



CORROSION IN REFINERY INDUSTRY FAILURE ATLAS

CASE HISTORY n° 5 Date 31 March 2008

Process: Continuous Catalytic Reforming
Equipment: Furnace tubes

DATE OF INCIDENT AND/OR INFORMATION: 2005/ inspection during a planned shut-down

NATURE OF THE INCIDENT :

A big mass of dust in the outlet tube header in third and fourth furnace. Erosion losses on the inside surface of the headers caused by dust. Slow and uniform thinning of furnace tube walls.

CONSEQUENCES :

Removal of dust from the tube headers and repairing the erosion losses. Collecting one tube from the fourth furnace to establish the reasons of the incident by means of destructive examinations. After examinations, the furnaces were put into operation for another four years.

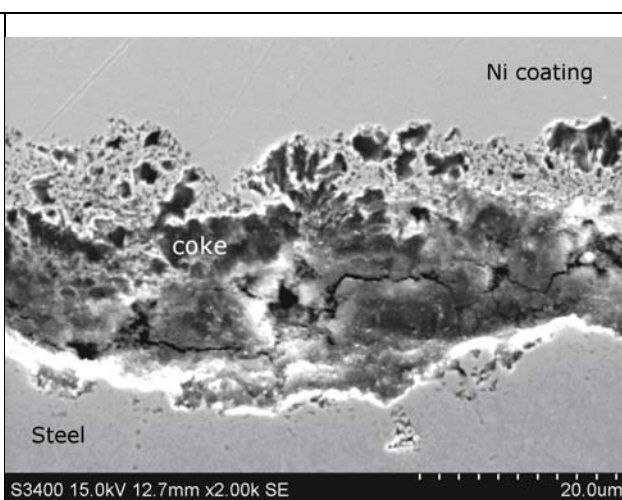
MATERIAL COMPOSITION and REFERENCES

Furnace tubes: ASTM A335 P9 (9% Cr – 1% Mo)

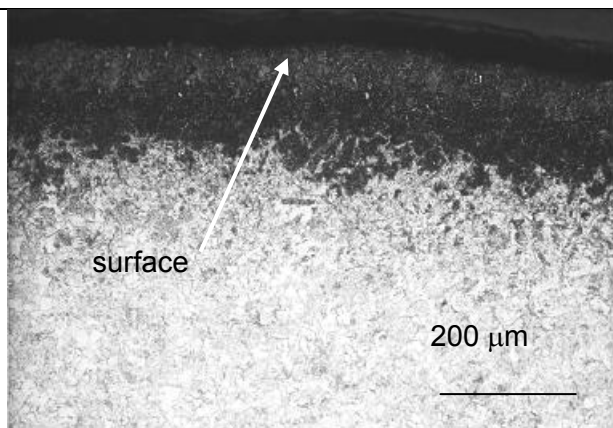
PICTURES AND SCHEMES :



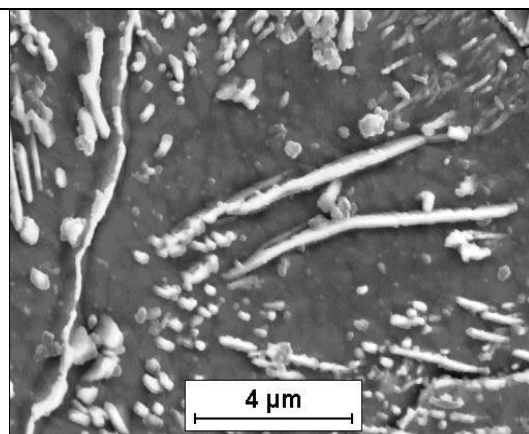
Erosion on the inside surface of a tube header. Dust in the header was composed of graphite, iron, Cr_7C_3 carbide, and traces of catalyst material



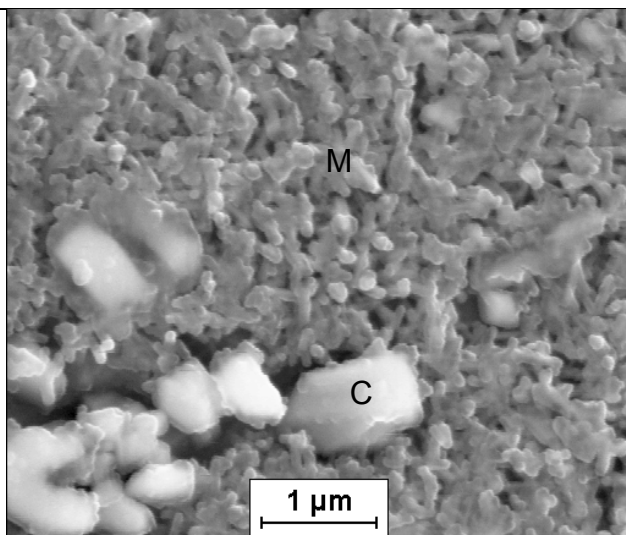
Coke layer on the inside surface of 9Cr-1Mo steel tube, composed of graphite, iron and Cr_7C_3 carbide



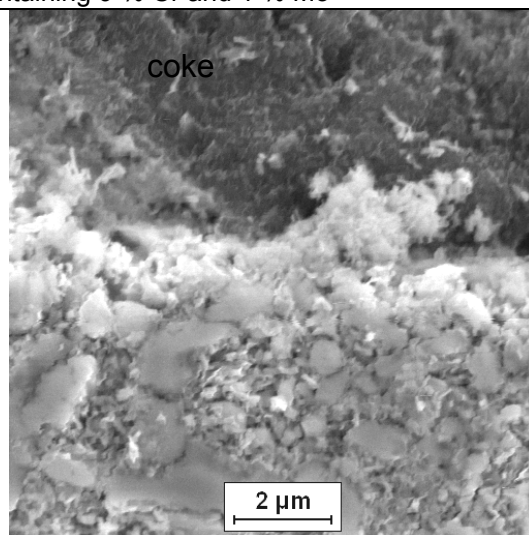
Carburized layer beneath the inside surface of 9Cr-1Mo steel tube



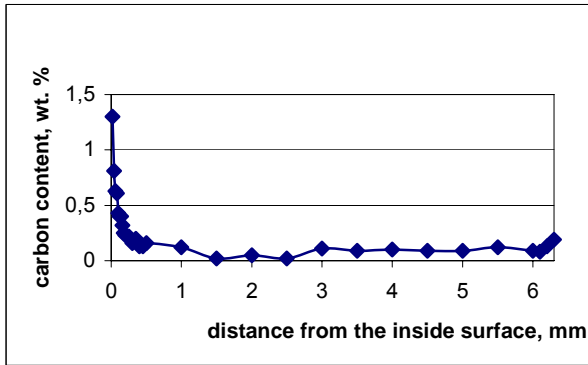
Middle-wall material of 9Cr-1Mo steel tube : degraded primary alloy carbides in metal matrix (alloy ferrite) containing 9 % Cr and 1 % Mo



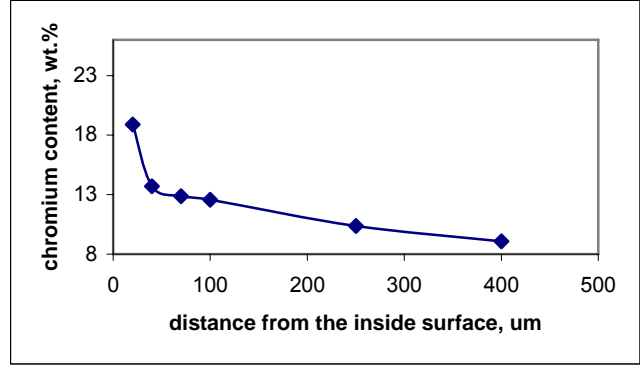
Degraded primary carbides (C) in the "matrix" (M) composed of fine carbides, 30 μm from the inside surface. Chemical composition in **C**: 25% Cr, 4% Mo, in **M**: 15% Cr, 2% Mo



A partly disintegrated layer of fine carbides at the inside surface covered with coke



Carbon profile beneath the inside surface of 9Cr-1Mo steel tube



Chromium profile beneath the inside surface of 9Cr-1Mo steel tube

ASPECT : Loose corrosion products on the inside surface of 9Cr-1Mo steel tube composed of graphite, iron and Cr_7C_3 carbides. Carburized layer beneath the inside surface of the tube. Degraded primary alloy carbides in alloy ferrite matrix in the middle-wall material, and degraded primary carbides in a porous "matrix" composed of fine alloy carbides within the carburized layer. Enrichment of carburized layer in chromium and molybdenum. Formation a layer of fine, low and high alloy carbides at the inside surface that constitutes a barrier for inward diffusion of carbon. Metal dusting due to mechanical separation of high alloy carbides and decomposition of low alloy carbides into graphite and iron.

MEDIA AND OPERATING CONDITIONS:

Skin tube temperature 550-600°C

Hydrotreated naphtha and recycle hydrogen gas, sulphur content in the naphtha ~ 0.2-0.3 ppm, 470-520°C (inside)

Fuel gas (outside)

TIME TO DETERIORATION : 10 years



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ANSWER

TYPE OF CORROSION : Metal dusting
API 571 CLASSIFICATION: 4.4.5

CAUSES :

Metal dusting attack under standard operating conditions connected with formation of dust containing hard, alloy carbides. Probable too high carbon activity in the third and fourth furnace.

REMEDY :

There is no remedy established till now. The operation temperature was under the project temperature. Some experiment were carried out to show that sulphur content in the feed higher than actually used in the discussed CCR platformer seems to be harmful when an advanced stage of metal dusting is reached. Destructive examinations of the tubes in the first, second and third furnace will be helpful to solve the question.

PUBLICATION - TECHNICAL REPORT:

J. Dampc, Z. Grzesik, J. Hucińska: Metal dusting in CCR platforming unit. EUROCORR 2007, WP 15. Freiburg im Breisgau, Germany 2007

BIBLIOGRAPHIC REFERENCES :