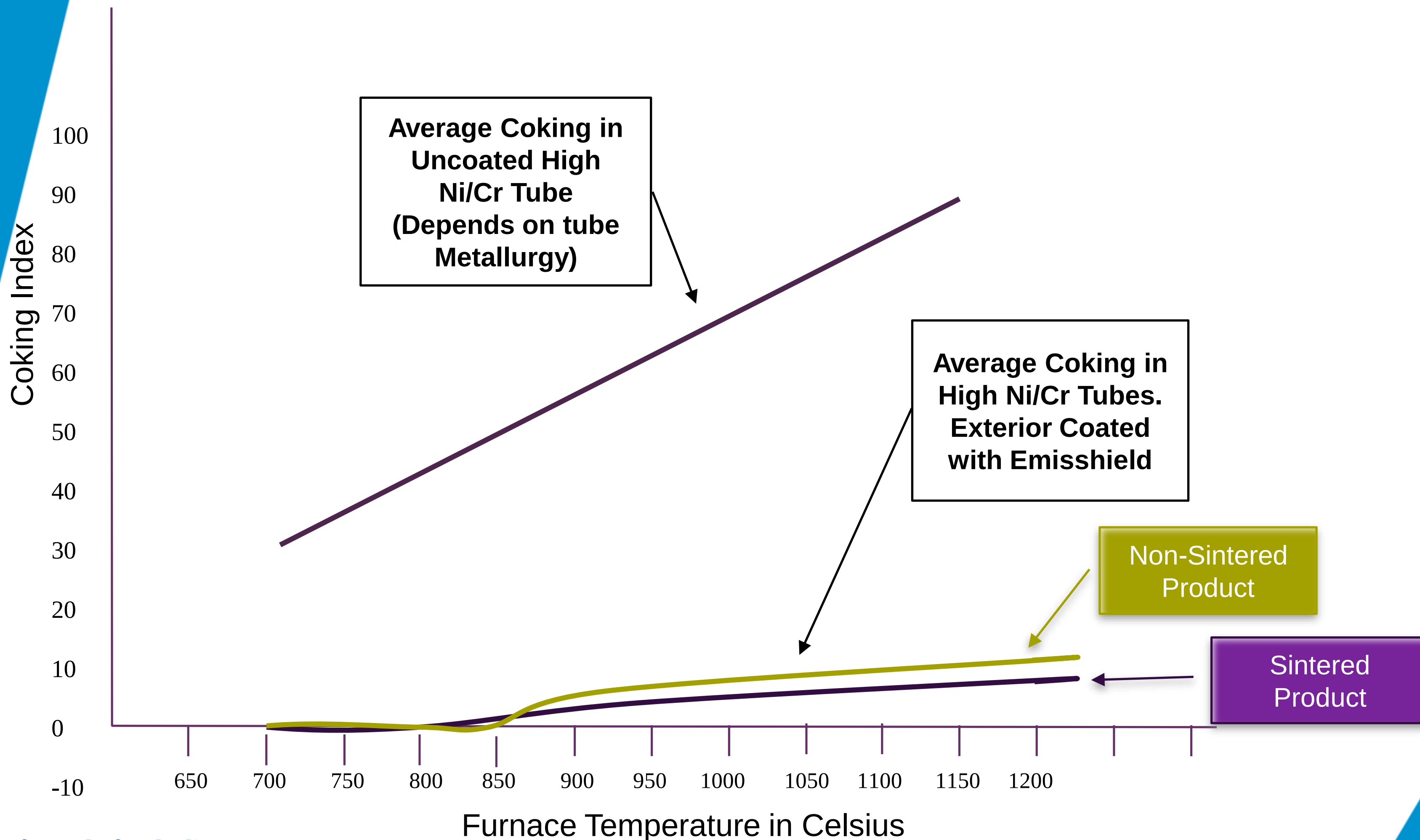
Process Tube Emissivty Theory Issues

Question:	Observations:
- **Does** higher emissivity on tube exterior surface reduce coking (Composite Tube)?	**Yes**, it may as an Intrinsic not Apparent emissivity.
- **Does** higher Intrinsic emissivity Lower TMT and improve reaction rate?	**Yes**, It lowers TMT (Up to 60°C), which may lead to less coke formation and the increased heat flux leads to improved reaction rate.
- **Does** ceramic coating with Intrinsic emissivity on tube exterior reduce tube exterior/interior hot spots?	**Yes**, and that, in turn, may reduce hotspots on tube interior and oxide nucleation sites - thus less coke.

Coking Index Ethylene Pilot Plant Continuous Flow



EMISSHIELD COATING Exterior of Process Tubes Theory

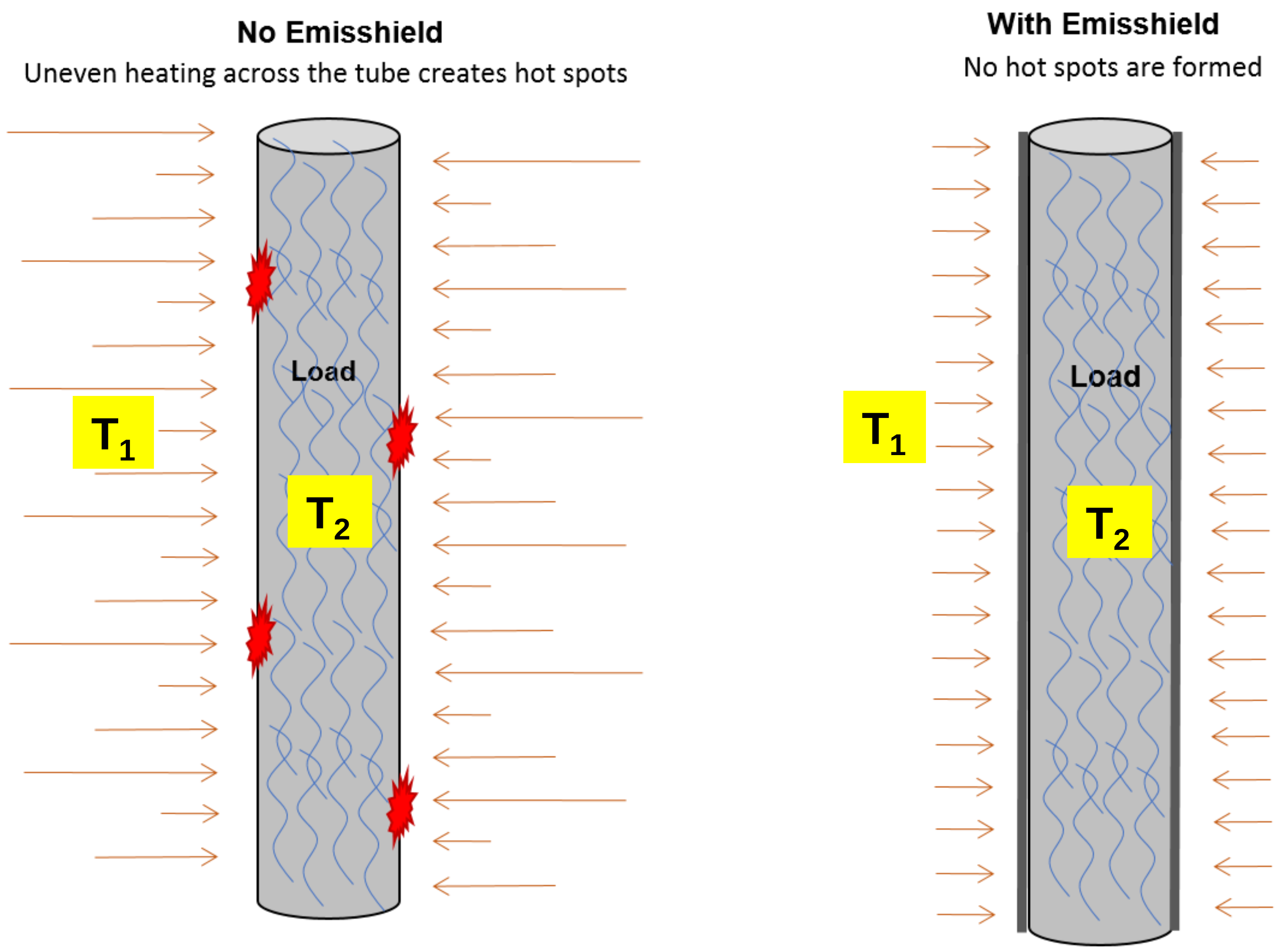
Coated Tube Overall Benefits:

1. Fuel Savings/Production Increase
2. Creates a uniform and increased heat flux/minimizes hot spots
3. Emissivity at temperature: 0.90 - 0.95
4. Minimizes insulative thermal oxide layer
5. Minimizes nucleation sites in interior
6. Reduces coking and carburization
7. Reduces TMT

Uncoated Ni/Cr Tube Conditions:

1. Emissivity at temperature: 0.5-0.8
2. Develops insulative thermal oxide layer
3. Hot spots across the process tube no-uniform oxide layer and spallation
4. Coking tendencies still present (Ni/Fe)
5. Higher TMT – Higher Coking
6. Tube creep

Increase Heat Transfer



Emisshield Process Tube / Radiant Wall Solutions

1. ***Developed by NASA*** - to Protect Human Life and Space Vehicles in extremely violent Thermal Conditions.

2. ***Thermal Stability*** - to 1350°C on Tubes and Radiant Walls

3. ***Thermal Shock*** - tested from -200^{0}C to 1500^{0}C in 3 seconds with no debonding.

4. ***Adhesion*** - Thermal Shock Bonding Strength > 5,000 psi.

5. ***Hemispherical Emissivity*** - > 0.9

6. ***Thin Filmed*** - Less than 75m in thickness for maximum performance.

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