8th Chemical Process Safety Sharing (CPSS)

CARBULIZATION in Steam Interchanger Dehydrogenation unit

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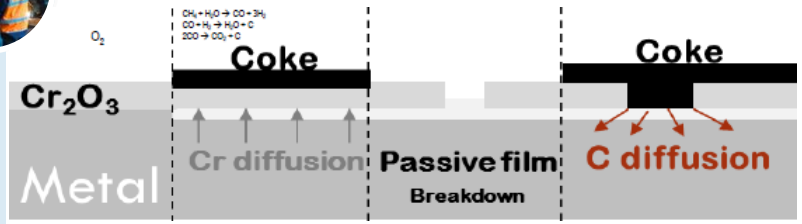
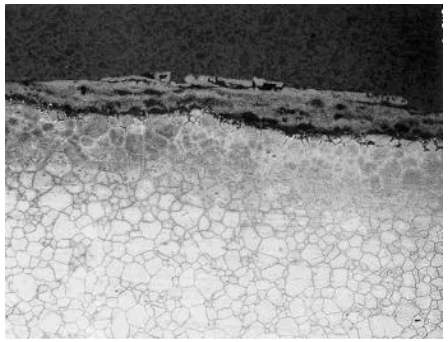
Contents

Introduction

- **What's the Carburization**
  - CARBULIZATION is a formation of metal carbide is absorbed into a material at elevated temperature while in contact with a carbonaceous material or carburizing environment.



A rule of thumb states that up to 50% carburization can be tolerated on stream before loss of strength materially affects tube life. **API 571,573**



A photomicrograph of a cross-section of a 304H cyclone from a fluid coker showing surface carburization after 24 years. Mag. 35X.

Critical Factors

•Three conditions must be satisfied:

a)Exposure to a carburizing environment or carbonaceous material.

b)Temperature high enough to allow diffusion of carbon into the metal [typically above 1100°F (595°C)].

c)Susceptible material

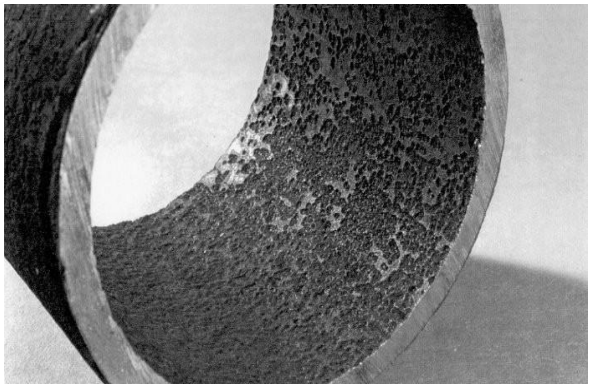
•Conditions favoring carburization include a high gas phase carbon activity (hydrocarbons, coke, gases rich in CO, CO2, methane, ethane) and low oxygen potential (minimal O2 or steam).

Affected Materials

•Carbon steel and low alloy steels, 300 Series SS and 400 Series SS, cast stainless steels, nickel base alloys with significant iron content (e.g., Alloys 600 and 800) and HK/HP alloys.

Introduction

- **METAL DUSTING**
  - METAL DUSTING is form of carburization resulting in accelerated localized pitting which occurs in carburizing gases and/or process streams containing carbon and hydrogen. Pits usually form on the surface and may contain soot or graphite dust.



Critical Factors

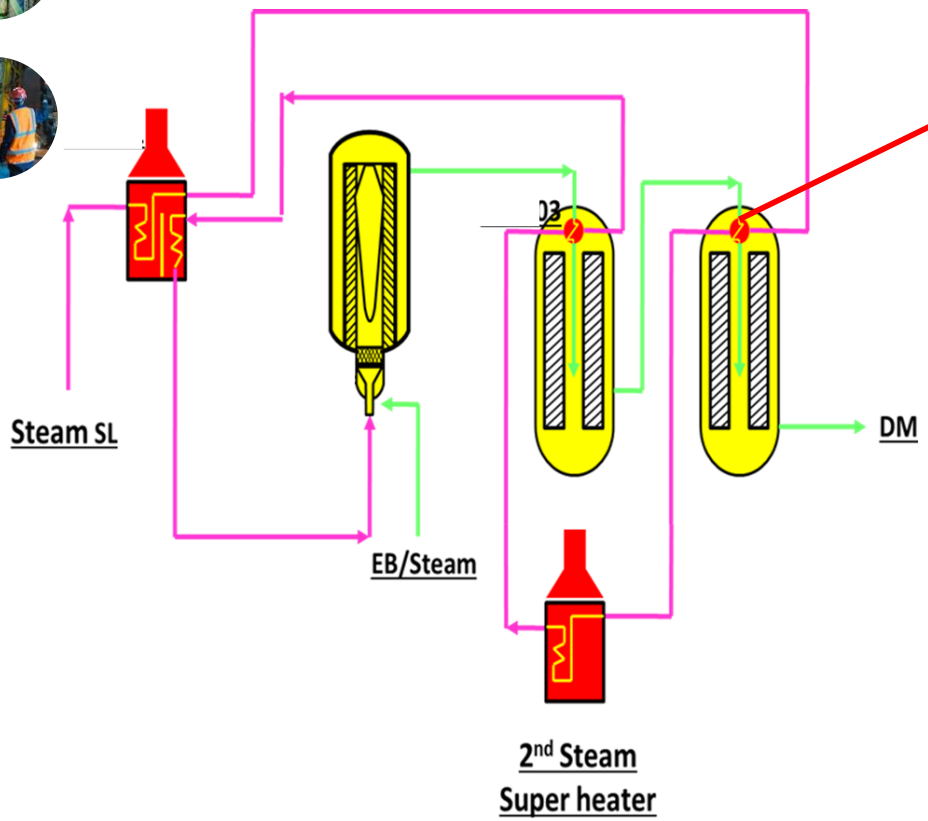
- **Process stream composition, operating temperature, and alloy** composition are critical factors.
- **Metal dusting is preceded by carburization and is characterized by rapid metal wastage.**
- Metal dusting involves a complex series of reactions involving a reducing gas such as hydrogen, methane, propane or CO.
- It usually occurs in the approximate operating temperature range of 900 °F to 1500 °F (480 °C to 815 °C)

Affected Materials

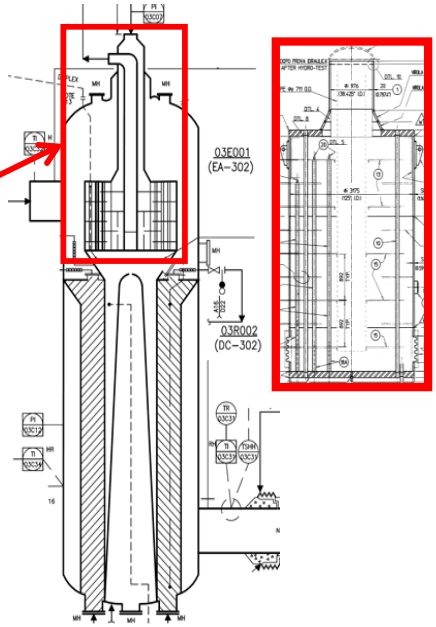
- Low-alloy steels, 300 series SS, nickel-based alloys, and heat resisting alloys. Aluminized coatings that form a protective alumina layer on the surface have been shown to provide some protection.

Introduction

Process overview : Dehydrogenation Unit



Steam interchanger



	Shell	Tube
Materials	SS304H	SS304H
Design temperature (°C)	700-910	650
Operating temperature (°C)	801 (in)/ 632 (out)	567.7 (in)/620 (out)
Design pressure (barG)	2.1	1.8
Operating pressure (barG)	0.6	0.5
Service media	Steam	Effluent
Years in service	23	23

Introduction

Steam interchanger Historical Timeline

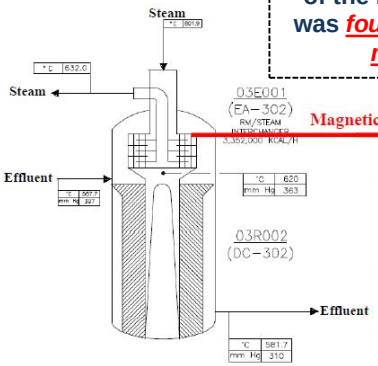
03E001 was operated in 1997

1997 — 2011 — Revamping 130% 2013 — 2016 — 2019

Specialist (LTI) informs that the *carburization* could be take placed on the *inter-exchanger*.

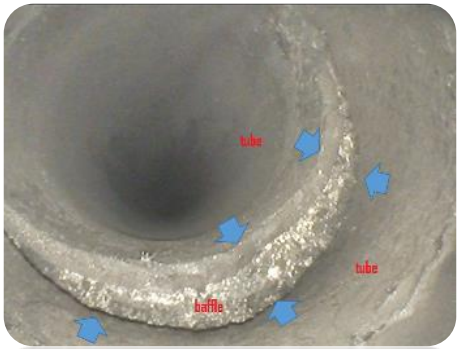
Inspection of the I.D of the inlet tubes of the RMI showed no signs of carburization.

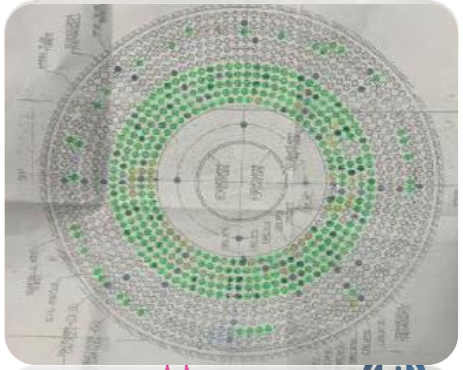
2013 and 2016: Top part of the inter-exchanger was *found initial sign of magnetic..*



Magnetic sign was found on the top part of inter-exchanger

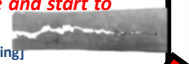
2019: The tube was cut and inspection finding found that the tubes were failed (green color-mark).





LUMMUS recommend :
The interchanger design life 100,000 hours

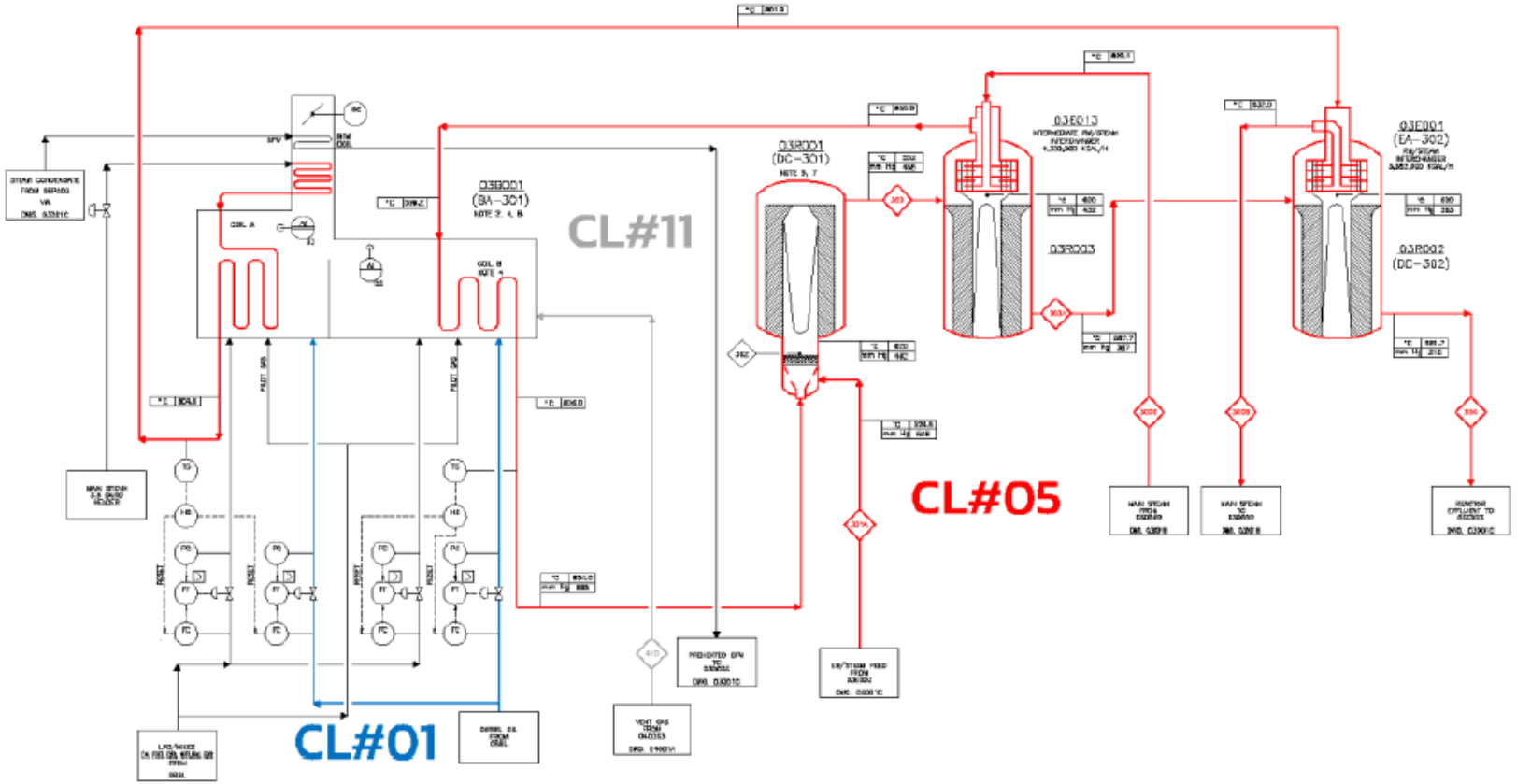
The carburization of the tubes in the first pass is confined to six or seven innermost rows of the exchanger because of *heat transfer from high temperature steam in the radial flow design. Over a period of time, the carburized tubes flake off from inside and start to crumble*



[From LUMMUS Sharing]

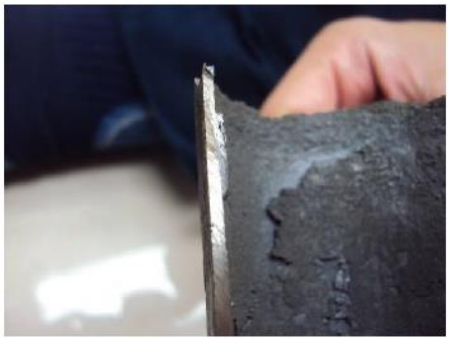
INFORMATION / FINDINGS

RBI indicated that *Carburization (CARBU), Metal dusting (METDUS),* Creep (CREEP), Sigma phase embrittlement (SIGPHEMB) and High temperature oxidation (HTOXID) could be take placed on the inter-exchanger .

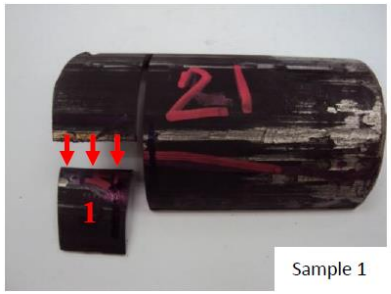


INFORMATION / FINDINGS

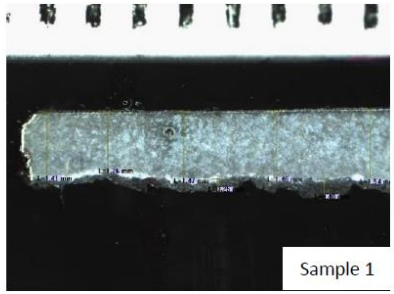
Visual testing: Internal surface was found scale and minimum thickness was 1.6 mm (design 3 mm).

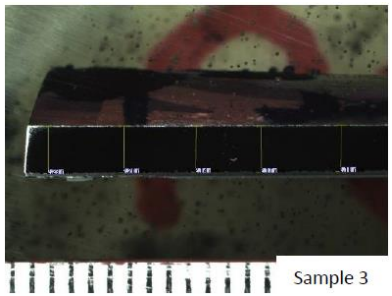

Stereo microscope: The minimum thickness of top part is 1.26 mm (sample 1) and bottom part is 2.14 mm (sample 3).



Sample 1


Sample 1

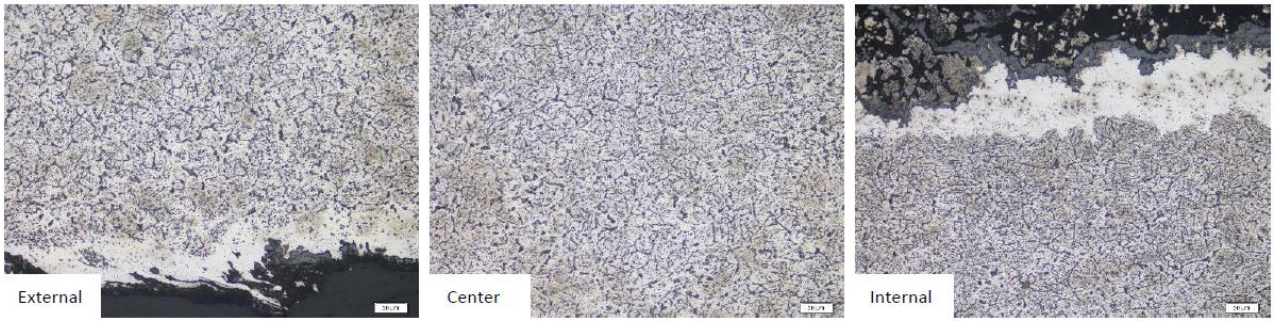
Sample 3


Sample 3

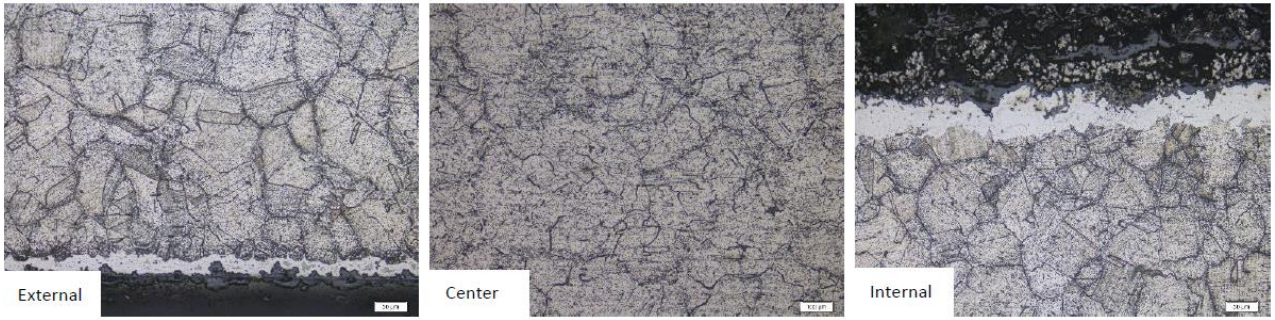
INFORMATION / FINDINGS

Optical Microscope:

- Sample 1 (top): The internal surface was found ***scale***, ***chromium depleted*** and ***degraded microstructure*** through cross-section thickness.



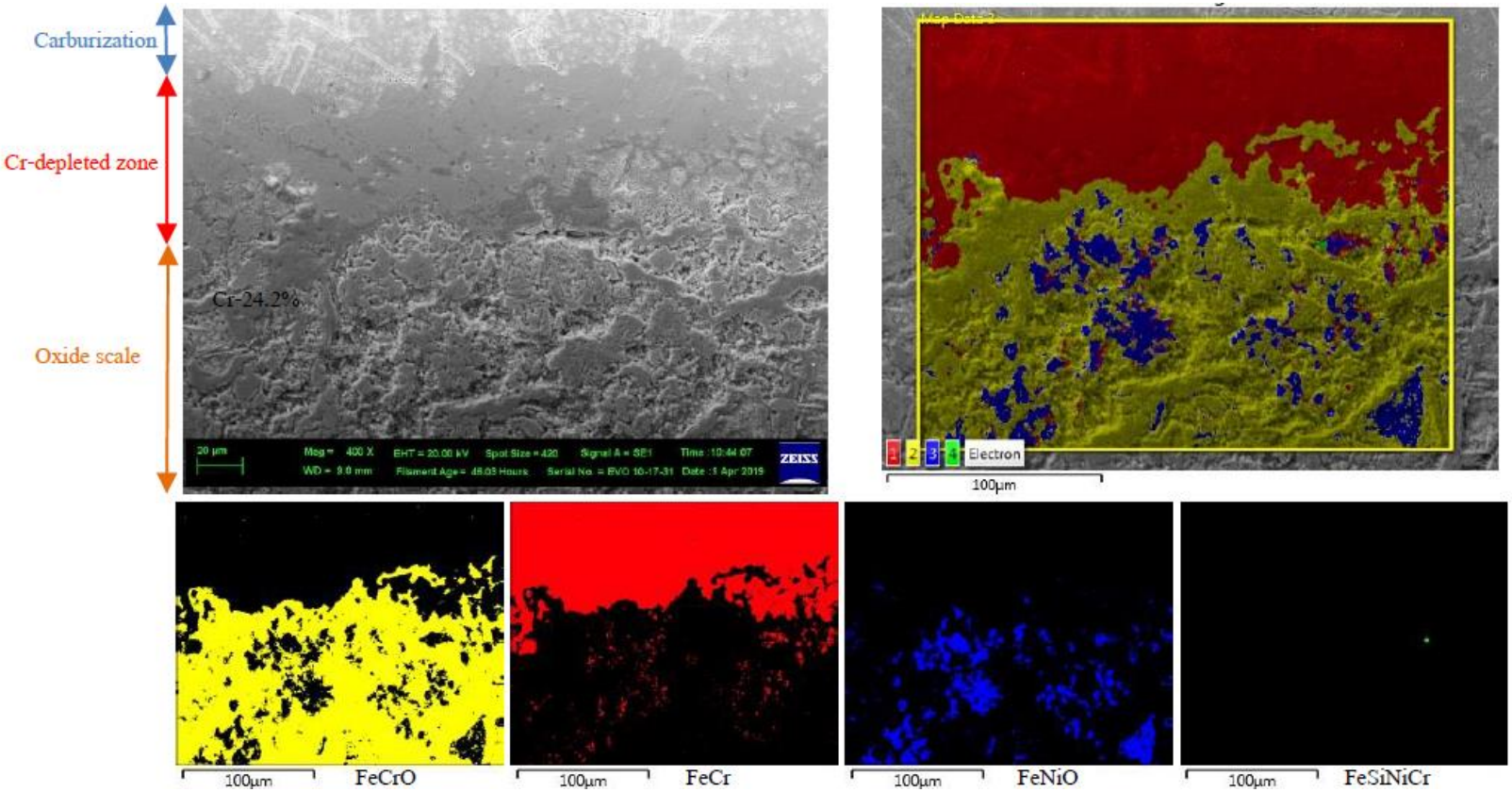
- Sample 3 (bottom): Internal surface was found ***scale*** and ***chromium depleted*** but the middle microstructure was normal.



INFORMATION / FINDINGS

Scanning Electron Microscope:

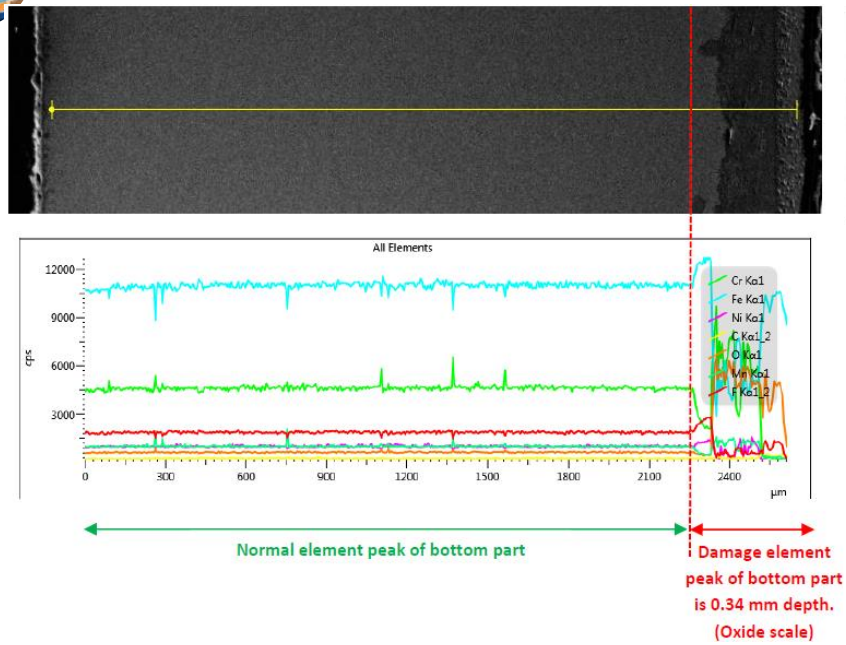
- Internal scale was ***found Chromium oxide layer***, ***Chromium depleted*** and ***carburization zone***

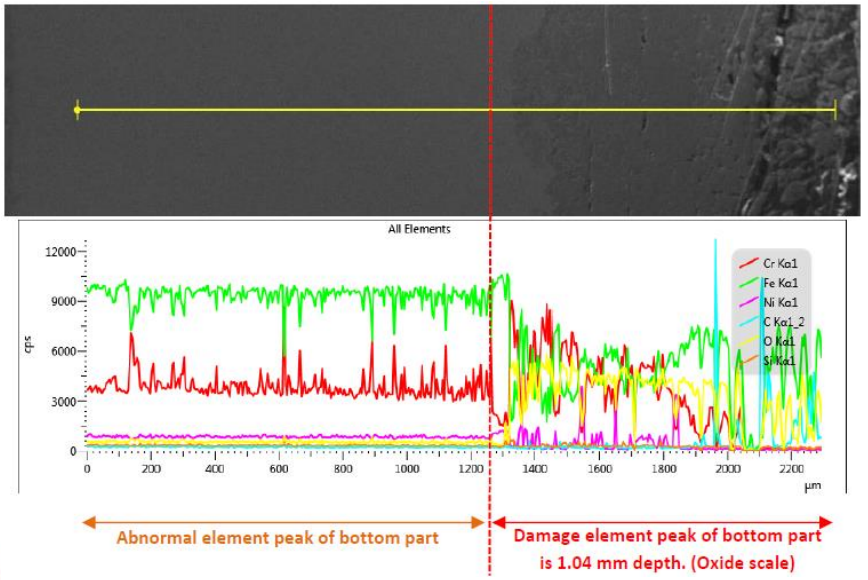


INFORMATION / FINDINGS

Scanning Electron Microscope:

- Linescanning by EDX indicated that the sample 3 - bottom damage is 0.34 mm depth even sample 1 – top damage is 1.04 mm depth.





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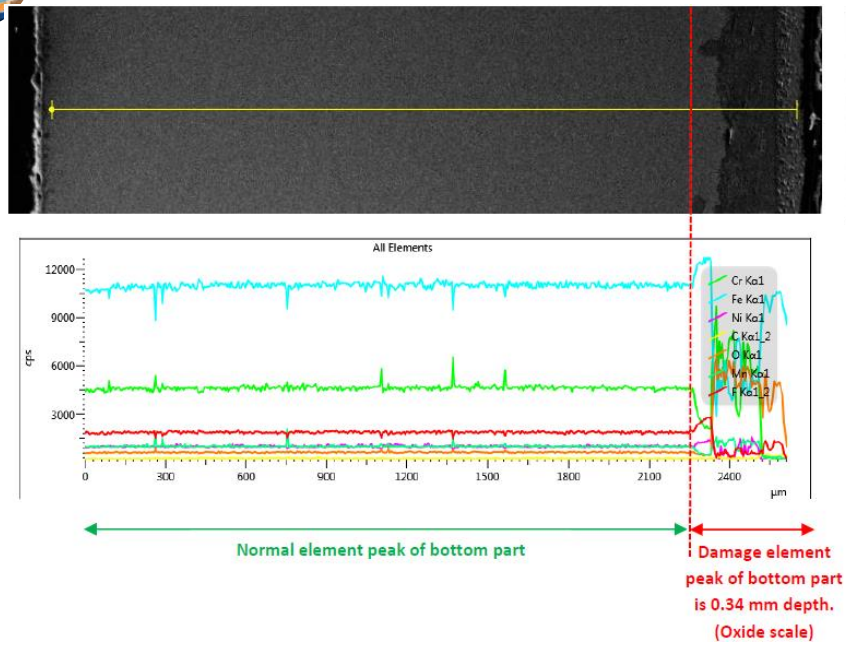
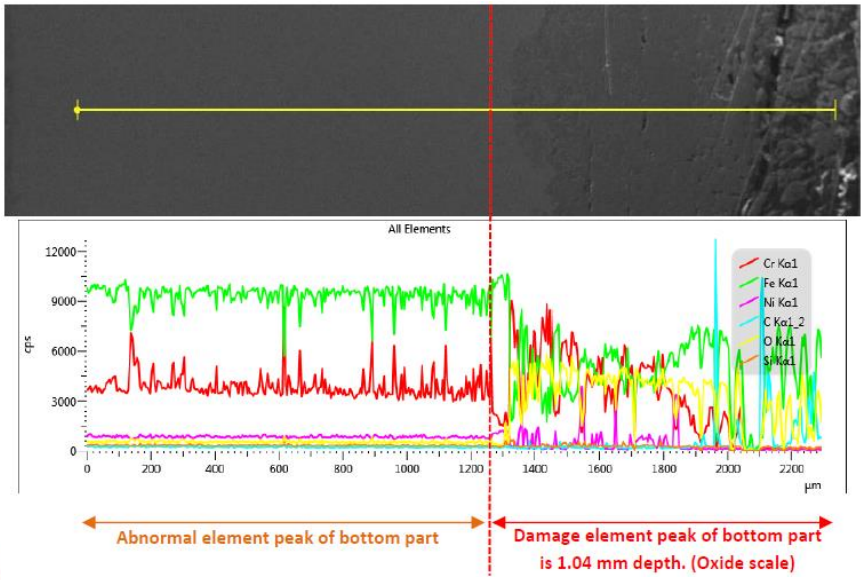




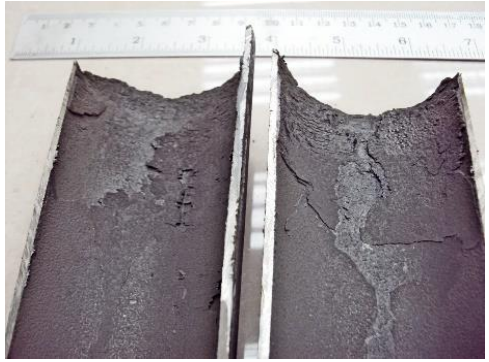
Conclusion and Recommendation

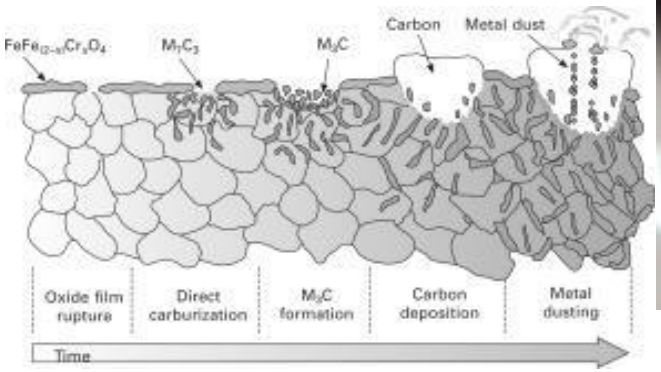
Conclusion

- The possible failure mode is ***Metal Dusting due to the form of carburization*** in accelerated ***localized pitting*** and ***thickness loss.***

- The carburization depth of each sample could be followed :
  - 0.3 mm of sample 3
  - All thickness of sample 1

When it is considered from contrast of hardness result.



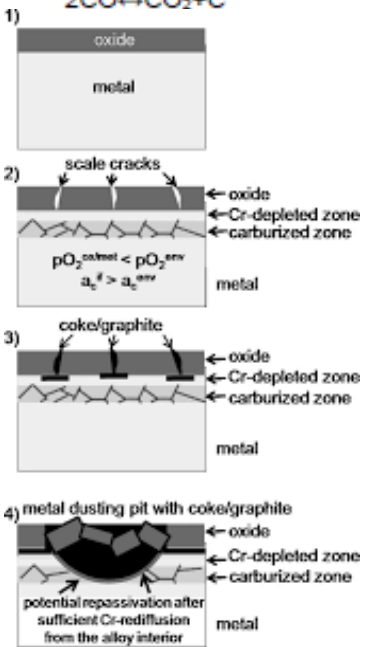


Water Gas Shift Reaction:

$CO+H_2O \leftrightarrow CO_2+H_2$

Boudouard Reaction:

$2CO \leftrightarrow CO_2+C$



Conclusion and Recommendation

Recommendation

Prevention / Mitigation

- **Materials selection must be made based on the specific application and environment. In case Interchanger, the material upgrade from 304H(Cr 18-20%) to 310H(Cr 24-26%)**

- **For other process, Sulfur in the carburizing atmosphere (usually as H2S or a disulfide), forms a protective sulfide that minimizes carburization and metal dusting. It is thought that sulfur retards the carbon transfer from the atmosphere to the metal.**

Inspection and Monitoring

- **VT can be effective in identifying areas of severe metal wastage, including localized areas of numerous rounded pits, uniform thinning.**
- **Magnetic testing on tube surface.**
- **Metal dusting is most accurately confirmed through destructive testing**

A rule of thumb states that up to 50% carburization can be tolerated on stream before loss of strength materially affects tube life.

API 573

Inspection of Fired Boilers and Heaters

Chemical Process Safety Sharing

Thank you for your attention